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Surface Walls on a Bistable Anchoring of Nematic Liquid Crystals

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Abstract. — We observe the defects separating nematic domains of two easy orientations, above a bistable orienting SiO evaporated glass plate. The defects are coreless walls. Their width depends on the bulk texture imposed by the nematic cell geometry. For thin enough samples, we have found situations where the wall thickness diverges, i.e., where the texture can force a surface orientation exactly along the surface barrier orientation. We model this new kind of surface transition. The barrier energy of the bistable anchoring is found small, with an extrapolation length $\approx 1 \mu m$. We observe also hysteresis effects which can be explained by a more or less permanent first molecular layer adsorbed on the surface. The corresponding non-elastic contribution to the anchoring is one order of magnitude larger than the elastic one.

1. Introduction

Nematic liquid crystal (NLC) can be oriented by solid surface [1]. Usually the solid substrate imposes only one surface orientation $n_0$ (the easy direction) of the NLC molecules. This anchoring is called monostable. To change the surface orientation from $n_0$ to $n$, one must spend some free energy, the anchoring energy, which depends on $n \cdot n_0$. Recently it has been demonstrated that, by evaporating SiO on a solid substrate in suitable conditions, two easy directions $n_0$ and $n'_0$ appear on the surface [2]. This anchoring is called bistable. Varying the evaporation parameters, one can induce anchoring transitions from monostable to bistable [3]. In this case, the anchoring energy has been found to vanish, as expected. In the range of bistable anchoring, there appears an energy barrier for surface orientations $n$ in-between the two energy minima $n_0$ and $n'_0$. The measurement of this barrier is important for basic and practical reasons. By using a horizontal or vertical electrical field, one can switch the surface orientation from $n_0$ to $n'_0$ and vice versa [4]. In this way, a complete $n_0$ domain goes toward the orientation $n'_0$ in a coherent way above the anchoring energy barrier. The threshold for this transition allows an estimation of the anchoring energy barrier in presence of the external electric field.

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In this paper we used another method to measure the anchoring energy barrier: the observation of the localized rotations of the surface director across surface defects [5] which separate the \( n_0 \) and \( n_0' \) domains. Across such defects the surface director goes from one easy \( n_0 \) to the order one \( n_0' \) by crossing a barrier of maximum anchoring energy \( W \). As usual, \( W \) can be characterized by an extrapolation length \( d \), defined by \( W = K/d \), where \( K \) is a curvature elastic constant of the nematic material. Another typical length associated with the nematic ordering is its coherence length \( \xi \), the length over which a variation of its order parameter modulus \( S \) relaxes. In absence of surface disorientation (i.e., when the director is along the easy axis) the surface order parameter results from the balance between a bulk effect, which tends to induced a non zero value, by continuity from the bulk, and a surface effects which for SiO surface tends to decrease the surface order. This balance depends on the anchoring strength. For weak anchoring \( (d \gg \xi) \), the bulk dominates and the surface ordering along the easy axis compares with the bulk value. The decrease of surface order induced by the disorientation is negligible [6], and the surface order parameter inside the defect, along the anchoring energy barrier, is nearly equal to that along the easy axis. Thus for \( d \gg \xi \) the texture of a surface defect is expected to be purely elastic, with just a continuous change of surface orientation. For strong anchoring \( (d \approx \xi) \), the surface dominates and \( S \) along the easy axis decrease with respect to the bulk value. Due to the disorientation, the surface value of \( S \) on the anchoring barrier is expected lower than along the easy direction and could even become zero inside a core. In this case the structure of the surface defect would not be purely elastic: a core discontinuity would appear. This defect would be a surface line. A priori, one does not know which kind of surface defect will appear on a bistable surface.

To study the type and structure of these surface defects, we have observed cells made with one SiO bistable anchoring plates coupled with a monostable counter-plate creating an antagonistic anchoring. We find that the surface defects are walls. Their structure depends not only on the SiO bistable surface anchoring properties, but also on the texture which connects the bistable anchoring toward the antagonistic monostable counter-plate anchoring. We have found that the elastic torque due to the bulk texture can destabilise the surface wall up to the point to induce a new kind of surface anchoring transition where the surface director orientation on the wall spreads all over the surface.

The plan of the paper is the following: in Section 1 we make the simplest naive prediction on the geometry and on the energy of surface lines and surface walls. In Section 2 we describe the experimental set-up used for the defect observations. In Sections 3, 4 and 5 we discuss the experimental results. Paragraph 3.1 is devoted to the experimental characterization of the nature of surface defects, Paragraphs 3.2, 3.3 and 3.4 to the study of the surface defects structure by varying the antagonistic anchoring of the counter-plate. In Paragraph 3.2 we also describe the new surface wall instability due to the competing effects of the surface anchoring and the bulk texture. Paragraph 3.5 is devoted to the summary of Section 3. In Section 4 we describe the observation of surface defects with high strength. In Section 5, finally, we discuss some new non-elastic surface effects associated with the past history of the sample.

1.1. GEOMETRY. — In this paragraph we describe the nematic bistable anchoring obtained by SiO oblique evaporation on glass and the expected geometrical properties of the surface lines (SL) or surface walls (SW) which are expected to separate two domains of the bistable easy orientations.

The bistable anchoring is obtained by grazing evaporation of SiO on a glass plate [2]. We call \( V \) the evaporation plane \( (x = 0) \), the substrate is the \( z = 0 \) plane (see Fig. 1). It has been shown experimentally that the two easy directions of the bistable anchoring \( n_0 \) and \( n_0' \) are always contained in an oblique plane \( P \) going throughout \( x \cdot P \) is defined by \( Z = 0 \), where
Fig. 1. — Any point on the hemisphere represents the surface director tip. The plane $z = 0$ is the substrate plane, the plane $V(x = 0)$ is the SiO evaporation plane. $n_0$ and $n'_0$ are the two bistable easy directions. $n_0$ and $n'_0$ are symmetrical with respect to the plane $V$ and they are contained in an oblique plane $P$, defined by $Z = 0$, where $Z$ normal to $P$ inside $V$, makes an angle $\alpha$ with $z(\alpha \approx 20^\circ)$. $n_0$ and $n'_0$ are characterized by a zenithal angle $\theta_0$ and azimuthal angles $\varphi_0$ and $-\varphi_0$, respectively. $\theta_0$ and $\varphi_0$ are linked together by the fact that $n_0$ is inside the plane $P$, thus only one angle $\phi_0 = (n_0, Y)$ in the plane $P$ is sufficient to describe the easy direction on an SiO bistable surface.

$Z(Z^2 = 1)$ normal to $P$ inside $V$, makes an angle $\alpha$ with $z(\alpha \approx 20^\circ)$. We take a Cartesian reference frame $XY$ in $P$ with $X$ parallel to $x$ (see Fig. 1). By changing the evaporation parameters, one obtains first a planar monostable orientation (along $X$), then two bistable easy directions which rotate inside $P$ and finally an oblique monostable orientation (along $Y$). In the bistable region of evaporation parameters, the surface presents many domains, each of them characterized by the two easy directions $n_0(\varphi_0, \theta_0)$ and $n'_0(-\varphi_0, \theta_0)$ where $\varphi$ is the azimuthal angle and $\theta$ is the zenithal angle (see Fig. 1). $n_0$ and $n'_0$ are contained in the plane $P$ then the angle $\phi$ between the $Y$-axis and the surface director in the plane $P$ is sufficient to describe the two easy axis: $\phi_0(n_0)$ and $-\phi_0(n'_0)$.

The two domains oriented along $n_0$ and $n'_0$ could be separated by SL or by SW. Whatever may be the defect structure (a core for SL, or a wall for SW) there are two possible ways for the surface director $n$ to go on the surface from one $n_0(\phi = \phi_0)$ domain to the other one $n'_0(\phi = -\phi_0)$. One way is to turn toward the $y$-axis, the other one is to turn toward the $x$-axis. In the first case $n$ has rotated of an angle $2\phi_0$ in the plane $P$, in the second case it has rotated of an angle $\pi - 2\phi_0$.

Let us discuss first the SL. When we have a SL the two bistable domains are separated by a core. The surface director $n$ across the SL starts parallel to one easy direction $n_0$ then jumps toward the other one $n'_0$ through the core. By analogy with the bulk disclination line (BL), the SL are classified by their strength. The strength $m$ of a BL is defined by the ratio between the angle which the director makes when we make a complete loop around the line and $2\pi$. Due to the symmetry $n \rightarrow -n$ only integer or semi-integer strength lines can exist in the bulk. The same classification apply to the SL with the difference that on the surface, the strength of the line is not limited to integer or semi-integer but can be any real number [7]. In our case we find $m_1 = \phi_0/\pi$, and $m_2 = 1/2 - \phi_0/\pi$ for the two types of SL.

In the case of a SW, $n$ across the SW turns in a continuous way from $\phi = \phi_0$ to $\phi = -\phi_0$ in the plane $P$ of a total angle $2\phi_0$ or $\pi - 2\phi_0$. By analogy with the SL, the SW can be classified by their strengths: $m_1 = \phi_0/\pi$ when $n$ rotates of $2\phi_0$ across the SW, and $m_2 = 1/2 - \phi_0/\pi$ for a rotation of $\pi - 2\phi_0$. 
1.2. ENERGY. — In this paragraph we discuss the cost in energy of the SL or SW on the bistable anchoring surface. We do not consider now the influence of the bulk textures, i.e. we treat the case of a semi-infinite sample. The surface energy $E$ per unit of length of SL or SW is defined as 

$$E = \int_{-\infty}^{+\infty} (W(\phi(x)) - W_0) \, dx$$

where $\phi(x)$ is the variation of the surface director along an axis perpendicular to SL or SW and $W_0$ is the anchoring energy for $n \parallel n_0$. The energy $E$ has been calculated in the case of planar bulk distortion around the SW or SL when the molecular field condition $\nabla^2 n \times n = 0$ reduces to the simpler equation $\nabla^2 \theta = 0$ [7], where $\theta$ is a generic angle describing the planar director orientation. In the hypothesis of isotropic elastic constant $K$, $E$ has then the simple expression:

$$E = 2\pi Km^2$$  \hspace{1cm} (1)

$E$ is independent from the anchoring energy, it depends only on the SL or SW strength $m$. There is a compensation between the anchoring energy and the surface director profile to give a SL or a SW energy independent from the anchoring energy. In our case the $n$ deformation along the SL or the SW is in the $P$ plane and the induced bulk deformation is not in a plane but depends on both angles $\theta$ and $\varphi$. The molecular field condition is not expressed by the simple equation $\nabla^2 \theta = 0$. In consequence, equation (1) is not valid, and $E$ has a more complicated expression. In particular it should depend now explicitly on the $W(\phi)$ expression. The $W(\phi)$ bistable anchoring energy has been recently measured [3]. Using the mirror symmetry with regard to $V$ and truncating the development to the 4th-order terms in $(n \cdot n_0)$ the anchoring energy is

$$W(\eta, \zeta) = a_1 \zeta^2 + a_2 \eta^2 + a_3 \zeta^4 + a_4 \eta^4 + a_5 \eta^2 \zeta^2 + a_6 \eta \zeta + a_7 \eta^2 \zeta + a_8 \eta \zeta^2$$  \hspace{1cm} (2)

where $\eta = (n \cdot Y), \zeta = (n \cdot Z)$ and $\xi = (n \cdot X)$. In equation (2) we have used $n^2 = \xi^2 + \eta^2 + \zeta^2 = 1$. Since all easy directions must be inside $P$, the surface director orientations to connect the two bistable easy directions must also be in the plane $P$. The anchoring energy (2), for $n$ in the plane $P(\zeta = 0)$, writes as

$$W(\eta) = a^2 \eta^2 + a_4 \eta^4$$  \hspace{1cm} (3)

where $\eta = \cos \phi$.

The extremum of $W(\eta)$ satisfies the equation:

$$(\partial W/\partial \eta)_{(n=n_0)} = 2\eta_0(a_2 + 2a_4 \eta_0^2) = 0$$  \hspace{1cm} (4)

From equation (4) we have $a_2 = -2a_4 \eta_0^2$ and by substituting $a_2$ in $W(\eta)$ (Eq. (3)) we obtain:

$$W(\eta) = a_4 [\eta^4 - 2\eta^2 \eta_0^2]$$  \hspace{1cm} (5)

By choosing $W(\eta = \eta_0) = 0$, we add a constant term $a_4 \eta_0^4$ in equation (5), and $W(\phi)$ now writes as:

$$W(\phi) = \frac{K}{2d} \left[ \cos^2 \phi - \cos^2 \phi_0 \right]^2$$  \hspace{1cm} (6)

where we have substituted $a_4 = \frac{K}{2d}$. In equation (6), $d$ is the anchoring extrapolation length.

In this approximation, the heights of the two $W(\phi)$ maxima on the $m_1$ and $m_2$ SL (SW) are different with the lower maximum along the lower strength SL (SW). Let us define $W_1$ and
$W_2$ the energy maxima at $\phi = 0$ and $\phi = \pi/2$ of the anchoring energy $W(\phi)$. From equation (6) we have:

$$W_1 = \frac{K}{2d} \sin^4 \phi_0$$

$$W_2 = \frac{K}{2d} \cos^4 \phi_0$$

(7a)

(7b)

Therefore, if $\phi_0 < \pi/4$ ($m_1 < m_2$) we have $W_1 < W_2$ and the opposite if $\phi_0 > \pi/4$. The first consequence of equation (3) is that if $d \approx \xi$ we can expect a decrease, or even a melting, of the order parameter $S$ along the maxima. In this limit a SL is favoured compared to a SW. This melting mechanism is totally different from that which creates the core of bulk lines. In the latter case the core is always present to relax the infinite elastic energy, from the infinite curvature around the line. In the case of the SL, the presence of the core would be due to a value of the anchoring energy barrier larger than the nematic condensation energy. In the opposite case when $d \gg \xi$, probably the more common case, the deformation is continuous and we expect a SW. One can then usually expect to find for $\phi_0 < \pi/4$ and $m_1$ SW and vice versa an $m_2$ SW for $\phi_0 > \pi/4$ between two domains of easy directions $\mathbf{n}_0$ and $\mathbf{n}_0'$.

In the previous paragraphs we have discussed the geometry and the energetics of surface defects in a simi-infinite cell. In a real situation the cell is never infinite, so the structure of the surface defects will depend also on the cell thickness and on the easy direction of the counter-plate. To study the influence of these textural effects, we have observed and characterized surface defects when the anchoring of the counter-plate, the cell thickness $h$ and the angle $\phi_0$ of the bistable domains are changed.

2. Experimental Set-Up

Using bistable plates and various counter-plates, we have built cells of various geometries, which present many domains separated by SL or SW. A typical cell is constituted by two glass plates separated with $0.5 - 5 \, \mu m$ mylar spacers. The lower plate is treated by SiO evaporation to present a bistable anchoring. The upper plate is treated by silane to give a strong monostable "homeotropic" orientation, perpendicular to the surface, or by SiO evaporation to give a strong monostable "planar" anchoring parallel to the surface. The planar monostable counter-plate is mounted with the planar orientation in the evaporation plane of the bistable plate (parallel to the $y$-axis) or with the planar orientation perpendicular with regard to the bistable plate evaporation plane (parallel to the $x$-axis). In the first case, we call the cell a bistable-planar-$y$ cell, in the second case we call it a bistable-planar-$x$ cell. The cell is filled with the nematic liquid crystal 5CB ($4'$-n-pentyl-cyanobiphenyl) in the isotropic phase at $T = 40 \, ^\circ C$. An electric oven is used to heat the nematic cell and to stabilize its temperature within $0.01 \, ^\circ C$. The texture measurements are made by using a polarizing microscope. For the bistable-homeotropic cell the azimuthal angle $\varphi$ of the bistable domains is found by measuring the light extinction directions between crossed polarizers. The zenithal angle $\theta$ is calculated from the measurement of the optical thickness by using a tilting compensator. For the bistable-planar cell the azimuthal angle is measured by assuming the validity of the optical adiabatic theorem [8]. This theorem says that, in the limit of twist distortion with characteristic length larger than the light beam wavelength, the light polarization follows the director orientation variation along the cell. By knowing the orientation on the counter-plate and by measuring the angle between the polarizer and analyzer for the extinction of the transmitted light we can measure the value of the azimuthal angle on the bistable plates.
3. Results and Discussion

3.1. Experimental Characterization of Bulk Lines, Surface Lines and Surface Walls

3.1.1. Surface or Bulk Defects? — By carefully controlling the SiO evaporation parameters (SiO thickness $\delta_{SIO} = 50 \, \text{Å}$ and SiO evaporation angle $\alpha_{SIO} = 75^\circ$) we first make a bistable-monostable planar cell with $\phi_0 = 85^\circ$. The nematic liquid crystal is introduced in the cell in the isotropic phase. After cooling down in the nematic phase we observe many domains, each of them characterized by one of the two orientations $\phi_0$ and $-\phi_0$ in the plane $P$. These domains are separated by surface defects or bulk defects. In Figure 2 one can see two different linear structures, A and B. Structure A has a regular curvature, it is mobile when we induce a flow in the cell, and finally it is visible also without polarizers. Moreover, by tuning the polarizer we cannot follow a black line on structure A, the director orientation across structure A is not continuous, a core is present. These characteristics correspond to that of a bulk line (BL). On the other hand structure B a less uniform curvature (it seems to follow the surface irregularities) and it is not mobile when subjected to a hydrodynamic flow. From this observation we can deduce that structure B is a surface defect, SL or SW.

3.1.2. Surface Line or Surface Wall? — In Figure 3, we show a typical surface structure for a bistable-homeotropic cell ($\delta_{SIO} = 45 \, \text{Å}$, $\alpha_{SIO} = 75^\circ$) with $\phi_0 = 60^\circ$. All the surface defects
Fig. 3 — Bistable-homeotropic cell with $\phi_0 = 60^\circ$ between crossed polarizers: (a) the polarizer is parallel to $\varphi_0(n_0)$, (b) the polarizers have been rotated counter-clockwise until their bisectrices coincide with those of the two bistable domains, (c) clockwise rotation of the polarizers until the analyzer is parallel to the bisectrice of the two bistable domains, (d) one polarizer is parallel to $-\varphi_0(n'_0)$. 
under crossed polarizers present black lines. To know if this defect is a SL or a SW, we follow the displacement of the black line in crossed polarizers when we turn the polarizers. In Figure 3a we start with one polarizer along $\varphi_0(n_0)$ and we turn the polarizers counter-clockwise (Fig. 3b) or clockwise (Fig. 3c) until one polarizer is along $-\varphi_0(n'_0)$ (Fig. 3d). One can see that the two white lines in Figure 3c are transformed in black lines in Figure 3b and vice versa, the white line in Figure 3b is transformed in black line in Figure 3c. We can follow in a continuous way the black line which goes from one domain oriented along $\phi = -\varphi_0$ to the other one $\phi = \varphi_0$. In particular, the surface director on the surface structure explores all orientations in the plane $P$ between the two easy orientations. We do not see any core. We can conclude that the surface defects that we observe are surface walls (SW). In fact, we have never observed surface lines.

3.1.3. Strength Measurement of Surface Walls. — To characterize the SW we measure $\theta_0$ and $\varphi_0$ of the two domains that are separated by the SW. From the values of $\theta_0$ and $\varphi_0$ we calculate the angle $\varphi_0$ in the plane $P$ by the relationship: $\sin \varphi_0 = \sin \theta_0 \sin \varphi_0$. In practice, $\theta_0 = 70^\circ + 90^\circ$ and qualitatively $\varphi$ and $\phi$ compare very much.

To distinguish the $m_1$ SW from the $m_2$ SW we can exploit (a) the total rotation angle across the SW, (b) the director orientation in the center of the SW. For a bistable-homeotropic cell method (a) is more convenient. If $\varphi_0 < \pi/4$ the total rotation angle across the $m_1$ SW is smaller than $\pi/2$. By turning the NLC cell between crossed polarizers we should always observe only one black line. For the $m_2$ SW, instead, the total angle of rotation is larger than $\pi/2$ and we should observe two black lines. The opposite is true when $\varphi_0 > \pi/4$: the $m_1$ SW should have two black lines, the $m_2$ SW should always have only one black line. We can also exploit method (b) and directly measure the director orientation on the center of the SW with a tilting compensator. This method is less accurate than the preceding one due to the small thickness of the SW. For a bistable-planar cell method (b) is the most efficient. We assume the validity of the adiabatic theorem, as we can verify by looking at the good extinction of the transmitted light when the polarizer is parallel to the orientation on the lower plate and the analyzer is perpendicular to the director orientation on the upper plate. We turn the polarizer until it is parallel to the surface director of the planar monostable plate. By turning the polarizer we try to extinguish the intensity in the center of the SW. If we obtain the extinction of transmitted light when the polarizers are parallel (crossed) the orientation direction of the SW is perpendicular (parallel) to the monostable planar plate. By knowing the easy axes azimuthal angle $\varphi_0$ and the orientation of the planar upper plate, we can know if we observe an $m_1$ or an $m_2$ surface wall.

3.2. Bistable-Homeotropic Cell

3.2.1. $\phi_0 < \pi/4$ Bistable Domains. — We now describe the surface defects observed in a cell which has just undergone a single $I \rightarrow N$ transition. The cell is made with a bistable surface with $\phi_0 < \pi/4$ and a counter plate homeotropic with easy axis parallel to the $z$-axis. Figure 4 shows a SW for a bistable-homeotropic cell when $\phi_0 = 25^\circ$ ($\delta_{SiO} = 35$ Å, $\alpha_{SiO} = 75^\circ$). By measuring the total rotation angle across the SW (method (a)), we find that the strength of the SW is $m_1$. The same $m_1$ SW is obtained after many $N \rightarrow I \rightarrow N$ cycles. This result is not surprising since, from equations (3a) and (3b) when $\phi_0 < \pi/4$, the anchoring energy barrier $W_1$ of the $m_1$ SW is lower than the corresponding barrier $W_2$ of the $m_2$ SW.

3.2.2. $\phi_0 > \pi/4$ Bistable Domains

3.2.2.1. $m_1$ Surface Wall. — Figure 5a shows a $\phi_0 = 60^\circ$ bistable-homeotropic cell just after the first cooling down from the isotropic phase in the nematic phase. The two black lines
Fig. 4. — $m_1 = (2\phi_0)/(2\pi)$ surface wall for a bistable-homeotropic cell with $\phi_0 = 25^\circ$ between crossed polarizers.

Fig. 5. — (a) $m_1 = (2\phi_0)/(2\pi)$ surface wall for a bistable-homeotropic cell with $\phi_0 = 60^\circ$ between crossed polarizers, just after the first cooling down from the isotropic phase in the nematic phase. (b) Schematical representation of the director orientation across the $m_1$ surface wall with the induced bulk texture in the case of a bistable-homeotropic cell. By starting from $B'(n_0)$ we go to $B(n_0)$ through the $m_1$ surface wall. The surface director rotates in the plane $P$ with a zenithal angle that, starting from $\theta_0$, goes to $\beta < \theta_0$, just at the energy barrier, and finally return to $\theta_0$. The surface director on the bistable surface is connected with the homeotropic plate $H$ by a splay-bend texture.

in Figure 5a suggest that we have an $m_1$ SW. Figure 5b we show schematically the director orientation across the $m_1$ SW with the induced bulk texture. Points $B(n = n_0)$ and $B'(n = n_0')$ represent the two easy axis orientations on the bistable anchoring. Point $H$ represents the homeotropic orientation on the upper plate. By starting from $B'(n = n_0')$ we go to $B(n = n_0)$
through the $m_1 = 2\phi_0/(2\pi)$ SW, then from $B$ to $H$ with the splay-bend texture of total distortion angle $\theta_0$ (texture (I)) and finally we return to $B'$ along the same texture (I). This result is surprising since from equations (3a) and (3b) when $\phi_0 > \pi/4$, the surface energy barrier $W_2 < W_1$ and the $m_2$ SW should be favoured instead of the $m_1$. In fact, what we know experimentally, is that the total energy (anchoring energy plus the bulk texture energy) of the $m_1$ SW is lower than the corresponding $m_2$ SW energy. Let us now vary the temperature. Figure 6 shows the $m_1$ SW for temperatures approaching $T_c$. From Figure 6a to Figure 6d the temperature goes from $\Delta T = T_c - T = 3.5 ^\circ C$ to $\Delta T = 0.02 ^\circ C$. We take as operative definition of the thickness $s_1$ of an $m_1$ SW the distance between the two black lines in Figure 6. We measure $s_1$ versus the temperature. The $s_1$ thickness diverges, at a temperature slightly above $T_c$. From Figure 6d $s_1 \approx 30 \mu m$ at $\Delta T = 0.02 ^\circ C$. To understand this effect, one must realize that the surface director across the $m_1$ SW goes from $\phi_0$ to $-\phi_0$ by passing through the evaporation plane with a zenithal angle $\beta = \pi/2 - \alpha = 70^\circ < \theta_0$ (see Fig. 5b). The unexpected observation of the $s_1$ critical divergence can be explained as follows: when the surface energy is maximum, at the barrier value $W_1$, the bulk energy of the hybrid cell is minimum, since the bulk curvature is $\beta/h < \theta_0/h$. As one will see in Paragraph 3.2.2.2., equation (19), the total free energy of the $m_1$ SW can be lower than that of the $m_2$ SW because of the weaker bulk curvature, although the surface barrier is higher. To find the equilibrium thickness $s_1$ we must minimize the bulk and surface energy of the $m_1$ SW. The energy per unit of SW length $E_{m_1}$
in the limit $s > h$ and in the isotropic elastic constants $K$ can be roughly estimated as:

$$E_{m1} = \frac{1}{2} K \left( \frac{2\phi_0}{s_2} \right)^2 sh + \frac{1}{2} K \left( \frac{\sin^4 \phi_0}{s_2} \right) s - \frac{1}{2} K h \left( \frac{\theta_0^2 - \beta^2}{s_2} \right) sh$$  \hspace{1cm} (8)

The first two terms in equation (8) represent the cost in elastic energy due to the bulk relaxation of the $\phi$ disorientation across the wall and the cost in the SW anchoring energy. The last term in the right hand of equation (8) represents the gain in the bulk elastic energy due to the smaller zenithal angle $\beta$ across the SW, compared to the zenithal angle $\theta_0$ of the bistable domains. By collecting the common factors in equation (8) $E_{m1}$ writes:

$$E_{m1} = \frac{1}{2} K \sin^4 \phi_0 \left[ \frac{A h}{s} + \left( \frac{h}{d} - B \right) \frac{s}{h} \right]$$  \hspace{1cm} (9)

where the positive constant $A$ and $B$ are given by:

$$A = \frac{(2\phi_0)^2}{\sin^4 \phi_0}$$  \hspace{1cm} (10a)\hspace{1cm} \hspace{1cm} B = \frac{\theta_0^2 - \beta^2}{\sin^4 \phi_0}$$  \hspace{1cm} (10b)

By substituting in equations (6a) and (6b) the measured value of $\theta_0 = 80.6^\circ$ and $\phi_0 = 60^\circ$ in Figure 6 we obtain: $A = 7.8$ and $B = 0.86$. If $h/d \leq B$, $E_{m1}$ (Eq. (9)) is minimized for $s \rightarrow +\infty$, i.e. we have an anchoring transition from the $\pm \phi_0$ bistable anchoring toward a monostable oblique anchoring with $\phi = 0$ and $\theta = \beta$. In the range $B \leq h/d \leq A + B$ the equilibrium thickness $s_1$ writes:

$$s_1 = h \sqrt{\frac{A}{h/d - B}}$$  \hspace{1cm} (11)

Equation (11) tells us that, by varying the anchoring extrapolation length $d$ (for instance when approaching the Nematic-Isotropic transition temperature) or the cell thickness $h$, we can obtain a surface anchoring transition at $d = h/B$ with the oblique orientation just at the center of the $m_1$ SW invading the two domains. Figure 7a shows the $m_1$ SW thickness $s_1$ versus the NLC temperature. Figure 7b shows the extrapolation length $d$ calculated via equation (7).

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**Fig. 7.** (a) $m_1$ SW thickness $s_1$ vs. $\Delta T = T_c - T$ (b) Anchoring extrapolation length $d$ vs. $\Delta T = T_c - T$. The extrapolation length is calculated by the measurement of the $m_1$ surface wall thickness $s_1$ via equation (11).
by the measured values of \( s_1 \) and \( h \cdot d \) increases when the temperature approaches \( T_c \) according to the quantitative measurements present in references [9, 10]. The value of \( d \approx 2 \mu m \) is in agreement with the azimuthal anchoring measurement on planar SiO substrate [11]. It is one order of magnitude larger than the equivalent polar anchoring. Moreover, it is one order of magnitude larger than the observed anchoring barrier of bistable anchoring when the surface transition is induced by an external electrical field [4]. This apparent disagreement will be deeper discussed in the conclusions of the paper. It is principally due to the different rotations of the surface director to pass from one stable state to the other one in the two cases. By substituting \( s_1 \) (Eq. (11)) in equation (9), \( E_{m_1} \) writes:

\[
E_{m_1} = K(2\phi_0)^2 \frac{h}{s_1} 
\]

This result will be used in the next paragraph.

3.2.2.2. \( m_2 \) Surface Wall. — We keep the same cell as in the previous paragraph. After a second heating in the isotropic phase and cooling back in the nematic phase the domains and the SW in Figure 5a transform in those shown in Figure 8. We now observe three different domains. Besides the two bistable domains \( 1(\phi_1 = \phi_0) \) and \( 2(\phi_2 = -\phi_0) \) we observe a new domain \( 1' \) with nearly the same surface angle \( \phi \) as \( 1 \), but with an optical thickness difference \( \Delta \ell_II \) larger than that of domain \( 1(\Delta \ell_I) \). We interpret the domain \( 1' \) as the one for which the

Fig. 8. — The same bistable-homeotropic cell with \( \phi_0 = 60^\circ \) as in Figure 5a, after a second heating in the isotropic phase and cooling back in the nematic phase. The cell is observed between crossed polarizers. We observe three different domains. Besides the two bistable domains \( 1(\phi_1 = \phi_0) \) and \( 2(\phi_2 = -\phi_0) \) there is a new domain \( 1' \) with \( \phi_0 \approx \phi_1 \), but an optical thickness difference larger than that of domain \( 1 \). We observe also three different surface walls: an \( m_1 \) surface wall between the domains \( 1 \) and \( 2 \), an \( m_2 = (\pi - 2\phi_0)/(2\pi) \) surface wall that separates the domains \( 2 \) and \( 1' \) and just at the point of passage from \( m_1 \) to \( m_2 \) a new surface wall that we call \( 1/2 \) that divides the domain \( 1 \) from the \( 1' \).
angular bulk distortion is not $\theta_0/h$ (texture (I)) but $(\pi - \theta_0)/h$ (texture (II)). The existence of the domain $1'$ gives us a simple method to measure the cell thickness $h$ and the surface zenithal angle $\theta$ [12]. We measure $\Delta \ell_1$ on the domain 1 and $\Delta \ell_{11}$ on the domain $1'$ in a point near to the domain 1. From the expression $\Delta \ell = 2\Delta n_0 \tan(\theta/2)h$, where $\Delta n_0$ is the anisotropy of the refraction index, we obtain the cell thickness $h : h = (\Delta \ell_1 + \Delta \ell_{11})/(2\Delta n_0)$ and the surface zenithal angle $\theta = 2\tan^{-1}(\sqrt{\Delta \ell_1/\Delta \ell_{11}})$. In Figure 8 from the measurement of $\Delta \ell_1$ and $\Delta \ell_{11}$ we calculate: $h = 1.7 \mu m$ and $\theta = 80.6^\circ$. The hybrid texture will always distort the bistable anchoring, from the bulk curvature torque. This results in a departure $\Delta n$ from $n_0$. The knowledge of $\theta$ allows us to estimate this departure $\Delta n$. From the measurement of $\varphi_0 = 62^\circ$ and by knowing that the easy axis is on the plane $P$ we calculate $\theta_0 = 80.3^\circ$. By comparing $\theta$ and $\theta_0$ we can conclude that the disorienting effect of the homeotropic counter plate is negligible. In Figure 8 one can see three types of SW. The $m_1$ SW (two black lines) that has been already discussed, an $m_2$ SW (one white line), and just in the point of passage from $m_1$ to $m_2$ another SW that we call 1/2 SW. We now discuss the structure of the $m_2$ SW, the 1/2 SW will be discussed later in Paragraph 3.2.2.3.

The $m_2 = 1/2 - m_1$ SW separates two bistable domains with different bulk texture: texture (I) and texture (II). In Figure 9 we represent schematically the director orientation across the $m_2$ SW with the induced bulk texture. We go from $B'(n = n'_0)$ to $B''(n = -n_0)$ by an

![Fig. 9. — Schematical representation of the director orientation across the $m_2$ surface wall with the induced bulk texture in the case of a bistable-homeotropic cell. By starting from $B'(n'_0)$ we go to $B''(-n_0)$ through the $m_2$ surface wall. Then from $B''$ to the homeotropic plate $H$ with a splay bend texture of total rotation angle $\pi - \theta_0$ (texture II) and finally we return in $B'$ with a splay-bend texture of total rotation angle $\theta_0$ (texture I).](image-url)
Fig. 10. — Schematic representation of the $m_2$ surface wall with the texture (I) and texture (II) domains.

the $x_2$ interface: the $m_2$ SW should shift toward the $x < 0$ and at the same time its thickness should increase. Because the wall remains at equilibrium, there must exists a counter pressure $P$ on the center of the wall to stop the SW, i.e., to balance the total pressure on the SW. The origin of this counter pressure will be discussed in Paragraph 3.5. The total energy per unit length of a pressure-stabilized $m_2$ SW is roughly:

$$E = E_0 - Ph \left(\frac{x_2 + x_1}{2}\right) + \frac{K}{2h^2}(\pi - \theta_0)^2hx_1 - \frac{K}{2h^2}\theta_0^2x_2 +$$

$$+ \frac{1}{2}\cos^4 \phi_0(x_2 - x_1) + \frac{K}{2(x_2 - x_1)^2}(\pi - 2\phi_0)^2 h(x_2 - x_1) + \frac{K}{2h^2}(\pi/2)^2 h(x_2 - x_1)$$ (13)

$E_0$ is an arbitrary constant energy. The first term in the left hand represents the work per unit of SW length gone by the external stabilizing pressure $P$. The third and the last terms in the first row of equation (13) represent the energy cost of a texture (II) extending from $x = 0$ to $x = x_1$ and the gain in energy of a texture (I) extending from $x = 0$ to $x = x_2$. The terms in $x_2 - x_1$ on the second row of equation (13) represent the energy cost of the $m_2$ SW. In particular, the first term is the anchoring energy cost of the SW, the second is the bulk energy of the induced deformation across the SW and finally the last term is the bulk energy of the splay-bend deformation which connects the surface director orientation on the SW with the homeotropic easy direction of the counter-plate. To find the equilibrium thickness $s_2$ of the $m_2$ SW, it is more convenient to express the energy $E$ (Eq. (13)) as a function of $s = x_2 - x_1$ and $X = x_1 + x_2$. $E_{m2} = E - E_0$ writes:

$$E_{m2} = \frac{1}{2}K \left\{ - \frac{Ph}{K}X + \frac{(\pi - \theta_0)^2 X - \theta_0^2 (X + s)}{h} \right\}$$

$$+ (\cos^4 \phi_0) \frac{s}{d} + (\pi - 2\phi_0)^2 \frac{h}{s} + (\pi/2)^2 \frac{s}{h}$$ (14)

By minimizing $E_{m2}$ (Eq. (14)) with respect to $X$, we find the pressure $P$ given by:

$$P = \frac{K}{2h^2} [(\pi - \theta_0)^2 - \theta_0^2]$$ (15)

By injecting $P$ in $E_{m2}$ (Eq. (14)) we get:

$$E_{m2} = \frac{1}{2}K \cos^4 \phi_0 \left[ C \frac{h}{s} + \left( \frac{h}{d} - D \right) \frac{s}{h} \right]$$ (16)
where $C$ and $D$ are positive angular factors given by:

$$ C = \frac{(\pi - 2\phi_0)^2}{\cos^4 \phi_0} \quad (17a) $$

$$ D = \frac{(\frac{\pi}{2} - \theta_0)^2}{\cos^4 \phi_0} \quad (17b) $$

By substituting the measured value of $\theta = 80.6^\circ$ and $\phi_0 = 60^\circ$ in equation (13a) and (13b) we find: $C = 17.5$ and $D = 0.43$. The equilibrium thickness $s_2$ of the $m_2$ SW is given by minimizing $E_{m2}$ (Eq. (16)) with respect to $s$. In the range $h/d < C + D(s > h), s_2$ writes:

$$ s_2 = h \sqrt{\frac{C}{h/d - D}} \quad (18) $$

$s_2$ (Eq (26)) presents also a critical behavior as $s_1$ but for a value $h/d = D = 0.43$ lower than the corresponding critical value for $s_1(h/d = B = 0.86)$. By increasing the temperature, the anchoring extrapolation length $d$ increases and the $m_1$ SW becomes critical before the $m_2$ SW. To test the internal consistency of our model we have measured the SW thickness $s_1 = 6.6 \mu m$ and $s_2 = 2.2 \mu m$ in Figure 8 and we have calculated the anchoring extrapolation length via equations (11) and (18). We find $d_1 = 0.9 \pm 0.2 \mu m$ and $d_2 = 0.3 \pm 0.3 \mu m$ which coincide within the experimental errors. This correspondence from two independent measurements is reasonable, and justifies the rough model used.

The energy $E_{m2}$ is given by:

$$ E_{m2} = K(\pi - 2\phi_0)^2 \frac{h}{s_2} \quad (19) $$

If we compare the $m_1$ total energy $E_{m1}$ (Eq. (12)) with $E_{m2}$ (Eq. (19)) we find that $E_{m2} < E_{m1}$. But we always observe an $m_1$ SW after the first $I \rightarrow N$ transition. Now we are able to explain why the $m_1$ SW (and not the $m_2$) appears after the first $N-I$ transition. We have shown that an $m_2$ SW separates one bistable domain of texture (I) from the other bistable domain of the more energetic texture (II). The $m_1$ SW, instead, separates two domains with the textures (II). Besides, even if the energy of $m_2$ SW $E_{m2}$ is lower than the corresponding energy $E_{m1}$ the total energy $E_2$ of the two textures (I) and (II) separated by an $m_2$ SW could be higher than the corresponding energy $E_1$ of the two equal textures (I) separated by an $m_1$ SW. To do this comparison, we calculate the total energy $E_2$ for a circular domain of radius $R$ oriented along n_0 of texture (II) (case (a) in Fig. 11) with $m_2$ SW and the energy $E_1$ of the same domain with texture (I) and $m_1$ SW (case (b) in Fig. 11). The differences in the total energy $\Delta E = E_1 - E_2$ come from the different energies $E_{m1}$ and $E_{m2}$ of the SW and from the different energy of the bulk texture (I) or (II). $\Delta E$ writes as:

$$ \Delta E = \frac{1}{2} \frac{K}{h} \left( \frac{\pi}{2} - \delta \right)^2 \pi R^2 - \frac{1}{2} \frac{K}{h} \left( \frac{\pi}{2} + \delta \right)^2 \pi R^2 + \Delta E_{SW} 2\pi R \quad (20) $$

where $\delta$ is given by the relationship: $\delta = \pi/2 - \theta_0$ and $\Delta E_{m1} - E_{m2}$ is given by:

$$ \Delta E_{SW} = E_{m1} - E_{m2} = Kh \left[ \frac{(2\phi_0)^2}{s_1} - \frac{(\pi - 2\phi_0)^2}{s_2} \right] \quad (21) $$

The first term in the left hand of equation (20) represents the elastic energy of texture (I), the second term is the elastic energy of texture (II), and the last term linear in $R$ represents
the difference in energy of the two SW. If $\Delta E_{SW} < 0$ we obtain from equation (20) $\Delta E < 0$ and the $m_1$ SW, which separates two domains with equal texture (I), should be realized. Vice versa if $\Delta E_{SW} > 0$, by collecting the common factors in equation (20) we obtain:

$$\Delta E = \Delta E_{SW}2\pi R(1 - \frac{R}{R_c})$$

(22)

where a critical radius $R_c$ is given by:

$$R_c = \frac{2h\Delta E_{SW}}{\pi \delta K}$$

(23)

For $R > R_c, \Delta E < 0$ and an $m_1$ SW with two domains of textures (I) should be realized. If $R < R_c$ we expect from equation (22) $\Delta E > 0$. In this case small domains $R < R_c$ of texture (II) separated from the domain with texture (I) by an $m_2$ SW should be possible. To conclude, the surface walls are coupled with the bulk textures which they separate: the $m_2$ SW is coupled with a texture (I) and a more energetic texture (II), the $m_1$ is coupled only with the less energetic texture (I). Thus for an $m_2$ SW one gains linearly on the line energy but one loses quadratically in the surface energy. From the measured values of $h = 1.7 \mu m$, $\delta = 9.4^\circ$, $\phi_0 = 60^\circ$, $s_2 = 2.2 \mu m$ and $s_1 = 6.6 \mu m$ in Figure 8 we find $R_c = 1.8 \mu m$ using equation (19). Since $R_c \approx s_2$ these domains are too small to be optically observed. In fact, we have seen only the $m_1$ SW after the first Isotropic-Nematic transition.

After a second N-I-N cycle the surface presents an $m_1$ SW as before, but most frequently the $m_1$ SW has left a trace of an $m_2$ SW. This trace can be due to the anisotropic adsorption of NLC molecules or impurities on the surface. The anisotropy of adsorption is due to the nematic anchoring energy: the anisotropic adsorption is more probable along the easy axis than along the anchoring energy barriers. Across the surface wall (anchoring energy maxima), the adsorbed first layer of molecules after the first I-N transition is almost isotropic and does not keep memory of the wall texture. After a second I-N transition the molecules across the surface wall choose the less energetic texture, i.e., the $m_2$ SW. A more detailed discussion on this point will be made in Section 5.

3.2.2.3. 1/2 Surface Walls. — In Figure 8 three types of SW are shown. The two SW $m_1$ and $m_2$, which separate two bistable domains, and a third one, which separates two domains 1 and 1′ with almost the same angle $\phi$ but with different bulk texture (I) and (II). The $\phi$ variation
across this wall is $\Delta \phi \approx \pi$, as one can deduce from the two black line in Figure 8. This SW is an 1/2 SW and its strength is reminiscent of an 1/2 BL which, after the Isotropic-Nematic transition, sticks itself on the surface. On the 1/2 SW, there are two possible ways to connect the two surface orientations: through $\phi = 0$, or through $\phi = \pi$. These two trajectories have nearly equivalent surface energies but induced bulk textures with different energies. Indeed, going above the surface energy barrier $\phi = \pi, \theta = \pi - \beta$ costs more bulk distortion energy compared to the other barrier at $\phi = 0, \theta = \beta$. By following the sense of rotation of the black line on the 1/2 SW, we have experimentally established that the director does go from 1 to 1' by passing across $\phi = 0$. This confirms our theoretical argument. The 1/2 SW is represented schematically in Figure 12. By making a complete revolution around the point where the three lines meet, we recover the same surface orientation: $m_1 + m_2 + 1/2 = 0$. This conservation law is expected, since there is no bulk $\pi$ line appearing at the junction point of the three SW.

![Diagram](image)

**Fig. 12.** — Schematic representation of the director orientation across the 1/2 surface wall with the induced bulk texture in the case of a bistable-homeotropic cell. The surface director across the 1/2 surface wall rotates in the plane $P$ with a zenithal angle that starts from $\theta_0 (n_0')$ and goes to $\pi - \theta_0 (n_0')$ by passing through the angle $\beta$. The surface director on the bistable surface is connected with the homeotropic plate $H$ by a splay-bend texture.

3.3. **Bistable-Planar-$y$ Cell**

3.3.1. **$\phi_0 < \pi/4$ Surface Wall.** — In Figure 13 is shown a SW for a bistable-planar-$y$ cell with $\phi_0 = 12^\circ$ ($\delta_{\text{SiO}} = 30 \, \AA, \alpha_{\text{SiO}} = 75^\circ$). As we can see in the figure, the center of the SW is black between crossed polarizers. There is not twist distortion on the SW, the director in the center of the SW is parallel to the planar anchoring of the counter plate along the $y$-axis. We have an $m_1$ SW. This result is not surprising since an $m_1$ SW has a lower surface energy and also induces a bulk deformation with lower energy compared to the $m_2$ SW. As matter of fact, from equations (7a) and (7b) the anchoring energy barrier $W_1$ of the $m_1$ SW is lower than the corresponding barrier $W_2$ of the $m_2$ SW. Moreover, the splay-bend bulk energy $K((\pi/2 - \beta)/h)^2$, induced by an $m_1$ SW, is lower than the twist bulk energy $K((\pi/2)/h)^2$ induced by an $m_2$ SW. By repeating many cycles of N $\to$ I $\to$ N transitions we keep observing the $m_1$ SW. The $m_2$ SW never appears.
3.3.2. $\phi_0 > \pi/4$ Surface Wall. — In Figure 14a we show a $\phi_0 = 70^\circ$ bistable-planar-$y$ cell ($\delta_{SiO} = 40$ Å, $\alpha_{SiO} = 75^\circ$) just after the first isotropic-nematic transition. We observe two bistable domains 1 and 2 separated by a SW. The center of the SW is black when the polarizers are crossed and the analyzer is parallel to the easy direction of the $y$-planar counter-plate. There is no twist to connect the center of the SW with the planar-$y$ counter-plate, the surface director is along $\phi = 0, \theta = \beta$ and we have an $m_1$ SW. Figure 14b schematically represents the orientation across the $m_1$ SW with the bulk texture which connects the bistable surface to the planar-$y$ counter-plate. The bulk texture on the two bistable domains is the same. These observations are surprising, since the surface anchoring barrier $W_1$ of the $m_1$ SW is larger than the corresponding barrier $W_2$ of the $m_2$ SW. We would expect the appearance of an $m_2$ SW.

We can explain this paradox by the same argument used previously (3.3.2.2.). The bulk texture energy can be more favourable for a SW with the highest surface energy barrier than for the lowest energy barrier. The bistable surface barriers $W_1$ and $W_2$ of the two walls are the same as in 3.3.2.2. with $W_1 > W_2$ from equations (7a) and (7b). The bulk energy of the texture which connects the surface orientation on the SW with the planar-$y$ counter-plate is lower for the $m_1$ SW (we have only a small splay-bend curvature $(\pi/2 - \beta)/h$) than for the $m_2$ SW, that has a twist curvature $(\pi/2)/h$. As in the case of 3.3.2.2., we expect a critical spreading of the $m_1$ SW by approaching $T_c$, but we have not made temperature measurements on this cell geometry. The $m_1$ SW separates two domains with equal texture (I) of twist curvature $\phi_0/h$. The $m_2$ SW, instead, separates two textures of different bulk twist energy: the texture (I) and the texture (II) of twist curvature $(\pi - \phi_0)/h$. Because the $m_2$ SW is at equilibrium, it must be subjected to a counter pressure $P$. The origin of $P$ will be discussed in Section 5. If the total energy $E_{m_1}$ along an $m_1$ SW is lower than the corresponding energy $E_{m_2}$ of an $m_2$ SW, the $m_1$ SW should be realized. On the contrary, when $E_{m_1} > E_{m_2}$, small domains of texture (II) separated from texture (I) domains by an $m_2$ SW should be possible. As in the case of a bistable-homeotropic cell with $\phi_0 = 60^\circ$, the texture (II) bistable domains separated by an $m_2$ SW are expected with a critical size too small to be optically observed.

In Figure 15 the same part of the surface depicted in Figure 14 after a second N-I-N cycle is shown. We see two other SW and two other domains. The two bistable domains 1 and 2 of Figure 14 are splitted into other two 1' and 2'. The transmitted light from the 1' domain is extinguished at almost the same polarizer angle as the domain 1, but the extinction is not perfect. This indicates that the angle at the bistable surface is the same for the 1 and 1' domains, but the twist distortion on the 1' is larger than the equivalent distortion on the 1 domain. The same is true for the domains 2' and 2. In Figure 15a the polarizers are crossed and one can see that the SW between 1 and 2', 2 and 1' domains is white when the $m_1$ SW is
Fig. 14 — (a) $m_1$ surface wall for a bistable-planar-$y$ cell with $\phi_0 = 70^\circ$ soon after the first isotropic-nematic transition. The polarizers are crossed with the analyzer along the monostable planar-$y$ orientation of the upper plate. (b) Schematical representation of the director orientation across the $m_1$ surface wall with the induced bulk texture in the case of a bistable-planar-$y$ cell. By starting from $n'_0$ we go to $n_0$ through the $m_1$ surface wall. The surface director on the two bistable domains is connected with the planar-$y$ plate by a texture with large twist distortion. In the opposite, the surface orientation on the $m_1$ surface wall is connected with the planar-$y$ plate with a simple splay-bend texture with no twist distortion.

black. In Figure 15b the polarizers are parallel to the planar-$y$ orientation of the upper plate and the black (white) lines are now white (black). We have a twist texture on the SW between the 1 and 2', 2 and 1' domains: the director in the center of the wall is perpendicular to the easy direction of the counter-plate and we have an $m_2$ SW. The domain 1 and 1' or 2 and 2' are separated by an 1/2 SW. The $m_2$ SW is schematically represented on Figure 16.
Fig. 15. — The same bistable-planar-γ cell with $\phi_0 = 70^\circ$ as in Figure 14a, after a second heating in the isotropic phase and cooling back in the nematic phase. The two bistable domains 1 and 2 in Figure 14a are split in other two $1'$ and $2'$ with surface orientations $\phi_1' \approx \phi_1$ and $\phi_2' \approx \phi_2$. The bulk distortion to connect the bistable orientations of these two new domains with the monostable planar-γ orientation of the upper plate is larger than the equivalent bulk distortion of the previous domains 1 and 2 (see Fig. 16). We observe also three different surface walls: (a) The polarizers are crossed with the analyzer along the monostable planar-γ orientation of the upper plate. The black lines between the 1 and 2 domains is an $m_1$ surface wall. The other black line is an $1/2$ surface wall that separates the domain 1 from the $1'$ and 2 from $2'$. The white lines represent an $m_2$ surface wall that separates the domain 1 from the $2'$ and $1'$ from 2. This wall is white between crossed polarizers due to the twist distortion which connect the orientation in the center of the wall to the orientation on the planar-γ of the upper plate (see Fig. 16). (b) The polarizers are parallel along the monostable planar-γ orientation of the upper plate. We observe that the white lines in (a) becomes black and vice-versa.

Fig. 16. — Schematical representation of the director orientation across the $m_2$ surface wall with the induced bulk texture in the case of a bistable-planar-γ cell. By starting from $n_0'$ we go to $-n_0$ through the $m_2$ surface wall. From $-n_0$ we go to the planar-γ orientation of the upper plate with essentially a twist distortion of total angle $\pi - \varphi_0$, then we return in $n_0'$ by a twist distortion of total angle $\varphi_0$. The surface orientation on the $m_2$ surface wall is connected with the planar-γ plate with a twist texture.
3.4. Bistable-Planar-x Cell

3.4.1. $\phi_0 > \pi/4$ Surface Wall. — In Figure 17 are depicted the SW and the bistable domains on a $\phi_0 = 58^\circ$ bistable-planar-x cell ($\delta_{SiO} = 40$ Å, $\alpha_{SiO} = 75^\circ$) after the first I-N transition. The SW between the two bistable domains is black when the polarizers are crossed; the director in the center of the SW is parallel to the planar anchoring of the counter plate along the $x$-axis.

![Image 17. Bistable-planar-x cell with $\phi_0 = 58^\circ$ between crossed polarizers with the analyser parallel to the monostable planar-x orientation of the upper plate. We always observe an $m_2$ surface wall.](image17.png)

Now, in contrast with the case of a bistable-planar-y cell discussed in 3.3.1, we have an $m_2$ SW. This result is not surprising since the $m_2$ SW costs less in surface energy than the $m_1$ SW, as shown the previous case (from Eqs. (7a) and (7b), $W_2 < W_1$), but also the bulk energy, connected to the distortion on the SW, costs less. There is no distortion to connect the center of the $m_2$ SW with the planar-$x$ counter-plate, whereas there is a twist deformation of $(\pi/2)/d$ for the $m_1$ SW. By repeating many N-I-N cycles the $m_1$ SW is never observed.

3.4.2. $\phi_0 < \pi/4$ Surface Wall. — Figure 18 represents a bistable-planar-x cell with $\phi_0 = 12^\circ$. The center of the SW is black between crossed polarizer. We have also an $m_2$ SW. The discussion of the observations is similar to that for the two previous cases of bistable-homeotropic cell with $\phi_0 > \pi/4$ and of bistable-planar-y cell with $\phi_0 > \pi/4$ in Section 3.3.2. The bistable surface barriers $W_1$ and $W_2$ of the two walls are the same as in the previous cases.

![Image 18. Bistable-planar-x cell with $\phi_0 = 12^\circ$ after the first cooling down from the isotropic phase to the nematic phase. The polarizers are crossed with the analyzer parallel to the monostable planar-x orientation of the upper plate.](image18.png)
with, from equation (7a) and (7b), $W_1 < W_2$. The bulk energy of the texture, connecting the surface orientation on the SW with the planar-$x$ counter-plate, is zero for the $m_2$ SW. The $m_1$ SW, instead, induces a bulk distortion energy with a twist energy $K((\pi/2)/h)^2$ and a splay-bend energy $K((\pi/2 - \beta)/h)^2$. Moreover the $m_2$ SW separates two domains with equal texture (I) of twist curvature $(\pi/2 - \phi_0)/h)$. The $m_1$ SW separates two textures of different bulk twist energy: the texture (I) and the texture (II) of twist curvature $(\pi/2 + \phi_0)/h)$. As the $m_1$ SW is at equilibrium it must be subjected to a counter pressure $P$. The origin of $P$ will be discussed in Section 5. If the total energy $E_{m2}$ along an $m_2$ SW is lower than the corresponding energy $E_{m1}$ of an $m_1$ SW, the $m_2$ SW should be realized. In the opposite, when $E_{m2} > E_{m1}$ a small domain of texture (II) separated from texture (I) domains by an $m_1$ SW should be possible. As in the case of a bistable-homeotropic cell with $\phi_0 = 60^\circ$, the texture (II) bistable domain separated with an $m_1$ SW are too small to be optically observed. The $m_1$ SW never appears even by repeating many N-I-N cycles.

3.5. Summary. — To summarize, we have studied how the observed surface walls on the bistable plates depend on the antagonistic anchoring of the counter-plate and on the angles $\phi_0$ and $-\phi_0$ of the bistable anchoring. We have studied six cell geometries made with a $\phi_0 < \pi/4$ or $\phi_0 > \pi/4$ bistable anchoring coupled with counter-plates of two different anchoring: strong homeotropic and strong planar-monostable. We have more particularly studied the case of thin cells, where the textural effects are the more important. In this limit, in all the six cell geometries analyzed, we always observe the surface wall with lower bulk energy. For half the observed situations, this also corresponds to the lowest surface anchoring barrier. For the other half, the bulk can force the existence of surface defects which present the highest surface energy barrier. Changing the temperature or decreasing the thickness, one can even force the surface orientation of the bistable plate to adopt an uniform orientation corresponding to its maximum of energy. This corresponds to a new kind of surface anchoring transition imposed by the bulk. The measurement of the critical thickness where the walls become unstable allows to determine the corresponding surface energy barrier.

4. Higher Strength Surface Walls

After the first $I \rightarrow N$ transition, besides the $m_1$ and $m_2$ SW, we often see higher-order surface walls. These walls disappear most often after the subsequent N-I-N cycles.

4.1. $\phi_0 > \pi/4$ Surface Walls. — Figure 19a shows a $\phi_0 = 60^\circ$ bistable-homeotropic cell with two bistable domains of identical texture (I) and two SW. Between crossed polarizers, one wall always shows one black line, while the other one may present three black lines or branches. The first SW is an $m_1$ SW, while the other is a new higher strength SW of strength $m_3 = (2\pi - 2\phi_0)/(2\pi) = 1 - m_1$. The $m_1$ SW is converted into an $m_2$ SW by one defect point of strength $\pm 1$ and then the $m_3$ is transformed back into an $m_1$ SW by a point defect of opposite sign. We have never observed light scattering around these points. This implies that around these points the surface director varies continuously. The structure of these coreless surface points is different from the usual bulk points with core. Figure 19b schematically represents an $m_3$ SW.

4.2. $\phi_0 < \pi/4$ Surface Wall. — Figure 20a shows a $\phi_0 = 3^\circ$ bistable-homeotropic cell ($\delta_{SiO} = 30$ Å, $\alpha_{SiO} = 75^\circ$) relatively thick ($h \approx 5$ μm) with two bistable domains of identical texture (I) and two SW $m_1$ and $m_3$. The influence of the bulk texture on the surface is negligible and we can assume to have a semi-infinite cell. Now the $m_3$ SW can show (between crossed
Fig. 19. — (a) Bistable-homeotropic cell with $\phi_0 = 60^\circ$ between crossed polarizers. Besides the $m_1$ surface wall (with one black line), we observe an $m_3 = (2\pi - 2\phi_0)/(2\pi)$ with three black lines. (b) Schematical representation of the director orientation across the $m_3$ surface wall with the induced bulk texture in the case of a bistable-homeotropic cell. By starting from $B'(n'_0)$ we go to $B(n_0)$ through the $m_3$ surface wall. From $n_0$ we go to the homeotropic orientation of the upper plate with a splay-bend texture (I), then we return in $n'_0$ with the same texture. The surface orientation across the $m_3$ surface wall passes three times along the polarizers.

polarizers) four black lines or branches as one sees in Figure 20a. The director orientation across the $m_3$ SW is not uniform but the central part of the line is twice larger than the two side parts. On this SW the surface director goes across the $W_2$ maximum in the surface plane ($\phi = \pi$), across the $W_1$ maximum inside the evaporation plane ($\phi = (3/2)\pi$) and finally again across the $W_2$ maximum ($\phi = 0$). In the central part of the wall, $n$ is oriented along $\phi = (3/2)\pi$ while in the two-side parts it is oriented along $\phi = 0$ and $\phi = \pi$. The different thickness of
the central part of the $m_3$ SW compared to the side parts reflects the difference in the surface barrier height $W_1$ and $W_2$. From Figure 20a we deduce that $W_1 < W_2$. This result is expected for $\phi_0 = 3^\circ$ since from equations (7a) and (7b) we have $W_1 < W_2$.

Figure 20b shows the same cell geometry with the same $m_3$ SW as in Figure 20a but with a thin cell of thickness $h \approx 0.5 \mu m$. Here, we can observe just the opposite of Figure 20a: the side parts of the $m_3$ SW are thinner than the central one. For cell thickness so small the reaction of the bulk texture on the surface is more important than the anchoring energy effect. On the central part of the SW, $n$ is along $\phi = (3/2)\pi, \theta = \pi - \beta$, while on the side parts it is parallel to $\phi = 0$ or $\phi = \pi$ and $\theta = \pi/2$. The bulk texture energy to connect the surface bistable director to the homeotropic counter-plate is higher for the central part ($\theta = \pi - \beta$) compared to the side parts ($\theta = \pi/2$). In this small thickness case, the gain in texture energy becomes more important than the cost in surface energy, as previously discussed. Anyway, the energy cost of the $m_3$ SW is higher than the $m_1$ and we have observed that $m_3$ SW is metastable and disappears, leaving an $m_1$ SW when we approach the nematic-isotropic transition.

5. Non-Elastic Effects

We have repeated many N-I-N cycles on all our samples. When we lower the temperature of the cell from the isotropic phase to the nematic phase, the transition is not homogeneous but the nematic phase appears first as bubbles in an isotropic background. The nematic director at the nematic-isotropic interface of the bubble is at the “magic” angle $\theta = 53^\circ$ from the interface normal [13]. The director orientations at the isotropic-nematic interface of two neighbouring bubbles can be in the same or just in the opposite directions (see Fig. 21). In the last case, by lowering the temperature, the isotropic phase in between two bubbles disappears leaving a nematic phase with director orientations just in opposite directions. The isotropic phase is not completely replaced: an 1/2 BL remains. These lines from always loops. If the loop has a small radius it annihilates before reaching the surface. *Vice versa*, if its dimensions are large, it goes toward the surface where it remains sticked on. By repeating many cycles of heating in the isotropic phase and cooling down deep in the nematic phase, we observe, in all the six cell geometries analyzed, that the bistable domains which appear after the first isotropic-nematic transition remain at the same place on the bistable surface. The new BL which are produced after the second I-N transition stick themselves preferentially along the trace left by the SW formed after the first I-N transition. If the second I-N transition is very fast, the BL can stick
at any region of the surface giving rise to 1/2 SW. In Figure 22 for instance we show the same $\phi_0 = 60^\circ$ bistable-homeotropic cell, as in Figure 5a, after five N-I-N cycles, going each cycle deep into the nematic phase at $\Delta T = T_c - T = 10$ °C. After the first I-N transition the surface presents only an $m_1$ SW. In Figure 22a, after the second N-I-N cycle, the surface presents an $m_1$ SW as before, but most frequently the $m_1$ has left a trace of an $m_2$ SW and an 1/2 SW has retransformed this trace in an $m_1$ SW. In Figure 22b, after a third N-I-N cycle the $m_2$ has been replaced by an $m_4$ SW and the 1/2 SW has left its trace on the surface. After a fourth N-I-N cycle one part of the $m_1$ SW is transformed back in an $m_2$ SW and new 1/2 SW appears (Fig. 22c). Finally in Figure 22d, all the walls between the two bistable domains are $m_2$. New 1/2 SW appear together with new 1/2 SW traces. These traces remain after many transitions in the isotropic phase. They disappear only after days in the isotropic phase.

On the opposite, if after the first transition the nematic is left at a temperature close to $T_c$ the surface orientation printing is much weaker. After a second N-I-N cycle we can obtain one bistable domain $n_0$ where before there was the orientation $n_0'$ and no traces are left by the $m_1$ SW. This memory effect is reminiscent of that already described in the pioneering work of Friedel [14] on glass surfaces. More recently it has been found on SiO surfaces [15] and on polymer surfaces [16]. It can be due to the adsorption of NLC molecules or impurities on the surface.

To understand this memory effect we imagine, as in reference [16], the surface with a distribution of assumed isotropic adsorption sites. An anisotropic adsorption energy is created by the nematic anisotropic anchoring energy: the anisotropic adsorption is more probable along the easy axis than along the anchoring energy maxima. The probability of anisotropic adsorption along the anchoring energy maxima decreases with respect to the equivalent adsorption along one easy direction, by a factor $\sigma$ given by: $\sigma = \exp\left(\frac{(K/d)\xi^2}{k_B T}\right)$, where $k_B$ is
the Boltzmann constant and $T$ the absolute temperature. The energy $(K/d)\xi^2$ represents the anisotropic surface energy of a NLC packet of dimension $\xi$ oriented along the anchoring energy maximum. By substituting the elastic constant $K$ with the expression $K = (k_B T S^2)/L$ ($L$ is the molecule length and $S$ the order parameter) and the coherence length $\xi$ by $\xi = L/S$, we obtain $\sigma = \exp[-L/d]$. At a $T \ll T_c$, $L/d \approx 1/10$ we find $\sigma \approx 0.9$, i.e. the anisotropic modulation of the adsorption due to the anchoring energy is small but not negligible. At a temperature close to $T_c$ the anchoring energy becomes very weak with a very long extrapolation length $d$. In this case $L/d \approx 1/1000$, the adsorption is almost isotropic ($\sigma \approx 1$) and no memory effect could be observed. After a second N-I-N cycle we observe that, where there was previously an $m_1$ SW, now there is a SW which presents the structure of an $m_2$ SW. This is not surprising since, as we have suggested, the anisotropic adsorption is strong along the surface easy axes $n_0$ and $n_0'$ and it is almost isotropic along the barrier of the anchoring energy, i.e. across the surface wall. Across the surface wall, the adsorbed first layer of molecules after the first I-N transition is almost isotropic and does not keep memory of the wall texture. After a second I-N transition the molecules across the surface wall choose the less energetic texture, i.e. the $m_2$ SW.

In Section 3.2.2.2 we have shown that the $m_2$ SW is unstable being subjected to a pressure. This pressure was supposed to be balanced by a counter-pressure $P$ of opposite sign. We can now understand a possible origin for the counter-pressure $P$ that prevents the $m_2$ SW to move: the surface memory effect gives a positional anchoring to the walls. This can be considered as a solid friction mechanism. We can estimate $P$ by looking at Figures 23a and 23b. In Figure 23a
we have a $\phi_0 = 85^\circ$ bistable-homeotropic cell with two domains 1 and 1' of equal surface orientations and different bulk textures separated by an 1/2 SW. Because the mechanism that produces the counter-pressure is the same in the case of an 1/2 SW and an $m_2$ SW, we can estimate the order of magnitude of $P$ on an 1/2 SW. Figure 23b shows the same part of the surface as Figure 23a just after another N-I-N cycle. One can see that, where there was the 1/2 SW, there remains now a weak trace. This trace is the memory of the 1/2 SW. In figure 23a we call $r$ the curvature radius of the 1/2 SW. For a variation $\Delta r$ of the 1/2 SW curvature radius, the total energy variation $\Delta E$ writes as:

$$\Delta E = \frac{K}{2h^2} \left( \frac{\pi}{2} - \delta \right)^2 h\chi r \Delta r - \frac{K}{2h^2} \left( \frac{\pi}{2} + \delta \right)^2 h\chi r \Delta r + E_{1/2} \chi \Delta r + Ph\chi r \Delta r$$  \hspace{1cm} (24)$$

where $r\chi$ is the length of the 1/2 SW, $\delta = \pi/2 - \theta_0$, $h$ is the cell thickness and $E_{1/2}$ is the elastic energy per unit length of the 1/2 SW. The two first terms in the right hand of equation (24) represent the variation of the bulk energy in the domain 1 and 1' when the 1/2 SW is displaced.
of $\Delta r$ from the domain 1 toward the domain 1'. The third term represents the variation in the elastic energy associated to the 1/2 SW. By analogy with the $E_{m1}$, $E_{m2}$ expression equations (12) and (19), the elastic energy per unit length of the 1/2 SW $E_{1/2}$ writes as

$$E_{1/2} = K \pi^2 \frac{h}{s_{1/2}}$$

(25)

where $s_{1/2}$ is the thickness of the 1/2 SW. The last term in the right hand equation (24) represents the work that must be done against the positional anchoring pressure $P$ to displace the 1/2 SW. By imposing the equilibrium condition $\Delta E/\Delta r = 0$ in equation (24) we obtain a lower limit $P_c$ of the solid friction counter-pressure given by:

$$P_c = \pi K \left[ \frac{\delta}{h^2} - \frac{\pi}{\tau s_{1/2}} \right]$$

(26)

By measuring $r = 96$ $\mu$m, $\delta = 5^\circ$, $h = 0.6$ $\mu$m and $s_{1/2} = 4$ $\mu$m, by knowing $K = 6.6 \times 10^{-7}$ (cgs), we find $P_c = 4.8 \times 10^4$ barye. The positional anchoring which gives rise to the counter-pressure $P$ can be interpreted as an orientational anchoring of the first layers of molecules with fixed positions [1]. The shift of the 1/2 SW is equivalent to disorient the first layers of molecules in the center of the SW from its direction to the easy direction of one domain and to disorient the molecules in the other domains along the direction in the center of the SW. By defining an anchoring extrapolation length of the bulk molecules above the first layer $d_c^*$, the energy per unit length associated with this first layer can be written as: $(K/d_c^*) s_{1/2}$. By equalizing this energy to the positional anchoring energy per unit of length $P_c h r$ we obtain for $d_c^*$:

$$d_c^* = \frac{K s_{1/2}}{P_c h r}$$

(27)

Using the measured value of $s_{1/2}$, $h$, $r$ and the known values of $K$ and $P_c$ in equation (26) we find an upper limit of the extrapolation length $d_c^*$ given by: $d_c^* = 8 \times 10^{-2}$ $\mu$m. This anchoring is one order of magnitude larger than the elastic one.

We have discussed the stability of the walls for displacements perpendicular to their orientation. We can now discuss the stability of surface walls for displacements parallel to their orientation. The question arises at a junction of three surface walls. In two dimensions, we locally recognize the same problem as the one of wetting a surface by a fluid. Projecting the surface tensions along the common direction, we obtain the Young-like relationship:

$$E_{m2} + E_{1/2} \cos \gamma = E_{m1}$$

(28)

where $\gamma$ is the angle between the direction of the 1/2 SW and the common direction of the $m_1$ and $m_2$ SW. We compare the angle $\gamma$ in equation (28) to the measured angle $\gamma_m$ at the attaching point of the 1/2 SW on the $m_2 - m_1$ SW in Figure 23a. The value of $E_{m1}$, $E_{m2}$ and $E_{1/2}$ are obtained from the measured values of $s_1$, $s_2$ and $s_{1/2}$ in Figure 23a by using equations (12), (19) and (25), respectively. We find $\gamma = 46^\circ$ in reasonable agreement with the measured value in Figure 23a of $\gamma_m = 45^\circ$.

6. Conclusion

We have the surface energy barrier which separates bistable orientations of a nematic liquid crystal. To do this, we have studied the nematic textures which appear above bistable anchoring plates obtained by oblique evaporation of SiO. These textures are constituted by domains of
either one of the two possible easy orientations on the surface. The domains are separated by linear surface defects. We have studied the structure of these defects. We have found a continuous variation of the surface director orientation across the defects. The defects are surface walls (without core) and not surface lines (with core). We find that usually two kinds of surface walls on a bistable surface exits. On one wall the surface director barrier orientation is inside the evaporation plane, on the second one, the barrier orientation is in the substrate plane, perpendicular to the evaporation plane. The sequence of these two walls is equivalent to a single $\pi$ wall.

To study how the surface wall type depends on the antagonistic anchoring of the counter-plate and on the bistable anchoring, we have made cells with different bistable surfaces coupled with monostable counter-plates with three different strong anchoring: homeotropic or two perpendicular planar ($x, y$) orientations. More particularly we have studied the case of thin cells, where the textural effects are the more important. In this limit, in all the six cell geometries analyzed, we always observe the surface wall with lower bulk energy. For half the observed situations, this also corresponds to the lowest surface anchoring barrier. For the other half, the bulk can force the existence of surface defects which present the highest surface energy barrier. Changing the nematic liquid crystal temperature or decreasing the cell thickness, one can even force the surface orientation of the bistable plate to adopt an uniform orientation corresponding to its maximum of energy. This corresponds to a new kind of surface anchoring transition imposed by the bulk. We have modelized this surface anchoring transition.

By measuring the surface wall thickness we have calculated, using our model, an anchoring barrier extrapolation length $d \approx 1 \mu m$. $d$ is found to diverge close to the Nematic-Isotropic transition temperature, in agreement with quantitative measurements in literature [9, 10]. This anchoring is relatively weak. Its value is in good agreement with independent measurements made with an external applied magnetic field [11], but it is one order of magnitude smaller than the observed anchoring barrier of bistable anchoring when an uniform surface switch is induced by an external electric field [4]. This is principally due to the different behaviour of the surface director in the two cases. The surface transition to pass from one stable surface state to the other one of the bistable anchoring can be described by a trajectory of the director on the hemisphere of Figure 1. In the case of a surface transition across defects, this trajectory lies on (or very close to) the oblique plane $P$. The bifurcation point [3] of such a transition is the oblique $Y$-axis. This corresponds to a rotation of the surface director with a large azimuthal variation $\Delta \phi$ and a small polar change $\Delta \theta$. In this case, for the sake of simplicity, we can imagine that the surface energy barrier $\Delta W$ depends only on $\phi$, $\Delta W = \Delta W(\phi)$. On the contrary, an electrically induced uniform surface transition between the two stable surface states describes on the same hemisphere of Figure 1a trajectory with a large azimuthal and polar variations $\Delta \phi'$ and $\Delta \theta'$. The large $\Delta \theta'$ is principally due to the dielectric coupling between the electric field and the nematic director. In this case, the bifurcation point is in the plane $V$, far from the $Y$-axis, towards the $y$- or $z$-axis. The surface energy barrier $\Delta W$ has to depend on both $\phi$ and $\theta$, $\Delta W = \Delta W(\theta, \phi)$. In conclusion, as the polar contribution to the anchoring energy on such surfaces is expected stronger than the azimuthal one, the energy barrier for the electrically induced transition is expected higher than in the case of the transition through surface defects, in agreement with our experimental results.

We also observe interesting hysteresis effects. After many N-I-N cycles, by going deep in the nematic phase, the bistable domains always appear in the same place. As a general rule, a region which was once oriented along one bistable easy direction maintains the same orientation. Orientational changes come from defects which, coming from isotropic-nematic interfacial bulk disclination lines, eventually intersect the surface, where they transform into surface walls. These new walls are printed on top of each other after each Isotropic-Nematic new transition.
This memory effect could be due to the well known adsorption of a first layer of nematic molecules on the surface, with forces larger than the typical nematic forces. The nematic anchoring energy, if sufficiently strong, generates an anisotropy of the adsorption. The first anisotropic layer of adsorbed molecules gives also a non-elastic contribution to the nematic anchoring energy which depends on the sample history. We have experimentally estimated an equivalent extrapolation length $d^*$ for the non-elastic anchoring energy of the first layer lower than $8 \times 10^{-2} \mu m$, i.e., an anchoring energy of more than one order of magnitude larger than the elastic one. This behavior is probably very general and should apply to monostable anchoring as well. It would be important to measure the non-elastic contribution to the previously measured surface anchoring of nematic liquid crystal. It will be important also to better understand this memory effect, which could disturb the making of displays with electrically controlled surface anchoring bistability [17] in nematic liquid crystals.

References