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Flexoelectricity and alignment phase transitions in nematic liquid crystals

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Abstract. — The influence of the flexoelectric effect on the phase diagram relevant to the order transition induced by an electric field on a nematic liquid crystal is considered. The analysis shows that this influence can be important. It is found that the order phase transition between the initially undistorted and distorted configurations always takes place. In contrast, the phase transition between the distorted and the saturated configurations is possible only if the dielectric anisotropy is large enough. The stability of the phases is analysed. The existence of a tricritical point is predicted. The dependence of the tricritical point on the flexoelectric coefficient is discussed too. The limits of our calculations and the performed simplifying hypotheses are critically analysed.

1. Introduction.

Nematic materials are characterized by anisotropic properties [1]. In particular their dielectric constant parallel to the symmetry axis ε_{\parallel} can be different from the one perpendicular to it ε_{\perp} . The dielectric anisotropy $\varepsilon_a = \varepsilon_{\parallel} - \varepsilon_{\perp}$ can be positive or negative. From this anisotropy, it follows that nematic materials can be oriented by means of an external electric field. If the nematic is uniform, i.e. its symmetry axis is position independent, and the electric field is parallel ($\varepsilon_a < 0$) or perpendicular ($\varepsilon_a > 0$) to it, an order phase transition is expected [2].

This well known transition is called Fréedericksz transition. The critical field giving rise to this transition depends on the elastic properties and on the anisotropy of the medium, on the thickness of the sample and on the surface properties. A lot of papers are devoted to this order instability. In particular special attention has been devoted to the undistorted \rightarrow distorted

transition [3] (usual Fréedericksz transition), and to the distorted \rightarrow saturated transition [4]. In the last case, everywhere the nematic symmetry axis \mathbf{n} (the director) is parallel to the distorting field when the applied field is larger than a critical one. The influence of the surface properties on these transitions has been discussed by different authors [5] by using a phenomenological expression for the surface free energy proposed a long time ago by Rapini and Papoular [6], or variants of it [7].

In this paper the phase diagram undistorted \rightarrow distorted \rightarrow saturated configuration *versus* the applied electric field will be considered. We use an expression for the surface free energy recently proposed [8], and we take into account the flexoelectric effect [9].

In the analysis the anchoring energy strength and the flexoelectric coefficient will be considered thickness independent. Consequently the obtained results have to be considered as a first approximation of the true ones. Our paper is organized as follows. In section 2 the main equations relevant to the interaction of the external field with the nematic are rapidly discussed in the usual frame. In section 3 the flexoelectric effect is considered and a few peculiar aspects discussed. In section 4 the phase diagram is reported and analysed. In section 5 the main conclusions of our paper are stressed.

2. Dielectric interaction nematic-electric field.

Let us consider a nematic liquid crystal characterized by positive dielectric anisotropy. Let the sample be of thickness d and the initial nematic orientation planar, i.e. the director \mathbf{n} be parallel to the surfaces in the absence of external field. In the limit of small ε_a [10] the total free energy of the nematic sample can be written in the form

$$F = \int_{-d/2}^{d/2} \left\{ \frac{1}{2} K \left(\frac{d\theta}{dz} \right)^2 - \frac{1}{2} \varepsilon_a E^2 \cos^2 \theta \right\} dz + f_s^- + f_s^+, \quad (1)$$

where : K = nematic elastic constant, ε_a = nematic dielectric anisotropy (supposed positive), E = external electric field, z = coordinate normal to the limiting surfaces, $\theta = \cos^{-1}(\mathbf{n} \cdot \mathbf{z})$ nematic tilt angle (see Fig. 1), f_s^- , f_s^+ surface free energy densities relative to the surface at $z = -d/2$ and $z = +d/2$ respectively. By minimizing (1) one obtains for θ the differential equation

$$\frac{d^2\theta}{dz^2} - \frac{1}{2} \xi^{-2} \sin(2\theta) = 0, \quad \forall z \in (-d/2, d/2), \quad (2)$$

with the boundary conditions

$$-K \frac{d\theta}{dz} + \frac{df_s^-}{d\theta^-} = 0 \quad \text{at } z = -d/2, \quad \text{and} \quad K \frac{d\theta}{dz} + \frac{df_s^+}{d\theta^+} = 0 \quad \text{at } z = +d/2. \quad (3)$$

In (2) $\xi = \sqrt{K/\varepsilon_a}(1/E)$ is the coherence length which it is useful to rewrite as $\xi = (d/\pi)(E_c/E)$. $E_c = (\pi/d) \sqrt{K/\varepsilon_a}$ is the threshold field for the Fréedericksz transition [11] in the strong anchoring situation. In equations (3), $\theta^\pm = \theta(\pm d/2)$ are the surface tilt angles.

In the following we suppose that in the absence of external field the planar orientation is stable. Consequently f_s^- and f_s^+ have a minimum for $\theta^- = \theta^+ = \pi/2$; hence

$$\left(\frac{df_s^-}{d\theta^-} \right)_{\pi/2} = \left(\frac{df_s^+}{d\theta^+} \right)_{\pi/2} = 0, \quad (4)$$

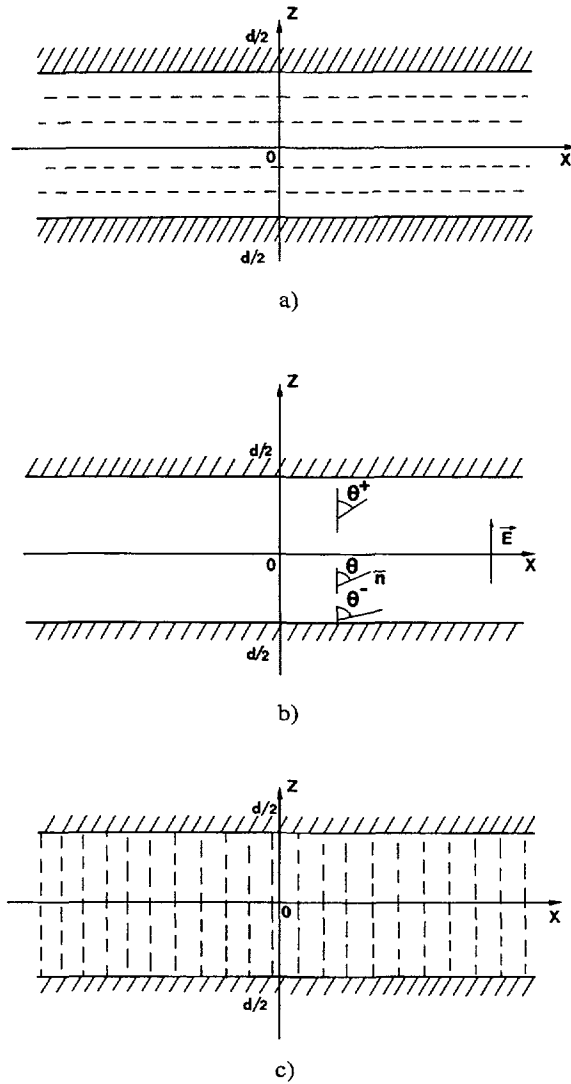


Fig. 1. — Geometry of the problem. A nematic slab of thickness d is considered. $\mathbf{n} = (\sin \theta, 0, \cos \theta)$ is the nematic director, θ is the tilt angle. a) In the absence of the external distorting field (parallel to the z -axis) \mathbf{n} is parallel to the x -axis (planar orientation). b) If an external field E , larger than a critical one is applied, \mathbf{n} is no longer uniform across the sample (distorted phase). c) If an external field larger than the saturation field is applied \mathbf{n} is uniform across the sample and everywhere parallel to the distorting field (homeotropic orientation).

and

$$\left(\frac{d^2 f_s^-}{d\theta^{-2}} \right)_{\pi/2} = W^- > 0, \quad \left(\frac{d^2 f_s^+}{d\theta^{+2}} \right)_{\pi/2} = W^+ > 0. \quad (5)$$

Furthermore we assume that f_s^- and f_s^+ have a maximum for $\theta^- = \theta^+ = 0$. This hypothesis

implies

$$\left(\frac{df_s^-}{d\theta^-} \right)_0 = \left(\frac{df_s^+}{d\theta^+} \right)_0 = 0, \quad (6)$$

and

$$\left(\frac{d^2 f_s^-}{d\theta^{-2}} \right)_0 = \tilde{W}^- < 0, \quad \left(\frac{d^2 f_s^+}{d\theta^{+2}} \right)_0 = \tilde{W}^+ < 0. \quad (7)$$

Finally the surface energies are supposed monotonic decreasing functions of $\theta \in (0, \pi/2)$. Consequently the surface torques $df_s^\pm/d\theta^\pm$ vanish only for the homeotropic and planar alignment. The threshold field for the undistorted \rightarrow distorted order phase transition is obtained by putting $\theta = (\pi/2) - \eta$, and considering the case $\eta \rightarrow 0$. In this limit equation (2) reduces to

$$\frac{d^2 \eta}{dz^2} + \left(\frac{\pi}{d} h \right)^2 \eta = 0, \quad (8)$$

where $h = E/E_c$ is the reduced applied field. Solution of (8) is

$$\eta(z) = A \cos \left(\frac{\pi}{d} h z \right) + B \sin \left(\frac{\pi}{d} h z \right). \quad (9)$$

By substituting (9) into (3), taking into account (4) and (5), we deduce that a nontrivial solution of the kind (9) exists only if the reduced field h is larger than a threshold field h' given by

$$\operatorname{tg}(\pi h') = \left[\frac{W^- + W^+}{K} \frac{d}{\pi h'} \right] / \left[1 - \frac{W^- W^+}{K^2} \left(\frac{d}{\pi h'} \right)^2 \right], \quad (10)$$

which is a generalization of the well known equation proposed a long time ago by Rapini and Papoular in the simple case in which $W^- = W^+$ ⁽¹²⁾. h' is called Fréedericksz's field.

The saturation field for the distorted \rightarrow saturated order phase transition is obtained by equation (2) in the limit of $\theta \rightarrow 0$. In this case equation (2) reduces to

$$\frac{d^2 \theta}{dz^2} - \left(\frac{\pi}{d} h \right)^2 \theta = 0, \quad (11)$$

whose solution is

$$\theta(z) = \tilde{A} \operatorname{ch} \left(\frac{\pi}{d} h z \right) + \tilde{B} \operatorname{sh} \left(\frac{\pi}{d} h z \right). \quad (12)$$

By substituting solution (12) into boundary conditions (3), and taking into account equations (6, 7) one obtains that the solution $\theta(z) = 0, \forall z \in (-d/2, d/2)$, is stable if the reduced applied electric field is larger than a critical value h'' given by

$$\operatorname{tg} h(\pi h'') = \left[\frac{|\tilde{W}^-| + |\tilde{W}^+|}{K} \frac{d}{\pi h''} \right] / \left[1 + \frac{|\tilde{W}^-| |\tilde{W}^+|}{K^2} \left(\frac{d}{\pi h''} \right)^2 \right], \quad (13)$$

which is a generalization of the saturation field given by Nehring, Kmetz and Sheffer [13]. h'' is called saturation field. Equations (10) and (13) are general, and they hold in the case in

which f_s^\pm are monotonic functions of θ , having a minimum for $\theta = \pi/2$ and a maximum for $\theta = 0$.

In the following we limit ourselves to consider the symmetric case in which

$$f_s^- = f_s^+ = K_{1s} \cos^2 \theta + K_{2s} \cos^4 \theta, \quad (14)$$

where K_{1s} and K_{2s} are phenomenological parameters temperature dependent. An expression for the surface free energy of the kind (14) has been proposed [14] in order to interpret recently observed spontaneous surface order transition [15] (see appendix A). By using for f_s expression (14), equations (10) and (13) are written

$$\operatorname{tg}(\pi h') = \frac{2(\delta_1/h')}{1 - (\delta_1/h')^2}, \quad (15)$$

and

$$\operatorname{tg} h(\pi h'') = \frac{2[(\delta_1 + 2\delta_2)/h'']}{1 + [(\delta_1 + 2\delta_2)/h'']^2}, \quad (16)$$

where

$$\delta_1 = \frac{2}{\pi} \frac{K_{1s}}{K} d \quad \text{and} \quad \delta_2 = \frac{2}{\pi} \frac{K_{2s}}{K} d, \quad (17)$$

are adimensional parameters taking into account the surface anchoring parameters K_{1s} and K_{2s} , the elastic properties of the medium K and the sample thickness d .

The standard analysis performed in this section to deduce the threshold and saturation fields is limited only to the vicinity of the phase boundaries. However the result obtained are meaningful, because the surface energies are supposed monotonic functions of θ , having a minimum for $\theta = \pi/2$, and a maximum for $\theta = 0$. The same kind of analysis will be performed in the next section, in which the flexoelectric effect is considered.

The phase diagram obtained by means of equations (15) and (16) has been recently considered [16].

3. Flexoelectric interaction nematic-electric field.

In the previous section only the dielectric interaction has been considered. As is well known it is proportional to the square of the electric field and it gives a bulk effect, resulting in a torque density proportional to the dielectric anisotropy. In compensated nematic ($\epsilon_a = 0$) this interaction vanishes.

In this section the flexoelectric interaction will be considered. As shown a long time ago [17] a distorted nematic usually presents an electric polarization proportional to the spatial derivative of the nematic director. This polarization is called flexoelectric polarization, and it is given by

$$\mathbf{P} = e_{11} \mathbf{n} \operatorname{div} \mathbf{n} - e_{33} \mathbf{n} \times \operatorname{rot} \mathbf{n}, \quad (18)$$

where e_{11} and e_{33} are the flexoelectric coefficients. The coupling of this polarization with an external electric field has been the subject of many theoretical and experimental investigations. The electric contribution to the energy density connected to the coupling of \mathbf{P} with the external field \mathbf{E} is of the kind $-\mathbf{P} \cdot \mathbf{E}$. The flexoelectric polarization introduces also a renormalization of the elastic constants [18], which can be neglected if we are looking for instabilities separating

an undistorted state from a distorted one. In the event in which the problem is unidimensional the flexoelectric contribution can be integrated, as discussed in detail by Durand [19]. In this case the effect of the flexoelectric polarization is a renormalization of the surface energies. Simple calculations [20] show that, near the undistorted orientation, the flexoelectric contribution reduces to

$$- \int_{-d/2}^{d/2} \mathbf{P} \cdot \mathbf{E} dz = - \frac{eE}{2} [\cos(2\theta^+) - \cos(2\theta^-)]. \quad (19)$$

where $e = e_{11} + e_{22}$.

It follows that the analysis reported in section 2 remains unchanged if f_s^\pm are substituted by

$$F_s^- = f_s^- + \frac{eE}{2} \cos(2\theta^-) \quad \text{and} \quad F_s^+ = f_s^+ - \frac{eE}{2} \cos(2\theta^+). \quad (20)$$

In particular by assuming for f_s^\pm the functional form (14), in equation (10) we have to put

$$W^- = 2(K_{1s} + eE) \quad \text{and} \quad W^+ = 2(K_{1s} - eE), \quad (21)$$

whereas in equation (13) the parameters \tilde{W}^- and \tilde{W}^+ are now given by

$$\tilde{W}^- = -2(K_{1s} + 2K_{2s} + eE) \quad \text{and} \quad \tilde{W}^+ = -2(K_{1s} + 2K_{2s} - eE). \quad (22)$$

Equations (21) show that the presence of the flexoelectric effect introduces an asymmetry in the surface energy, and consequently in the problem we are analysing. In particular in the event in which $E > 0$, the flexoelectric effect stabilizes the lower surface and destabilizes the upper one. By substituting equations (21) and (22), into equations (10) and (13) we obtain for the Fréedericksz field and for the saturation field the expression

$$\text{tg}(\pi h') = \frac{2(\delta_1/h')}{1 - (\delta_1/h')^2 + (4e^2/K\varepsilon_a)}, \quad (23)$$

and

$$\text{tg} h(\pi h'') = \frac{2[(\delta_1 + 2\delta_2)/h'']}{1 + [(\delta_1 + 2\delta_2)/h'']^2 - (4e^2/K\varepsilon_a)}, \quad (24)$$

respectively. By equations (23) and (24) simple calculations give

$$\delta_1 = \left\{ -\cotg(\pi h') + \sqrt{\cotg^2(\pi h') + [1 + (4e^2/K\varepsilon_a)]} \right\} h', \quad (25)$$

and

$$\delta_1 = -2\delta_2 + \left\{ \cotg h(\pi h'') - \sqrt{\cotg^2 h(\pi h'') - [1 - (4e^2/K\varepsilon_a)]} \right\} h'' \quad (26)$$

Equation (25) in the limit $\varepsilon_a \rightarrow 0$ gives for the critical field E' of the flexoelectric instability the value

$$E' = \frac{K}{2ed} \left[\left(2 \frac{K_{1s}}{K} d + 1 \right)^2 - 1 \right]^{1/2}, \quad (27)$$

which generalizes a formula obtained in a different way some years ago [21]. By using equation (27) we can estimate the order of magnitude of the threshold for the flexoelectric

instability in nearly compensated ($\varepsilon_a \sim 0$) nematic liquids crystals. By assuming $K \sim 10^{-6}$ dyn [2], $e \sim 10^{-3} \sqrt{\text{dyn}}$ [22], $K_{1s} \sim 10^{-2}$ erg/m² [13] and $d \sim 10$ μm one obtains for the threshold voltage $V' = E' d \sim (1-2)$ V, i.e. of the same order of the threshold voltage of the Fréedericksz transition in usual nematics.

We point out that the analysis presented in this section refers to one-dimensional director deformation. But as it is well known, in the event in which $e_{11} \neq e_{33}$, the planar nematic cell considered in our analysis can present a bidimensional instability. This bidimensional pattern, due to the flexoelectric effect, may have a threshold field lower than the one connected to the one-dimensional instability, as discussed in detail in references [23, 24]. As it is shown in the quoted references, the bidimensional instability appears at the threshold voltage V_c given by

$$V_c = \frac{2 \pi K}{e^*(1 + \mu)},$$

where $e^* = e_{11} - e_{33}$ and $\mu = \varepsilon_a K/4 \pi e^{*2}$. At the threshold the wave-vector of the bidimensional structure q_c is

$$q_c = \frac{\pi}{d} \sqrt{\frac{1 - \mu}{1 + \mu}}$$

As it is evident from the expression of q_c the bidimensional instability exists only if $\mu < 1$, which implies $e^{*2} > \varepsilon_a K/4 \pi$. It follows that the analysis presented in our paper is valid for $e^{*2} < \varepsilon_a K/4 \pi$, which we assume to be verified.

Note that equation (27), deduced in the limit of $\varepsilon_a \rightarrow 0$, is correct, in the sense that it refers to a unidimensional instability, only if also the other limitation $e_{11} - e_{33} \ll e_{11} + e_{33}$ is introduced, as we have assumed in deducing the above mentioned equation.

4. Phase diagram of the order phase transition h vs. δ_1 .

To obtain the phase diagram δ_1 vs. h we have to consider the stability of the three phases, i.e. planar ($\theta = \pi/2$, $\forall z \in [-d/2, d/2]$) distorted ($\theta = \theta(z)$), and homeotropic ($\theta = 0$, $\forall z \in [-d/2, d/2]$). To this end let us rewrite the total energy F of the nematic sample given by (1), in which f_s^\pm have the functional form (14), as

$$G = \int_{-\pi/2}^{\pi/2} \left\{ \left(\frac{d\eta}{du} \right)^2 - h^2 \sin^2 \eta \right\} du + \delta_1 (\sin^2 \eta^+ + \sin^2 \eta^-) + \delta_2 (\sin^4 \eta^+ + \sin^4 \eta^-) + rh [\cos (2 \eta^+) - \cos (2 \eta^-)], \quad (28)$$

where $G = (2 d/\pi K) F$ is the reduced total free energy, $u = \pi z/d$, $r = \sqrt{4 e^2/K \varepsilon_a}$, $\eta^\pm = \eta(\pm d/2)$, and $\eta = \pi/2 - \theta$. In the limit $\eta \rightarrow 0$ (near the P-phase), at the second order in η , G is given by

$$G = \int_{-\pi/2}^{\pi/2} \left[\left(\frac{d\eta}{du} \right)^2 - h^2 \eta^2 \right] du + (\delta_1 - 2 rh) \eta^{+2} + (\delta_1 + 2 rh) \eta^{-2} \quad (29)$$

In the considered limit $\eta(u) = A \cos(hu) + B \sin(hu)$, as follows from equation (9). By substituting this expression of $\eta(u)$ into (29), simple calculations give G in terms of A and B only, i.e.

$$G(A, B) = \left[-h \sin(\pi h) + 2 \delta_1 \cos^2\left(\frac{\pi}{2} h\right) \right] A^2 + \left[h \sin(\pi h) + 2 \delta_1 \sin^2\left(\frac{\pi}{2} h\right) \right] B^2 - 2 rhAB \sin(\pi h). \quad (30)$$

The P-phase corresponds to $A = B = 0$. The stable phase is obtained by minimizing $G(A, B)$ with respect to A and B . By imposing

$$\frac{\partial G}{\partial A} = \frac{\partial G}{\partial B} = 0 \quad (31)$$

we obtain the system

$$\begin{aligned} \left[-h \sin(\pi h) + 2 \delta_1 \cos^2\left(\frac{\pi}{2} h\right) \right] A - rhB \sin(\pi h) &= 0, \\ \left[h \sin(\pi h) + 2 \delta_1 \sin^2\left(\frac{\pi}{2} h\right) \right] B - r h A \sin(\pi h) &= 0, \end{aligned} \quad (32)$$

which admits always the solution $A = B = 0$. This solution is stable if

$$\left(\frac{\partial^2 G}{\partial A^2} \right)_{A=B=0} = 2 \left[-h \sin(\pi h) + 2 \delta_1 \cos^2\left(\frac{\pi}{2} h\right) \right] > 0, \quad (33)$$

and furthermore

$$\begin{aligned} H(0, 0) &= \left[\frac{\partial^2 G}{\partial A^2} \frac{\partial^2 G}{\partial B^2} - \left(\frac{\partial^2 G}{\partial A \partial B} \right)^2 \right]_{A=B=0} \\ &= \left[\left(\frac{\delta_1}{h} \right)^2 + 2 \left(\frac{\delta_1}{h} \right) \cotg(\pi h) - (1 + r^2) \right] h^2 \sin^2(\pi h) > 0. \end{aligned} \quad (34)$$

Equation (33) gives

$$\delta_1 > h \left\{ -\cotg(\pi h) + \sqrt{1 + \cotg^2(\pi h)} \right\} = \delta_1^*, \quad (35)$$

whereas from equation (34) one derives

$$\delta_1 > h \left\{ -\cotg(\pi h) + \sqrt{1 + \cotg^2(\pi h) + r^2} \right\} = \delta_1^{**} > \delta_1^*. \quad (36)$$

Consequently the P-phase is stable for $\delta_1 > \delta_1^{**}$. The condition $\delta_1 = \delta_1^{**}$ gives again the threshold (25).

We wish to underline that for $E > K_{1s}/e$ and $K_{2s} > 0$ i.e. for $\delta_1 < \delta_1^+ = 2hr$ the easy axis on the upper surface is different from $\pi/2$, as discussed in detail in appendix B. However the threshold for the $P \rightarrow D$ transition is the one given by equation (25), since the δ_1^+ does not take into account the bulk contribution to the total energy.

To analyse the stability of the H-phase we move in the same way as done for the P-phase. By substituting now in G , written in terms of θ and expanded up to the second order, solution (12) one obtains $\tilde{G} = \tilde{G}(\tilde{A}, \tilde{B})$. By imposing again

$$\frac{\partial \tilde{G}}{\partial \tilde{A}} = \frac{\partial \tilde{G}}{\partial \tilde{B}} = 0,$$

it is easy to show that $\tilde{A} = \tilde{B} = 0$, i.e. the H-phase, is always a solution. This phase is stable if

$$\left(\frac{\partial^2 \tilde{G}}{\partial \tilde{A}^2} \right)_{\tilde{A}=\tilde{B}=0} > 0, \quad (37)$$

and

$$\tilde{H}(0, 0) = \left(\frac{\partial^2 \tilde{G}}{\partial \tilde{A}^2} \frac{\partial^2 \tilde{G}}{\partial \tilde{B}^2} - \frac{\partial^2 \tilde{G}}{\partial \tilde{A} \partial \tilde{B}} \right)_{\tilde{A}=\tilde{B}=0} > 0. \quad (38)$$

Equation (37) gives

$$\delta_1 < -2 \delta_2 + \left\{ \cotg h(\pi h) - \sqrt{\cotg^2 h^2(\pi h) - 1} \right\} = \tilde{\delta}_1^*, \quad (39)$$

whereas from condition (38) one obtains

$$\delta_1 < -2 \delta_2 + \left\{ \cotg h(\pi h) - \sqrt{\cotg^2 h^2(\pi h) - 1 + r^2} \right\} h = \tilde{\delta}_1^{**} < \tilde{\delta}_1^*. \quad (40)$$

Note that in the hypothesis $K_{1s} + 2K_{2s} > 0$, giving $\delta_1 + 2\delta_2 > 0$, the saturation phenomenon can take place only if $r < 1$, i.e. $4e^2/K\varepsilon_a < 1$ (see appendix C).

Previous analysis shows that for $h < h'$ the nematic sample is in planar orientation. Consequently the region of the (δ_1, h) -plane limited by the line $\delta_1 = \delta_1(h')$ and the δ_1 -axis corresponds to a planar phase. On the contrary for $h > h''$ the stable phase is the homeotropic one (i.e. \mathbf{n} is everywhere parallel to the distorting field). Hence the region of the (δ_1, h) -plane limited by the line $\delta_1 = \delta_1(h'')$ and the h -axis corresponds to a homeotropic phase.

The line $\delta_1 = \delta_1(h')$ is shown in figure 2. In figure 2a the two lines correspond to $4e^2/K\varepsilon_a = 0.1$ (dashed) and to $4e^2/K\varepsilon_a = 0.9$. As expected the two lines coincide in the limit of $\delta_1 \rightarrow \infty$, which corresponds to strong anchoring. In fact in this limit the flexoelectric contribution can be neglected. In figure 2b the curve δ_1 vs. h' is reported in the limit of weak anchoring, for the same values of $4e^2/K\varepsilon_a$ considered above. In this limit $4e^2/K\varepsilon_a$ plays an important role on the critical line. As stated in section 2, in the absence of external field the planar orientation corresponds to a stable state having minimum energy, whereas the homeotropic one to a unstable configuration, whose energy is maximum. Consequently $K_{1s} > 0$ and $K_{1s} + K_{2s} > 0$, which are equivalent to δ_1 and $\delta_1 + 2\delta_2 > 0$. In the following figures 3, 4 and 5, in which the phase diagrams δ_1 vs. h are reported we have to underline that :

- i) for $\delta_2 > 0$, the phase-diagram is meaningful for $\delta_1 > 0$
- ii) for $\delta_2 < 0$, the phase-diagram is meaningful for $\delta_1 > -2\delta_2$.

In the opposite case, in the absence of the external field the sample is not planar, nor homeotropic. Hence the reorienting phenomenon connected to the external field is not a threshold phenomenon. The curve $\delta_1 = \delta_1(h'')$ is reported in figure 3 by considering the cases $4e^2/K\varepsilon_a = 0.1$ and $4e^2/K\varepsilon_a = 0.9$ and furthermore $\delta_2 = -0.25$. Note that in the case $\delta_2 > 0$, h'' , for $\delta_1 = 0$, is given by

$$\left\{ \cotg h(\pi h'') - \sqrt{\cotg^2 h^2(\pi h'') - [1 - (4e^2/K\varepsilon_a)]} \right\} h'' = 2\delta_2.$$

In contrast, in the case $\delta_2 < 0$, to $h'' = 0$ corresponds $\delta_1 = 2|\delta_2|$.

In figure 4 are reported the lines $\delta_1 = \delta_1(h')$ and $\delta_1 = \delta_1(h'')$ for $\delta_2 > 0$. In this case by increasing the applied electric field one observes the order phase transitions

$$\text{Planar} \rightarrow \text{Distorted} \rightarrow \text{Homeotropic} .$$

h'
 h''

All the phase transitions are of second order. In figure 5 the event $\delta_2 < 0$ is considered. In this case for $\delta_1 > \delta_1^{\text{TCP}}$ the situation is similar to the previous one. In contrast, for $\delta_1 < \delta_1^{\text{TCP}}$ the distorted phase is never stable, and the P \rightarrow H order phase transition is of the first order. Of course our analysis is valid only for $\delta_1 > 2|\delta_2|$, as stated by means of equation (7). The coordinates of the tricritical point TCP in figure 5 depend on the flexoelectric coefficient as shown in figure 6.

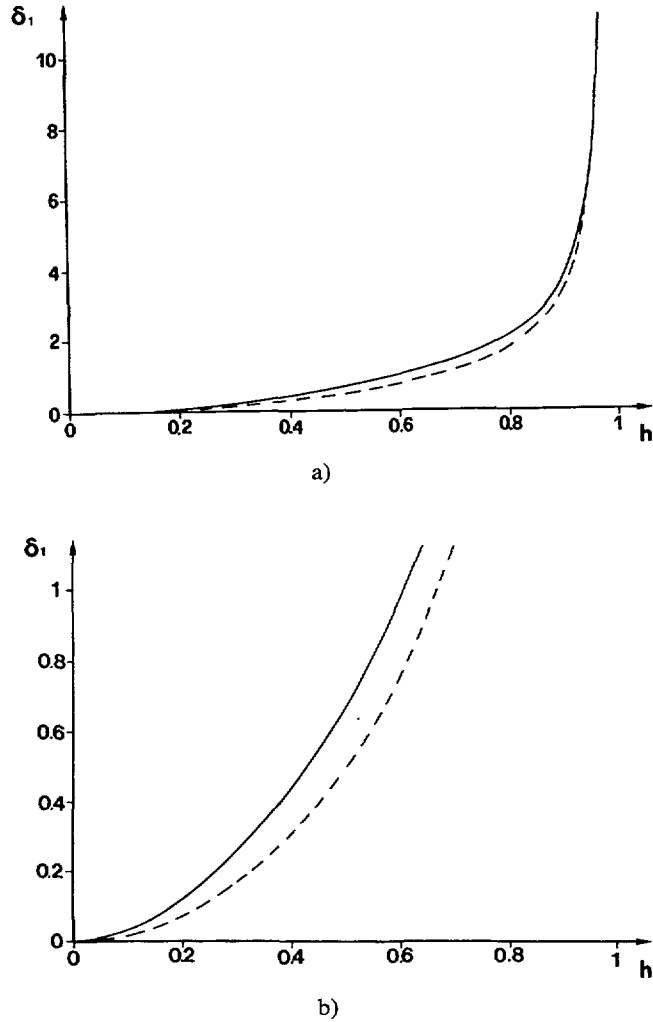


Fig. 2. — Phase diagram $\delta_1 = \delta_1(h')$ for the Planar \rightarrow Distorted phase transition for different values of the flexoelectric parameter $4 e^2/K \epsilon_a$. $4 e^2/K \epsilon_a = 0.9$ (continuous curve), $4 e^2/K \epsilon_a = 0.1$ (dashed curve). For $h < h'$ the stable configuration is the undistorted (Planar) one. For $h > h'$ the stable configuration is the distorted one. a) $0 \leq \delta_1 \leq 10$. Note that for large δ_1 (i.e. for strong anchoring) the h' is nearly independent of the flexoelectric parameter. b) $0 \leq \delta_1 \leq 1$. This sub-case refers to very weak anchoring. For $h' \sim 0$, $\delta_1 = (\pi/2)[1 + (4 e^2/K \epsilon_a)] h'^2$, as follows from equation (25).

We underline that the phase-diagram $\delta_1 - E$ are, actually, phase diagram $d - E$. They are meaningful only if K_{1s} , K_{2s} , ϵ_a and e are thickness independent. Recent experimental investigations [25] show that the anchoring parameters K_{1s} and K_{2s} seem to depend strongly on the thickness of the sample. As it has been shown in reference [26] this is connected to long range surface forces, like electrostatic forces, due to selective ions adsorption. Furthermore, as discussed in reference [27], the flexoelectric coefficient can also depend on the thickness, as a consequence of the spatial variation of the nematic scalar order parameter.

It follows that the phase-diagram presented in our paper have to be considered as a first approximation of the true ones. However it is important to underline that if the Debye

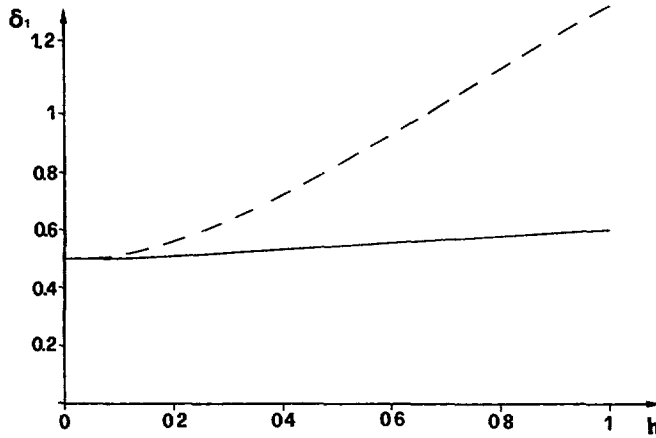


Fig. 3. — Phase diagram $\delta_1 = \delta_1(h'')$ for the Distorted \rightarrow Homeotropic phase transition for $\delta_2 = -0.25$ and for different values of the flexoelectric coefficient $4 e^2/K \epsilon_a$. $4 e^2/K \epsilon_a = 0.9$ (continuous curve), $4 e^2/K \epsilon_a = 0.1$ (dashed curve). Note that h'' (the saturation field) is different from zero for $\delta_1 = 0$, whereas h' (the critical field) goes to zero when $\delta_1 \rightarrow 0$. For $h < h''$ the stable configuration is the distorted one; for $h > h''$ the stable configuration is the homeotropic one. The phase diagram is meaningful in the region $\delta_1 > 0.5$ (see the text).

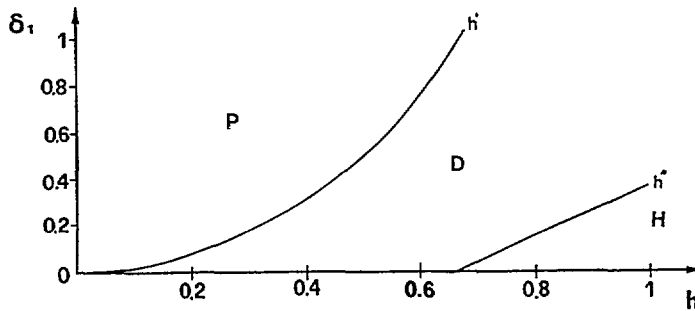


Fig. 4. — Phase diagram $\delta_1 = \delta_1(h)$ for the Planar \rightarrow Distorted \rightarrow Homeotropic phase transition for positive δ_2 ($\delta_2 = 0.25$) and $4 e^2/K \epsilon_a = 0.1$. The phases transition P \rightarrow D and D \rightarrow H are of second order. The phase diagram is meaningful in the region $\delta_1 > 0$ (see the text).

screening length is small enough the dependence on the thickness of the sample of the anchoring parameters disappear. Furthermore, the dependence on the thickness of the sample of the flexoelectric coefficients is important only for very small thicknesses [28]. Consequently our results are expected to work well for thicknesses of the sample larger than a few microns.

5. Conclusions.

The influence of the flexoelectricity on the phase diagram of the order transition on the plane external field-anchoring parameter has been considered. The analysis shows that in the limit of weak anchoring, the flexoelectric effect can change drastically the phase transition. In

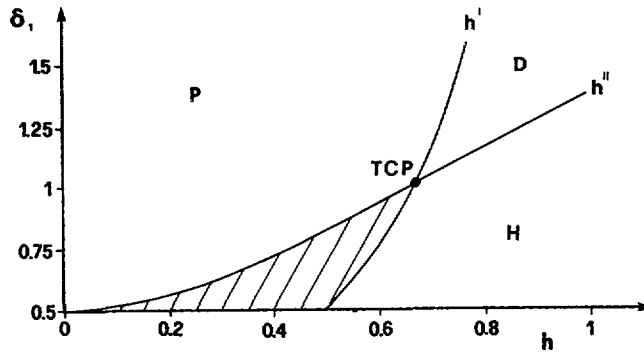


Fig. 5. — As in figure 4, with $\delta_2 < 0$ ($\delta_2 = -0.25$). Note that for $\delta_1 < \delta_1^{\text{TCP}}$ the P \rightarrow H transition is of first order. For $\delta_1 > \delta_1^{\text{TCP}}$ all the order transitions P \rightarrow D and D \rightarrow H are of second order. δ_1^{TCP} , h^{TCP} are the coordinates of the tricritical point. The phase diagram is meaningful in the region $\delta_1 > 0.5$ (see the text).

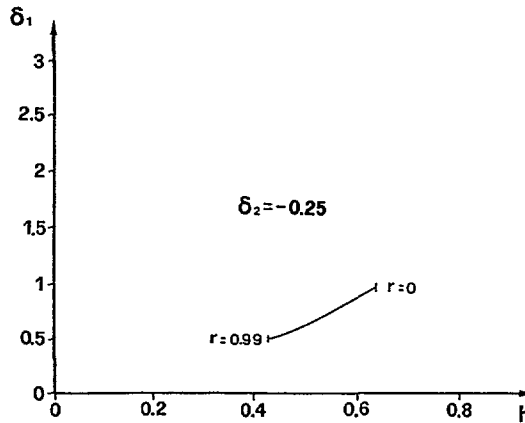


Fig. 6. — Tricritical line for the case $\delta_2 = -0.25$. It represents the tricritical points for different values of the flexoelectric coefficient $4 e^2/K \epsilon_a$, for $0 \leq 4 e^2/K \epsilon_a \leq 0.99$. The phase diagram is meaningful in the region $\delta_1 > 0.5$ (see the text).

particular in the limit of very weak anchoring, the flexoelectric interaction is more important of the dielectric one, and hence the effect is strongly polar. The existence of a tricritical point has been shown and its connection with the flexoelectric effect discussed.

6. Acknowledgments.

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Appendix A.

As discussed in reference [7] expression (14) for the surface energy at first sight can appear not very useful because the set of functions $\{\cos^{2n} \theta\}$ is not orthogonal.

It has been shown in reference [8] that the above mentioned expression is obtained by expanding f_s in terms of the symmetry elements of the surface and of the nematic liquid crystal. If the substrate can be supposed flat and isotropic, its symmetry elements reduce to its geometrical normal \mathbf{K} . On the other hand the liquid crystal is characterized by its quadrupolar tensor order parameter $Q_{ij} = S(T)(n_i n_j - 1/3 \delta_{ij})$, where $S(T)$ is the scalar order parameter [2]. Hence expression (14) is found by means of the expansion

$$f_s = \beta_{11}(K_i Q_{ij} K_j) + \beta_{21}(K_i Q_{ij} Q_{ie} K_e) + \beta_{22}(K_i Q_{ij} K_j)^2, \quad (A1)$$

where β_{ij} are phenomenological parameters temperature independent. From the preceding discussion it follows that even if $\{\cos^{2n} \theta\}$ is not a set of orthogonal functions, the previous expansion for f_s is correct, since it has to be considered as an expansion, in the sense of Landau, in terms of S and not in term of orthogonal functions. However it is also possible to obtain (14) by expanding f_s in term of orthogonal functions. As discussed in reference [7] a set of functions useful for this expansion is $\{P_{2n}(\cos \theta)\}$, where $P_{2n}(\cos \theta)$ are the Legendre polynomials. In this framework one writes

$$f_s = aP_2(\cos \theta) + bP_4(\cos \theta), \quad (A2)$$

where $P_2(\cos \theta) = (1/2)(3 \cos^2 \theta - 1)$, and $P_4(\cos \theta) = (1/8)(35 \cos^4 \theta - 30 \cos^2 \theta + 3)$. Simple calculations show that f_s in term of $P_{2n}(\cos \theta)$ can be written in the form (14).

It is important to underline that in (A1) the phenomenological parameters β_{ij} are temperature independent (the temperature enters in f_s via the scalar order parameter $S(T)$), whereas in (A2) a and b depend on T .

Appendix B.

In the considered case, as follows from equations (20) and (14), the effective surface energies are

$$F_s^\pm = K_{1s} \cos^2 \theta^\pm + K_{2s} \cos^4 \theta^\pm \mp \frac{eE}{2} \cos(2\theta^\pm). \quad (B1)$$

The easy directions are defined as the ones minimizing the effective surface energies. Simple calculations give

$$\begin{aligned} \frac{dF_s^\pm}{d\theta^\pm} &= - [(K_{1s} \mp eE) + 2 K_{2s} \cos^2 \theta^\pm] \sin(2\theta^\pm), \\ \frac{d^2 F_s^\pm}{d\theta^{\pm 2}} &= - 2 \{ [(K_{1s} \mp eE) + 2 K_{2s} \cos^2 \theta^\pm] \cos(2\theta^\pm) - K_{2s} \sin^2(2\theta^\pm) \}. \end{aligned} \quad (B2)$$

In the event in which $K_{1s} > 0$ and $K_{1s} + 2 K_{2s} > 0$, from equations (B2) we deduce that $\theta^- = \pi/2$ corresponds to a minimum of F_s^- for every applied electric field. Let us consider now the easy direction of the upper surface, θ^+ . If $K_{2s} > 0$, by equations (B2) we obtain that $\theta^+ = \pi/2$ corresponds to a minimum of F_s^+ for $E < E_1 = K_{1s}/e$. On the contrary $\theta^+ = 0$

minimizes F_s^+ , for $E > E_2 = (K_{1s} + 2K_{2s})/e$. For $E_1 < E < E_2$ the easy direction is tilted and given by

$$\cos^2 \theta^+ = \frac{eE - K_{1s}}{2K_{2s}} \quad (\text{B3})$$

Simple calculations show that: i) for small $E - E_1$, $\eta^+ = \sqrt{(e/2K_{2s})(E - E_1)}$, where $\eta^+ = (\pi/2) - \theta^+$; ii) for small $E_2 - E$, $\theta^+ = \sqrt{(e/2K_{2s})(E_2 - E)}$. The easy direction θ^+ vs. E in the case $K_{2s} > 0$ is shown in figure 7a.

If $K_{2s} < 0$, by equations (B2) we deduce that $\theta^+ = \pi/2$ is stable for $E < E_1 = K_{1s}/e$, whereas $\theta^+ = 0$ is stable for $E > E_2 = (K_{1s} - 2K_{2s})/e < E_1$. In the range $E_2 < E < E_1$, $F_s^+(\pi/2)$ and $F_s^+(0)$ are two minima of $F_s^+(\theta^+)$. Simple calculations show that for $E_2 < E < E_3 = (K_{1s} - |K_{2s}|)/e$, $F^+(\pi/2) < F^+(0)$, i.e. $\theta^+ = 0$ is metastable. However, for $E_3 < E < E_1$, $F^+(0) < F^+(\pi/2)$, i.e. $\theta^+ = \pi/2$ is metastable. The trend of θ^+ vs. E in the event $K_{2s} < 0$ is shown in figure 7b.

For a nematic liquid crystal cell like the one considered in reference [29], K_{2s} is of the same order of magnitude as K_{1s} (and of the order of magnitude of 10^{-2} erg/cm²). More precisely $|K_{2s}/K_{1s}| \sim 0.25$. This experimental result shows that the critical fields above evaluated are of the same order of magnitude for the sample analysed in reference [29]. Consequently the phase-diagram shown in figure 7b is expected to be experimentally detectable.

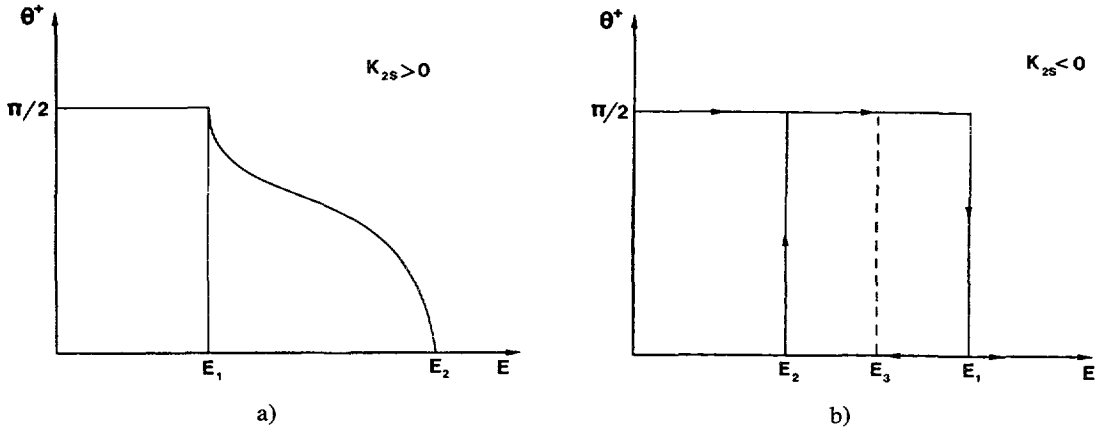


Fig. 7. — Easy direction of the upper surface (at $z = d/2$) vs. the applied electric field. a) $K_{2s} > 0$. In this case θ^+ vs. E shows two critical behaviours, typical of second order transitions near to $E_1 = K_{1s}/e$ and $E_2 = (K_{1s} + 2K_{2s})/e$. b) $K_{2s} < 0$, but $K_{1s} + 2K_{2s} > 0$. In this case θ^+ vs. E shows the critical behaviour of a first order transition of which the hysteresis loop is drawn.

Appendix C.

The condition $4e^2/K\varepsilon_a < 1$ to observe the $D \rightarrow H$ phase transition may seem strange. It follows from the fact that, if e is too large the flexoelectric contribution to the surface energy prevents the saturation transition. This order phase transition takes place only in the weak anchoring case. To understand the effect of the flexoelectric polarization on the $P \rightarrow D \rightarrow H$ phase

transitions we consider in appendix C the case of a compensated nematic ($\varepsilon_a = 0$). In this situation the reduced total free energy G is given by

$$G = \int_{-\pi/2}^{\pi/2} \left(\frac{d\eta}{du} \right)^2 du + \delta_1(\sin^2 \eta^+ + \sin^2 \eta^-) + \delta_2(\sin^4 \eta^+ + \sin^4 \eta^-) + \frac{eEd}{\pi K} [\cos(2\eta^+) - \cos(2\eta^-)], \quad (C1)$$

whereas in the general case it is given by equation (28).

The solution of the Euler-Lagrange associated to equation (C1) is

$$\eta(u) = \frac{\eta^+ - \eta^-}{\pi} u + \frac{\eta^+ + \eta^-}{2}, \quad (C2)$$

where η^+ and η^- have to be determined by minimizing the total energy. By putting (C2) into (C1) simple calculations give

$$G(\eta^+, \eta^-) = \frac{(\eta^+ - \eta^-)^2}{\pi} + \delta_1(\sin^2 \eta^+ + \sin^2 \eta^-) + \delta_2(\sin^4 \eta^+ + \sin^4 \eta^-) + \frac{eEd}{\pi K} [\cos(2\eta^+) - \cos(2\eta^-)]. \quad (C3)$$

It follows that η^+ and η^- are deduced by solving the system of equations $\partial G/\partial \eta^+ = \partial G/\partial \eta^- = 0$, i.e.

$$\begin{aligned} \frac{2}{\pi} (\eta^+ - \eta^-) + \left(\delta_1 - 2 \frac{eEd}{\pi K} \right) \sin(2\eta^+) + 2\delta_2 \sin^2 \eta^+ \sin(2\eta^+) &= 0, \\ -\frac{2}{\pi} (\eta^+ - \eta^-) + \left(\delta_1 + 2 \frac{eEd}{\pi K} \right) \sin(2\eta^-) + 2\delta_2 \sin^2 \eta^- \sin(2\eta^-) &= 0. \end{aligned} \quad (C4)$$

As is known the solution is stable if $\partial^2 G/\partial \eta^+ > 0$ and $H = (\partial^2 G/\partial \eta^{+2})(\partial^2 G/\partial \eta^{-2}) - (\partial^2 G/\partial \eta^+ \partial \eta^-)^2 > 0$. Let us consider the solution $\eta^+ = \eta^- = 0$ (the P-phase). In this case

$$\begin{aligned} \left(\frac{\partial^2 G}{\partial \eta^{+2}} \right)_{0,0} > 0 \rightarrow E < \frac{K}{2ed} (\pi\delta_1 + 1) \\ \text{and } H(0,0) > 0 \rightarrow E < E' = \frac{K}{2ed} \sqrt{(\pi\delta_1 + 1)^2 - 1}. \end{aligned}$$

Consequently in a compensated nematic initially in planar orientation, the undistorted configuration is stable for $E < E'$. Note that E' coincides with the one given by equation (27).

The other homogeneous configuration, i.e. the H-phase, is characterized by $\eta^+ = \eta^- = \pi/2$. In this event

$$\begin{aligned} \left(\frac{\partial^2 G}{\partial \eta^{+2}} \right)_{\pi/2, \pi/2} > 0 \rightarrow E > \frac{K}{2ed} (\pi\delta_1 - 1) \\ \text{and } H(\pi/2, \pi/2) > 0 \rightarrow E < \frac{K}{2ed} \sqrt{(\pi\delta_1 - 1)^2 - 1}. \end{aligned}$$

These two conditions are incompatible: this means that the H-phase is never stable for compensated nematics. In figure 8 the function $G(\eta^+, \eta^-)$ given by (C3) for different values of the external field E is shown. This figure shows that for $E < E'$, $G(\eta^+, \eta^-)$ has a unique minimum for $\eta^+ = \eta^- = 0$. For $E > E'$ the minimum of $G(\eta^+, \eta^-)$ corresponds to

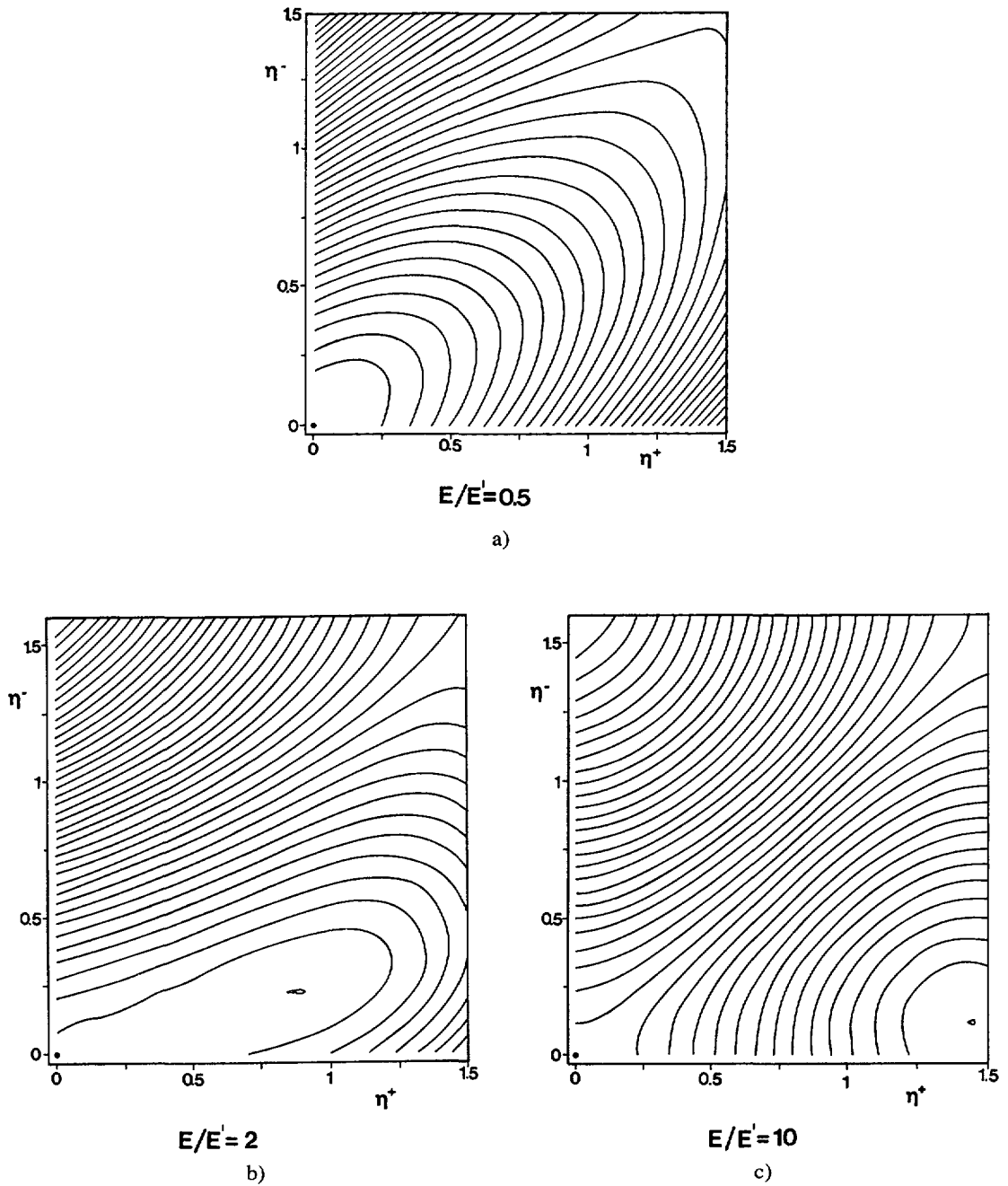


Fig. 8. — Total energy G for a compensated nematic vs. the surface tilt angles η^+ and η^- . a) $E < E'$. The minimum of G is reached for $\eta^+ = \eta^- = 0$ (P-phase). b) $E > E'$. G reaches its minimum for η^+ and η^- different from zero (D-phase). c) $E \gg E'$. The minimum of G corresponds to $\eta^+ \sim \pi/2$ and $\eta^- \sim 0$. The alignment of the nematic is nearly hybrid.

η^+ and η^- different from zero. If the field is very large with respect to E' , $G(\eta^+, \eta^-)$ reaches its minimum for $\eta^+ \sim \pi/2$ and $\eta^- \sim 0$. This fact shows that a compensated nematic submitted to a large electric field tends to assume the hybrid configuration. The trend of η^+ and η^- vs. the field is reported in figure 9. Figure 9a shows that η^+ is a monotonic function of E , whereas η^- presents a maximum for a field a little larger than E' , after that it tends to zero.

This analysis shows that the dielectric anisotropy can be responsible of the stability only if it overcomes the effect of the flexoelectricity.

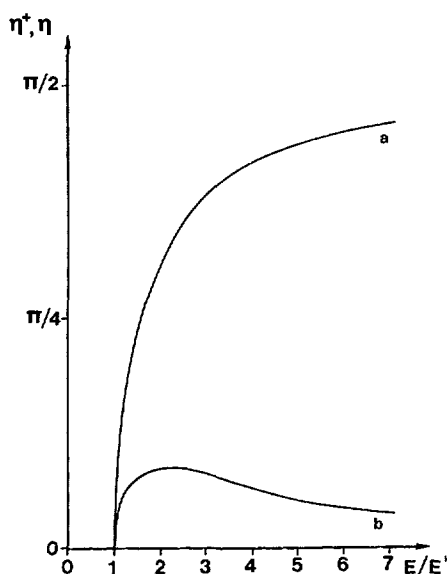


Fig. 9. — Surface tilt angle η^\pm vs. the applied field. For $E = E'$ the trend of η^\pm vs. E is typical of second order phase transition. a) η^+ vs. E is an increasing monotonic function tending to $\pi/2$ for large field. b) η^- vs. E presents a maximum for a field near to E' . For large E , η^- tends to zero.

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