Theory of the anticlinic pretilted surface phase in tilted chiral smectic films

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In freely suspended chiral smectic films, the molecules tilt at the surfaces above the bulk ferroelectric transition temperature. The tilt angle at the two surfaces can be either equal (*synclinic* surface phase) or opposite (*anticlinic* surface phase) on each surface of the film. We propose a realistic theoretical model accounting for the stability and properties of these two structures, based on competing surface interactions. The anticlinic phase is stable for sufficiently thin samples and high temperatures. We predict a reentrant Sm*A* phase merging with the surface phases at a three-phase point.

Free standing films have been widely used to elucidate the structures and confinement effects in chiral tilted smectic mesophases [1]. These mesophases present complex tilt orders associated with one (SmC^*), two (SmC_A), three (SmC_{FI1}) or four layers (SmC_{FI2}) [2] or even with incommensurate (SmC_α) superstructures [3]. In the chiral ferroelectric SmC^* phase all the molecules are tilted to the same angle with respect to the normal to the smectic layers. In the antiferroelectric SmC_A phase the direction of the tilt is reversed from one layer to the next. Both phases condense below the same parent paraelectric SmA structure [4]. Due to their chiral character they exhibit induced ferro- or antiferroelectric ordering. A number of these phases are also stabilized in thin films [5,8], where their structures are modified by the interactions of the tilt order with the sample walls. For negative coupling energy, the low symmetry state is favored and the ordering process begins at the surface, above the bulk transition temperature. This effect has been evidenced in several compounds and theoretically studied by Heinekamp *et al.* [6] and by Tilley and Zeks [7]. In SmC^* if the walls are isotropic and if the sample thickness is much smaller than the helix pitch, then the molecular tilts are equal at the two surfaces. This defines the geometry of the "synclinic" surface phase.

Recent experiments [5,6] have evidenced a radically different situation in homeotropic freely suspended films: The tilt is reversed from the upper to the lower surface. The corresponding phase was termed the "anticlinic" surface phase by Link *et al.* [8], in order to distinguish it from the previous "synclinic" surface phase. Its structure has been described within another context by Tilley and Zeks [7], who predicted that the anticlinic state is unstable. It was finally observed [9] under an applied electric field. The stability of the anticlinic structure was then explained by the coupling of the induced polarization with the field. Later on, Link *et al.* [8] evidenced an anticlinic state stable at arbitrarily small fields and claimed that it was stable even at zero field strength. In some materials the phase behavior is complicated by the existence of a ferroelectric-antiferroelectric transition, both bulk orders possibly yielding their own surface states [10]. The anticlinic

and synclinic surface states have also been evidenced in quite thick suspended films made with achiral banana-shaped molecules [11]. Although the molecular structure of the corresponding unconventional bulk "tilted" phase (B2) has not yet been clarified, its helical nature was claimed in a recent theoretical model [12] stating the secondary character of the layered smectic order in the B2 phase. So the synclinic and anticlinic surface states have been observed in a variety of compounds for a large range of film thicknesses. In order to account for the anticlinic vs synclinic stabilization, bulk effects have been proposed, based on effective intersurface long range electric forces [13] resulting from in-plane thermal fluctuations of the polarization. The aim of this article is to propose a simpler mechanism accounting for the anticlinic phase stability, even in absence of applied electric field and without recourse to any effective intersurface coupling. Our model is less specific and may be applied *a priori* to any tilted compound, whatever the thickness of the film, the chiral character of the molecules, or the nature of the bulk interactions. The proposed mechanism results only from the combined effects of a tilt-surface interaction depending on the derivative of the tilt order parameter and of the elastic bulk energy. This surface coupling favors a nonconstant tilt in the vicinity of the surfaces, and is associated with nonlocal interactions of the tilt with the walls (their range is greater than one interlayer distance d but can be much smaller than a typical sample width $\approx 10d-100d$). It competes with the standard tilt-surface interaction which forces the first layer to tilt and stabilizes only the synclinic structure [7]. The proposed mechanism can happen in either ferroelectric or antiferroelectric materials and is independent of a possible transition between these two types of order. For clarity we shall only present the model for ferroelectric (SmC^*) materials.

The order parameter (OP) associated with the transition from the paraelectric SmA phase to the ferroelectric SmC^* phase is an axial vector denoted $\boldsymbol{\tau}$ (perpendicular to the projection of the molecular axis onto the smectic x-y planes). Its components $\tau_x = \rho \cos \phi$ and $\tau_y = \rho \sin \phi$ describe the amplitude (ρ) and direction (azimuthal angle ϕ) of the molecular tilt vector [2]. The tilt vector and the induced polarization precess so as to form the typical helicoidal structure observed in chiral mesophases. In order to account for confinement effects, let us consider a sample of thickness $2L$ limited

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by two identical isotropic surfaces parallel to the smectic planes, for instance, a homeotropic SmA phase bounded by glass, liquid, or gas interfaces. Let z be the coordinate in the direction normal to the smectic layers, with $z=0$ at the center of the sample. Within the framework of the Landau theory of phase transitions [14], the bulk free energy associated with the tilting process reads [2] $F_{\text{bulk}} = \int \rho^2 [A + (\phi' +1)^2] + \rho^4 + \rho'^2 dz$ (in dimensionless form), where $\rho' = d\rho/dz$ and $\phi' = d\phi/dz$. The single critical coefficient A varies as $(T - T_{c0})$, where T_{c0} is the SmA $\leftrightarrow$ SmC* bulk transition temperature. Since the walls are isotropic, the free energy resulting from the interaction of the OP with the sample surfaces is invariant to the two-dimensional continuous rotation group of the smectic layers, and may be written

$$F_{\text{surf}} = \{\alpha \rho_+^2 + \beta(\rho_+'^2 + \rho_+^2 \phi_+'^2)$$
$$+ \gamma \rho_+^2 \phi_+' + \omega \rho_+ \rho_+'\} + \{\alpha \rho_-^2 + \beta(\rho_-'^2 + \rho_-^2 \phi_-'^2)$$
$$+ \gamma \rho_-^2 \phi_-' - \omega \rho_- \rho_-'\} \qquad (1)$$

plus higher degree terms. The subscripts $\pm$ denote the values of ρ, ρ', and ϕ' at the interfaces ($z = \pm L$). The first and second curly brackets in Eq. (1) represent the interactions with the upper and lower walls, respectively. α, β, ω, and γ are phenomenological coefficients depending on external parameters, such as temperature or concentration (but not on L). The form of the surface contribution to the free energy is identical to that of the bulk contribution plus a term $\rho_+ \rho_+' - \rho_- \rho_-'$ resulting from the breaking, by the walls, of the twofold bulk symmetry axes parallel to the surfaces. Let us notice that no linear term appears in Eq. (1). Indeed, the order parameter is a planar vector that is invariant under translations [i.e., $\boldsymbol{\tau}(z) \to \boldsymbol{\tau}(z + a)$]. Thus, at variance with the smectic order parameter (density wave $\delta\rho = \psi e^{ikz} + $c.c.) which transforms nontrivially under translations [i.e., $\psi(z) \to e^{ika}\psi(z + a)$], the breakdown of the translational symmetry, due to the presence of the surfaces, does not yield linear invariants at the interface [15].

Let us note that, although it is permitted by symmetry, the term proportional to β in Eq. (1) has not yet been used in previous phenomenological approaches while, as we shall see presently, it is the key for stabilizing the anticlinic phase. F_{surf} has no term breaking the continuous rotational symmetry and can only lead to spontaneous breakdown of the SmA point group as at least one phenomenological coefficient becomes negative. In the bulk the homogeneous SmC* phase is stabilized when A becomes negative. Inhomogeneous states are induced as the coefficient below ρ'^2 in F_{bulk} or the coefficients α and β in F_{surf} become negative. The former leads to incommensurate bulk structures [17] whereas the latter tend to stabilize the synclinic and anticlinic surface states, respectively. The microscopic interpretation of the coefficient β is beyond the scope of a phenomenological approach and depends on the physical properties of the walls. In the case of suspended films we can, however, notice the following obvious contribution to β. The microscopic couplings $\delta\boldsymbol{\tau}_{i-1} \cdot \boldsymbol{\tau}_i$ and $\delta\boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_{i+1}$ between the smectic layer number i and its nearest neighbors lead, in the continu-

ous approximation, to the $(\rho'^2 + \rho^2 \phi'^2)$ term in the bulk free energy, with a positive coefficient since δ is negative for a ferroclinic ground state. Since the last layer of the sample interacts with only one neighbor, it contributes in a different way to the free energy and gives rise to a separate surface term, corresponding to $\beta(\rho_+'^2 + \rho_+^2 \phi_+'^2)$ in Eq. (1). Transforming the discrete sum $\delta\Sigma_i [\boldsymbol{\tau}_{i-1} \cdot \boldsymbol{\tau}_i]$ into an integral and expanding in a series up to d^2 yields $\beta = \delta d^2/2$. Let us note that the corresponding negative sign of β, which favors the anticlinic structure, could surely be modified by taking into account interactions with next nearest neighbors or by a less crude microscopic approach.

The equilibrium states are determined by minimizing the total free energy $F_{\text{bulk}} + F_{\text{surf}}$ with respect to $\phi(z)$ and $\rho(z)$. In order to avoid spurious difficulties in solving the corresponding differential equations, one allows ρ to be negative. Then one identifies any point in the (ρ, ϕ) plane with the lattice of equivalent points $(\rho, \phi + 2\pi p)$ and $(-\rho, \phi + \pi + 2\pi p)$, for any integer p. The direction of the vector $\boldsymbol{\tau}$ is given by ϕ if ρ is positive, and by $\phi + \pi$ if it is negative. In the bulk, Euler-Lagrange equations readily yield the following results.

(a) The solutions corresponding to a minimum of the free energy are always either even or odd functions of z. Indeed, when considering a nonsymmetric configuration $\rho(z)$ whose upper part ($z > 0$) has a smaller energy than its lower part ($z < 0$) one can build a new even (or odd) solution coinciding with $\rho(z)$ for $z > 0$ and with $\rho(-z)$ [or $-\rho(-z)$ if $\rho(0) = 0$] for $z < 0$. The corresponding energy is obviously smaller than that of the asymmetric configuration since no second derivative (which would diverge at $z = 0$) is present in the bulk free energy.

(b) $\phi'(z) = -1$. Therefore, as in a system without boundary, the tilt vector precesses and forms a periodic helix with a helix pitch $\lambda = 2\pi$ (in normalized units).

(c) The OP amplitude $\rho(z)$ satisfies the elliptic equation

$$d^2\rho/dz^2 = A\rho + 2\rho^3. \qquad (2)$$

The solutions to Eq. (2) are associated with an effective free energy which depends only on A, $g = \beta/1 + \omega$, and $h = (\alpha + g - \gamma)/1 + \omega$. $g < 0$ favors the anticlinic structure while $h < 0$ favors the synclinic structure. In the following we shall only consider temperatures above T_{c0} ($A > 0$), i.e., in the bulk the untilted smectic A phase is stable. Thus, at the limits of stability of the surface states, the order parameter vanishes. Close to these limits the term $2\rho^3$ in the equation of state (2) can be neglected with respect to the first linear term $A\rho$. The solutions to the corresponding linear equation, namely, $\rho(z) = \rho_c \cosh(Az) + \rho_s \sinh(Az)$, have a triclinic symmetry group C_1 in the general case. According to the point (a) stated above, the minimum of the free energy can only happen for even ($\rho_s = 0$) or odd ($\rho_c = 0$) special solutions with monoclinic symmetry C_2. The even and odd solutions describe the synclinic and anticlinic surface states, respectively.

(i) $\rho(z) = \rho_c \cosh(z\sqrt{A})$. The tilt $\rho(z)$ is maximum at the surface and decreases with a length scale $1/\sqrt{A}$ down to a finite minimum at the center of the sample. The tilt configu-
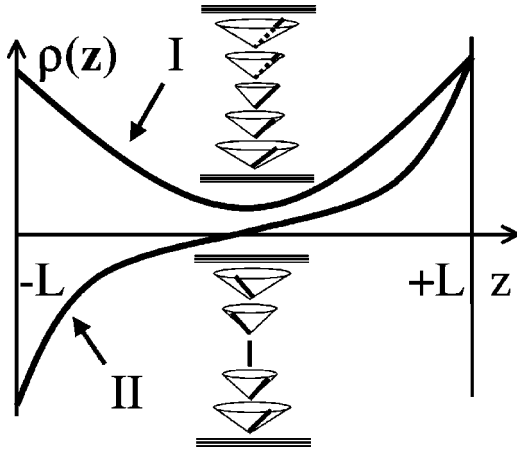
FIG. 1. Tilt ρ versus z for the synclinic (I) and anticlinic (II) solutions of Eq. (2).

FIG. 2. Theoretical phase diagrams in the space of the phenomenological coefficients $h/\sqrt{A}$, $L\sqrt{A}$. (a) $g>0$. (b) $0>g\sqrt{A}>-1/2$. (c) $g\sqrt{A}<-1/2$ and $1+\omega>0$. (d) $1+\omega<0$ and $0>g\sqrt{A}>-1/2$.

ration depends on two lengths: the deformation length $1/\sqrt{A}$ and the helix pitch $\lambda=2\pi$. In a thick sample the minimum of $\rho(z)$ at the center is much smaller than the tilt on the surfaces. On the contrary, in a film much thinner than $1/\sqrt{A}$, $\rho(z)$ is almost constant. In both cases, the direction of the order parameter is continuous at $z=0$. If the film thickness is smaller than the helix pitch then the direction of the vector order parameter is the same at both surfaces. This situation justifies the word synclinic for denoting this state. In the opposite case, the helical winding of $\tau(z)$ yields a periodic variation of $\phi_+-\phi_-$ versus the sample thickness L.

(ii) $\rho(z)=\rho_s\sinh(z\sqrt{A})$. This solution is depicted in Fig. 1. It differs from the synclinic state in two respects. The modulus $\rho(z)$ vanishes exactly at the center and the helix is broken: The tilt vector rotates to an angle π at $z=0$ (ρ changes its sign). In a film whose thickness is much smaller than the helix pitch and the deformation length, the OP direction is almost homogeneous in the sample, and its modulus varies linearly with z. The two surfaces are then *anticlinic* with respect to one another. For thicker samples $\rho(z)$ exhibits a nonlinear odd variation and, as in the synclinic state, $\phi_+-\phi_-$ varies with the sample thickness.

Introducing the hyperbolic solutions into the total free energy and minimizing with respect to ρ_c or ρ_s provides the limits of stability of the anticlinic and synclinic states respectively. The resulting theoretical phase diagram depends only on three phenomenological coefficients $h/\sqrt{A}$, $g\sqrt{A}$, and $L\sqrt{A}$. The equations describing the limit of stability of the synclinic and anticlinic phases are

$$(g\sqrt{A}+h/\sqrt{A})\cosh[2L\sqrt{A}]+\sinh[2L\sqrt{A}]$$
$$=-h/\sqrt{A}+g\sqrt{A},$$

$$(g\sqrt{A}+h/\sqrt{A})\cosh[2L\sqrt{A}]+\sinh[2L\sqrt{A}]$$
$$=h/\sqrt{A}-g\sqrt{A}, \tag{3}$$

respectively.

The two limits of stability can superimpose at one point in the phase diagram. Thus, a first order transition line relating the two surface states appears. Close to this line the order
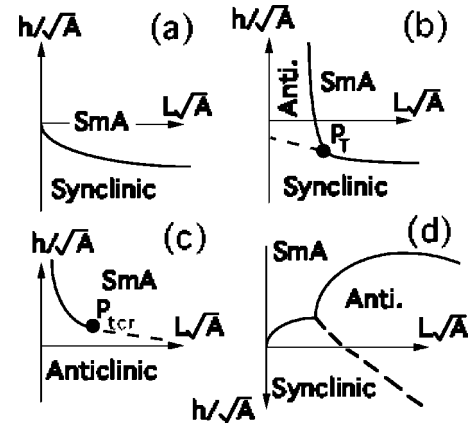
parameter is not small and the linear approximation fails. The solutions to the complete nonlinear equation (2) must be taken into account. A first integral of this equation is given by $\rho'^2=H_0+\rho^4+A\rho^2$, where H_0 is a constant of integration which vanishes in the high symmetry phase. Minimization of the effective free energy with respect to H_0 yields the following three stable solutions.

(1) The high symmetry SmA phase $\rho(z)=0$ for $H_0=0$.

(2) For $H_0<0$. The "synclinic" surface phase, corresponding to an even elliptic solution to Eq. (2), $\rho(z)=p\,\mathrm{nc}\{\sqrt{(p^2-q^2)}z,q^2/q^2-p^2\}$, where nc (and sc for $H_0>0$) are Jacobian elliptic functions [18], $2p^2=-A+\sqrt{(A^2-4H_0)}$, and $2q^2=-A-\sqrt{(A^2-4H_0)}$. Close to the Sm$A$ transition temperature, this solution is proportional to $\cosh(z\sqrt{A})$.

(3) For $H_0>0$. The "anticlinic" surface phase, described by the odd elliptic function $\rho(z)=p'\,\mathrm{sc}\{q'z,1-p^2/q^2\}$, where $q'^2=-q^2$ and $p'^2=-p^2$. This solution is proportional to $\sinh(z\sqrt{A})$ close to the SmA transition temperature.

Let us determine the theoretical phase diagram associated with these solutions. Equation (3), along with similar expressions involving elliptic functions that describe the anticlinic-synclinic transition, permits to us calculate the transition lines. Various situations may arise. Figures 2(a)–2(c) show typical phase diagrams in the plane ($h/\sqrt{A},L\sqrt{A}$) for $1+\omega>0$. For $g>0$ [Fig. 2(a)], the anticlinic phase is never stable. For $0>g\sqrt{A}>-1/2$ [Fig. 2(b)], the three phases are stable and merge at a three-phase point P_T. For $g\sqrt{A}<-1/2$ [Fig. 2(c)], the SmA and anticlinic phases are stable and are separated by a transition line which can change its order, from second to first, at a tricritical point P_{trc}. The transition lines from the SmA phase are second order, whereas the transition between the low symmetry states is always first order.

For $1+\omega<0$ and $g>0$, the anticlinic and SmA states are stable, whereas for $1+\omega<0$ and $g\sqrt{A}<-1/2$ the synclinic and SmA states are stable. Both surface phases are stabilized when $0>g\sqrt{A}>-1/2$ and they are separated by a first order transition line as depicted in Fig. 2(d).

Close to the bulk transition temperature T_{c0}, g and h remain constant while $A\simeq T-T_{c0}$. Assuming g and h negative
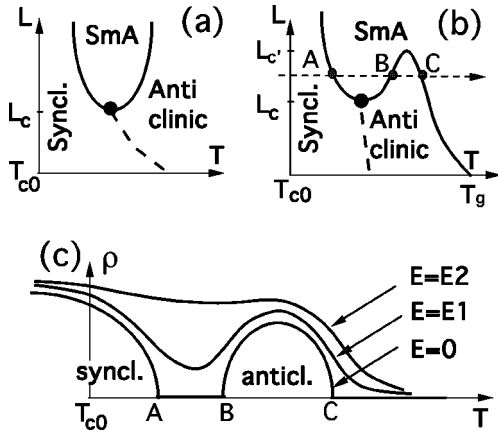
FIG. 3. (a) Phase diagram in the thickness (L)–temperature (T) plane, for g and h constant and negative and $1+\omega>0$. Dashed and full lines indicate first and second order transition lines, respectively. (b) Phase diagram for g and h becoming positive above T_g and T_h ($<T_g$), respectively. (c) Surface tilt $|\rho|$ vs temperature for various electric fields ($E2>E1>0$) and $L'_c>L>L_c$. The corresponding thermodynamic path ABC is represented in (b).
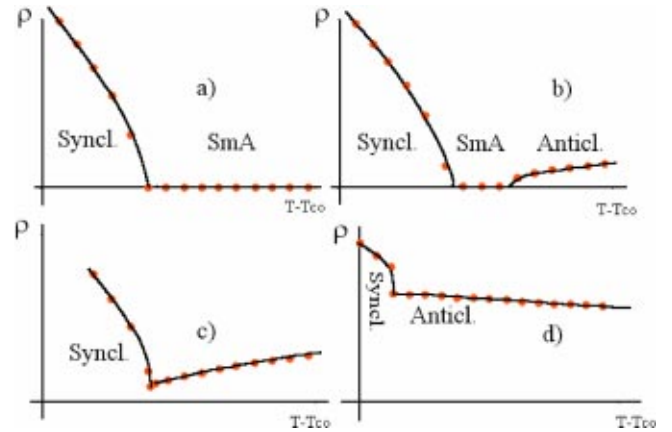

FIG. 4. Tilt at the surface versus temperature. The dots are numerically calculated. The phenomenological coefficients are chosen in such a way that, unlike in Figs. 3(a) and 3(b), the synclinic-anticlinic transition thickness increases with T. (a) For $L>L'_c$. (b) For $L_c<L<L'_c$. (c) For $L<L_c$. (d) For $L\ll L_c$.

and constant in Eqs. (3) yields the temperature thickness phase diagram depicted in Fig. 3(a). The anticlinic phase is stable at high temperature whereas the SmA phase is stable within an intermediate temperature range provided that the sample thickness is large enough. If L is smaller than a critical length L_c (defined by $\tanh[2L_c\sqrt{h/g}]=2\sqrt{hg}$), then the Sm$A$ domain is replaced by a first order anticlinic$\leftrightarrow$synclinic transition line. For values of the phenomenological coefficient corresponding to Fig. 3(a), the anticlinic-synclinic transition temperature increases with decreasing L. For other values, the temperature decreases and the anticlinic phase can be stabilized below the bulk critical temperature for small L. As the product gh becomes larger than 0.25, L_c is shifted toward infinity and the SmA stability domain disappears.

Since h and g are *spontaneous* symmetry breaking Landau coefficients, in the most likely situations they must become positive at high temperature ($h\approx T-T_h,g\approx T-T_g$). Accordingly, the parent SmA phase is also stable at high temperature. The T-L phase diagram shown in Fig. 3(a) is then modified as presented in Fig. 3(b). The SmA domain extends toward the high temperatures and the anticlinic phase is only stabilized for small thicknesses as reported experimentally by Link *et al.* [8]. This limitation defines a second critical thickness L'_c above which the anticlinic phase cannot be stable.

The SmA or the surface phases are usually observed over a rather small temperature interval ($\approx$10 K) between the isotropic phase and the bulk SmC^* phase. Thus it is not likely that $T_{g,h}$ fall within this interval and the high temperature SmA stability domain may be hidden by the isotropic liquid. To summarize, by decreasing T one should observe the following phase sequences: Iso$\rightarrow$Sm$A\rightarrow$anticlinic$\rightarrow$SmA $\rightarrow$synclinic or more likely Iso$\rightarrow$anticlinic$\rightarrow$SmA $\rightarrow$synclinic for $L'_c>L>L_c$. In the former case, the low temperature SmA domain is *reentrant*. Furthermore, below T_{c0} the synclinic structure smoothly transforms into the bulk SmC^* structure. For $L<L_c$ the following sequences are pre-

dicted: Iso$\rightarrow$Sm$A\rightarrow$anticlinic$\rightarrow$synclinic or Iso$\rightarrow$anticlinic $\rightarrow$synclinic.

The tilt at the surface versus temperature exhibits a complex behavior represented in Fig. 4. Above L'_c the tilt appears in the synclinic state and increases with decreasing temperature. Between L_c and L'_c the tilt presents two peaks separated by zero in the small temperature interval corresponding to the reentrant SmA stability domain. Below L_c the SmA domain is replaced by the first order anticlinic$\rightarrow$synclinic transition temperature. The tilt is discontinuous and has a (sharp close to L'_c) minimum at the transition. For the thinnest films [Fig. 4(d)], the minimum of the tilt at the transition disappears. For some specific values of the phenomenological coefficients, the tilt is not monotonic in the synclinic phase where it presents a minimum in the neighborhood of the bulk transition temperature T_{c0}.

A variety of theoretical phase diagrams can be foreseen by assuming a different order in the sequence of critical temperatures $T_{c0}/T_h/T_g$. In the experimental phase diagram reported by Chao *et al.* [10], the high temperature SmA phase is hidden by the stability domain of the liquid state and the higher temperature phase is anticlinic. This situation corresponds to the lower part of Fig. 3(a) with an increasing of the anticlinic-synclinic transition temperature with decreasing L.

In thin films of ferroelectric MHPOOCBC, Schlauf *et al.* [19] observed a surface state above the SmC^* phase. Moreover, within the stability domain of the surface state and under small applied electric field, they observed a strong decreasing of the ellipsometric quantity $\Delta_+-\Delta_-$, which is related to the tilt. In some cases, this quantity vanishes over a narrow temperature interval. Link claimed [8] that this interval coincides with the domain of stability, under electric field, of the anticlinic state. As we shall see below, in our approach the anticlinic state is deformed by the electric field and thus must yield nonzero $\Delta_+-\Delta_-$. For this reason we assume that the cancellation of $\Delta_+-\Delta_-$ corresponds rather to the reentrant SmA phase, stable between the high temperature anticlinic state and the low temperature synclinic state. In the cases when an exact cancellation is not evidenced, we

interpret the sharp decreasing of $\Delta_+ - \Delta_-$ as an effect of the lowering of the tilt in the neighborhood of the anticlinic-synclinic first order transition temperature (see Fig. 4). Although it seems likely that the complex behavior evidenced by Schlauf *et al.* involves the anticlinic structure, a confirmation of the reentrant Sm*A* domain needs further experimental studies.

The two surface phases are qualitatively different but have the same monoclinic symmetry group C_2. Accordingly, their structures are *macroscopically polar*, the polarizations being parallel to the smectic layers. Despite their common symmetry group, they are distinct phases. Strictly speaking, they are *anti-isostructural* states [20]. Unlike an isostructural phase transformation (e.g., liquid-gas), the anticlinic structure cannot transform continuously into the synclinic structure. Consequently, the corresponding first order transition line has no critical end point. This critical point is replaced by the three-phase point displayed in Figs. 2(b), 3(a), and 3(b).

In the anticlinic phase the upper half helix is rotated to an angle π with respect to the lower one. The symmetry and free energy of the anticlinic state are not modified if the angle shift is changed from π to any other finite value. This means that there is no energy barrier preventing the respective rotation of the upper and lower helices. We shall refer to this free rotation effect to as the "decoupling" of the two half helices. These two previous striking properties, namely, the rotational freedom and the absence of a critical end point, result from the fact that we have used a single vector OP for describing the ordered states. Taking into account a "secondary" OP with the same symmetry, e.g., the polarization $\mathbf{P}$ (in chiral systems polar and axial vectors have the same symmetry properties), together with flexoelectric ($\mathbf{P} \cong d\boldsymbol{\tau}/dz$) and inverse flexoelectric ($\boldsymbol{\tau} \cong d\mathbf{P}/dz$) couplings, modifies our model in several qualitative respects. First, a continuous method of transformation between the anticlinic and the synclinic phases is made possible by changing successively the signs of the primary ($\boldsymbol{\tau}$) and secondary ($\mathbf{P}$) OP moduli (to restore the rotational symmetry both OPs must simultaneously vanish). Accordingly, a critical end point may be found in a more general phase diagram. Along the same line, a small energy barrier is generated by this coupling and fixes the value of the central angle shift in the anticlinic phase. A similar effect can be produced by nonlocal electrostatic interactions. The present simplified approach holds when the secondary OP or the inverse flexoelectric coupling is sufficiently small.

Let us now return to the simplified model involving a single critical OP and discuss the electric field influence. The response of thin ferroelectric films to a small applied electric field $\mathbf{E}$ (parallel to the smectic layers) is different in the anticlinic and in the synclinic states. In both cases the two-fold symmetry axes are rotated toward the direction of $\mathbf{E}$ without breaking their polar symmetry groups. However, the second order transition line separating the reentrant Sm*A* phase from the low symmetry states disappears (in the same way as the Curie point of a ferromagnetic material disappears on applying an external magnetic field). Thus, the three-phase point becomes a critical end line in the (E,L,T)

phase diagram. At given small electric field and $L > L_c$ the tilt sharply decreases in the neighborhood of the limit of stability of the underlying Sm*A* reentrant temperature interval, but it never vanishes [Fig. 3(c), $E = E1$]. On the contrary, the synclinic↔anticlinic first order transition line [Figs. 3(a) and 3(b)] remains, but its position varies with E. The shifting direction of the transition line is controversial [5–7] and depends on the material properties. Let us consider the case when the line is shifted toward high temperatures. If the line is sufficiently shifted, then an anticlinic point in the phase diagram becomes synclinic at the corresponding field. This field-induced transition results from the following mechanism. In the anticlinic phase, the "decoupling" of the helix orientation in each half of the sample allows them to rotate independently, so as to align their *average* polarizations along the field direction. Even for arbitrarily small fields the resulting structure is close to that of the synclinic state although a residual angle shift persists at $z = 0$, due to the helical twisting of $\boldsymbol{\tau}$ and to the flexoelectric effect. Thus, to provoke the phase transformation into the actual synclinic structure, a finite field is necessary. It permits one to cancel the residual ($\boldsymbol{\tau}$) angle shift and to overcome the corresponding energy barrier. Above L_c, this barrier vanishes and the transformation from the anticlinic to the synclinic configurations is continuous and involves no phase transition. The threshold field, denoted E_c, has been observed in freely suspended films of DOBAMBC and of chiral TFMHPOBC by Link *et al.* [8], who report an anticlinic →synclinic field-induced transition. The converse synclinic →anticlinic transition has been proposed by Andreeva [9], assuming very strong flexoelectric longitudinal polarizations. It corresponds to a low temperature shifting of the transition line in Figs. 3(a) and 3(b). This mechanism is only possible at higher fields because, in thin synclinic films, the relative rotation of the upper and lower half helices must overcome a high elastic energy barrier associated with the rigid structure of the unbroken helix.

In summary, we have reported a simple phenomenological theory accounting for the stabilization of both anticlinic and synclinic surface phases in ferroelectric smectics at zero applied electric field. Taking into account an unusual surface energy allows us to predict the stability domain of the anticlinic phase at high temperature and small sample thickness. We have used the continuous approximation in which the smectic layered structure is neglected. This approximation fails to describe quantitatively the thinnest samples. However, since our approach is based on a surface-induced effect, the layer structure surely plays a secondary role for the stabilization of the various surface phases. Close to the bulk transition temperature, a reentrant Sm*A* phase can be stabilized, owing to the competition between the two surface states. We expect the same surface behavior in antiferroelectric materials. The order parameter $\boldsymbol{\tau}$ represents then the difference between the tilt vectors in two adjacent layers. In this case the difference between anticlinic and synclinic surface phases is subtler to show experimentally than for ferroelectrics and has not yet been reported to our knowledge.

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