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Theory of longitudinal ferroelectric smectics

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Abstract. — Recently, it was discovered that *a*-chiral smectic layers can undergo a phase transition into a polar smectic. The new phase is fundamentally different from that of the existing chiral Sm-C* ferroelectrics. In this paper we examine the underlying mechanism responsible for the new form of ferroelectricity. A Landau theory is presented to discuss the competition between ferroelectricity and other forms of ordering such as anti-ferroelectricity. An effective free energy is constructed to describe the coupling between layer undulations and the polarizability of the sample. We find that in the new phase the Landau-Peierls instability is absent and that second sound can propagate along the layers. Our considerations call for a number of experiments which we believe are crucial for a clarification of the true nature of the observed phases.

1. Introduction.

Ferroelectric liquid crystals have found extensive usage in both display and switching devices [1]. The classic ferroelectric liquid crystal materials are all in the chiral smectic-C (Sm-C*) phase [2]. In this phase, the molecules are organized in layers with the axes of the molecules tilted with respect to the layer normal. The ferroelectricity is due to the fact that the constituent molecules are chiral : in the Sm-C* phase chirality breaks reflection symmetry in a plane containing the layer normal, leading to an in-plane polarization. Recently the discovery of a ferroelectric smectic liquid crystal made from *a*-chiral molecules has been reported [3]. The lack of chirality already indicates that an unusual mechanism is involved. Indeed, optical and piezoelectric studies reveal that at least one of the new phases has uniaxial symmetry, unlike Sm-C* materials which are intrinsically biaxial. This means that the polarization must be along the layer normal — which corresponds to a *longitudinal* ferroelectric smectic. This implies that the polarization cannot be easily rotated by electric fields as there is no continuous symmetry for the polarization vector. Curiously, on cooling from the high temperature Sm-A

phase, the sample loses nearly all of its birefringence on entering the ferroelectric phase. We will show how this observation is compatible with the uniaxiality of the sample.

The constituent molecules of the new phase have a « polyphilic » structure. They are a linear assembly of four sub-groups : A-B-C-A. Here, A is a perfluorinated moiety, C is an apolar alkyl chain, and B is a biphenyl group which carries a significant dipole moment oriented along the chain. We will call this molecule, whose length is about 41 \AA , F^+ in the following. A chemically very similar molecule, F^- , has an A-B'-C-A structure with the dipole on B inverted. F^- molecules are completely miscible with F^+ . As mentioned, the ferroelectric phase is entered by cooling from a SmA phase. X-ray studies reveal that the SmA phase consists of a stack of densely packed layers — with an intermolecular spacing of order $3\text{--}4 \text{ \AA}$ — and with a layer spacing close to the F^+/F^- molecular length. For pure F^+ , the low-temperature phase — called SmX — has a complex, striped structure [4] with in-plane modulation. A bias electric field is required to observe the development of a strong piezoelectric signal. For a 70/30 mixture of F^+ and F^- molecules, the low-temperature phase — called SmX' — has a simple lamellar structure with a layer spacing $\sim 34 \text{ \AA}$ and it does develop a spontaneous polarization on cooling (somewhat below the critical temperature T_F). The natural explanation of the reduced layer spacing in the SmX' phase is that the molecular axis is tilted with respect to the layer axis, as appears to be confirmed by the X-ray data [4]. There can, however, be no long-range order of the Sm-C type due to this tilt, in view of the optical uniaxiality of the phase. In other words, the in-plane projection of the tilt must be disordered at large length scales.

The possibility of constructing ferroelectric liquid crystals from molecules which are a-chiral but which lack inversion symmetry has been hotly debated over the last twenty years [5]. Molecules with an A-B-C structure were suggested [6] as good candidates for promoting longitudinal ferroelectricity. We will see that in general this would promote *antiferroelectric* order. Polyphilic molecules with an A-B-C-A structure [3, 6] seem more likely candidates for ferroelectric smectics since (i) they naturally self-assemble into lamellae if A, B, and C have different polarizabilities ; (ii) they lack inversion symmetry, and (iii) the tendency to promote antiferroelectric order should be much less than for simpler A-B or A-B-C molecules. On further consideration, there appear to be strong objections against ferroelectric smectics based on an A-B-C-A molecular structure. First, a layer of dipoles acts as a *capacitor* with no electrical field outside the plates. The layer-to-layer dipolar coupling — which would have to produce the ferroelectric polarization — is thus extremely weak. On the other hand, the van der Waals attraction tends naturally to favor antiferroelectricity : (A-B-C-A) (A-C-B-A) (A-B-C-A) (A-C-B-A). To see why, assume that B is more polarizable than C. Antiferroelectric layering allows closer B-B spacing as is favored by the van der Waals attraction, while the same argument holds if C is more polarizable than B. A second problem is that a layer of vertical dipoles suffers from strong in-plane electrostatic repulsion. Assuming, for instance, molecules with (vertical) dipole — moments $p_0 = q_0 \times 1 \text{ \AA}$ — with q_0 the elementary charge — then the repulsive energy $p_0^2/\epsilon a^3$ between dipoles with a lateral separation $a \simeq 3 \text{ \AA}$ in a dielectric medium with $\epsilon \simeq 10$ is of order 500 K.

Finally, the whole concept of a *liquid* crystal developing ferroelectricity merely because the constituent molecules lack head-tail inversion symmetry seems suspect. If the molecules had their heads all pointing in the same direction, then we should expect a spontaneous splay in the sample [5]. For lamellae with no inversion symmetry this translates into a spontaneous curvature of the lamellae. For a solid, the crystallographic axes prevent the splay but for a liquid crystal the splay could develop and destroy the molecular alignment and thus the ferroelectric order.

In this article we want to investigate how these objections have been circumvented in the

SmX' phase. In section 2, we will examine qualitatively the balance between competing forces at the molecular level to argue that we are dealing with a « frustrated » system. We also discuss the relation between molecular tilt and birefringence. In section 3, we develop a Landau theory for rigid-layer ferroelectric ordering. Particular attention is paid to the dipolar coupling. We will show that the « capacitor argument » is inapplicable due to the development of in-plane domain structure, either at the macroscopic or at the microscopic level. In section 4, we introduce layer undulations and show that the macroscopic response of the SmX' phase is fundamentally different from ordinary smectics : there is no Landau-Peierls effect (i.e. there are sharp Bragg spots) and second sound can propagate along the layers.

2. Energy scales.

2.1 INTRA-LAYER. — Figure 1 shows a layer of pure F⁺ molecules in the high-temperature para-electric Sm-A phase ($T > T_F$). In the para-electric Sm-A phase, some of the dipolar B groups must be in an a-polar alkyl environment due the required disorder in the up-down orientation of the molecules (since half of the dipoles must point up and half down). Let ΔE_c be the energy cost, excluding the dipolar coupling, of flipping an F⁺ molecule in an otherwise aligned sample. If the alkyl chains are not too short, this « demixing » energy is of order $10 k_B T$ or more [13]. In the absence of the dipolar coupling, we should expect, at room temperature, the layers to be ordered and to encounter an Ising-type phase transition at a high temperature (around $k_B T_c \approx \Delta E_c$).

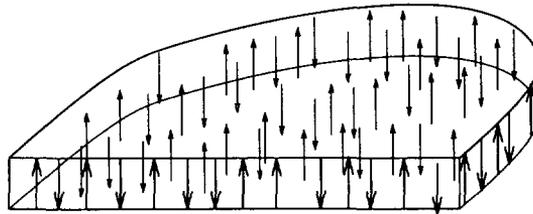


Fig. 1. — Schematic structure of an F⁺ layer, in the paraelectric smectic A phase.

X-ray data suggest that the molecules are locally tilted, although there is no long range azimuthal order as revealed by the optical uniaxiality. We will define θ to be the tilt rotation angle of the dipolar part B of the molecules with respect to the layer normal. The dipolar B groups and the apolar C alkyl chains in the ordered phase ($T < T_F$) are all in their proper dipolar respectively a-polar environment. In the ordered phase, we have to include the intra-layer dipolar repulsion we neglected in the para-electric phase. To estimate it, let p_0 be the molecular dipolar moment, ρ the dipole area density and ϵ the dielectric constant. Using the dipole approximation, for a two dimensional liquid of tilted dipoles, gives for the repulsion per molecule ΔE_c .

$$\begin{aligned} \Delta E_c(\theta) &= \frac{1}{2} \frac{p_0^2 \rho}{\epsilon} \int d^2r \left\{ \frac{1}{r^3} - 3 \sin^2 \theta \frac{x^2}{r^5} \right\} \\ &\approx \frac{1}{8} \frac{p_0^2 \rho}{\epsilon a} (3 \cos^2 \theta - 1) \end{aligned} \quad (2.1)$$

where we estimated already $p_0^2 \rho / \epsilon a$ to be of order 500 K.

According to equation (2.1), we could make $\Delta E_c(\theta)$ *negative* by letting the tilt angle θ exceed the « magical » angle $\theta_m = \arccos(1/\sqrt{3})$. The actual equilibrium angle θ results from a compromise between the dipolar interaction and all other inter-molecular forces. The energy cost (or gain) of tilting the B segment by an angle θ may be written as :

$$W(\theta) = f(\cos \theta) + \Delta E_c(\cos \theta) \quad (2.2)$$

in which $f(\cos \theta)$ contains all contributions to the tilt energy other than dipolar. We will assume that $f(\cos \theta)$ has a minimum for $\cos \theta = 1$. At a given temperature, the average tilt θ^* is then found by demanding that of $W(\theta)$ is minimal. The energy per molecule gained on entering the ordered phase is then of order :

$$E = \Delta E_c + W(\theta^*) . \quad (2.3)$$

Recall that ΔE_c and $W(\theta^*)$ are both of the order of $10 k_B T$ or more. *Under those conditions, ordering should either occur at temperatures much higher than $k_B T$ or not at all, depending on the sign of E .* The only case where we can have ordering near room temperature, will be when $\Delta E_c + W(\theta^*) \approx k_B T$. Considering that the natural energy scale of E is much larger than $k_B T$, this tells us that $|E|$ must be close to a minimum upon varying the material parameters. Suppose we minimize $E(p_0, \theta = \theta^*)$ with respect to the material parameter p_0 , i.e. we set

$$\begin{aligned} dE/dp_0 &\equiv \left. \frac{\partial E}{\partial \theta} \right|_{p_0} \left. \frac{\partial \theta}{\partial p_0} \right|_{\theta = \theta^*} + \left. \frac{\partial E}{\partial p_0} \right|_{\theta = \theta^*} \\ &= 0 . \end{aligned}$$

Since $\partial E/\partial \theta|_{p_0} = 0$ for $\theta = \theta^*$ — by definition of θ^* — we only must make sure that $\partial E/\partial p_0|_{\theta = \theta^*} = 0$. From equations (2.1) and (2.3), it follows that $\partial E/\partial p_0|_{\theta = \theta^*} = \partial \Delta E_c/\partial p_0|_{\theta = \theta^*} = 0$ when $\cos^2 \theta^* = 1/3$. The energy scale $|E|$ is thus minimized if we choose $\theta^* = \theta_m$, the magical angle. We thus should expect A-B-C-A polyphilic longitudinal ferroelectric smectics with transition temperatures around room temperature to assume tilt angles close to the magical angle !

The above (very heuristic) argument also implies that longitudinal ferroelectric ordering near room temperature of such a frustrated system should be accompanied by a strong drop in optical birefringence, (as indeed observed experimentally). To see why, let α_{\parallel} and α_{\perp} be the molecular polarizabilities of the B part of the molecules along, respectively perpendicular to its axis (the anisotropy is principally due to the conjugated ring on the biphenyl group B). Next, assume the molecules to have a fixed angle θ with the layer normal (z axis) but with a random in-plane azimuthal angle (recall that there is no net in-plane polarization). After performing an azimuthal average, the polarizability tensor in the laboratory frame becomes :

$$\vec{\alpha} \approx \begin{pmatrix} \alpha_{\perp} + (\alpha_{\parallel} - \alpha_{\perp}) \frac{\sin^2 \theta}{2} & 0 & 0 \\ 0 & \alpha_{\perp} + (\alpha_{\parallel} - \alpha_{\perp}) \frac{\sin^2 \theta}{2} & 0 \\ 0 & 0 & \alpha_{\perp} + (\alpha_{\parallel} - \alpha_{\perp}) \cos^2 \theta \end{pmatrix} \quad (2.4)$$

For tilt-angles close to the magical angle, the eigenvalues of $\vec{\alpha}$ become degenerate and the macroscopic birefringence vanishes.

2.2 INTER-LAYER. — We now turn to the interlayer forces. More precisely we want to know the energy difference between two layers with parallel dipoles, e.g. (A-B-C-A) (A-B-C-A), and with anti-parallel dipoles (A-B-C-A) (A-C-B-A). The strongest coupling is obviously due to the A-A interaction but this term is independent of the layer orientation.

Turning first to dipolar coupling, if we treat the dipoles on B as a capacitor plate then there is no dipolar coupling for infinite layers, (finite size effects will be discussed in the next section). It could be objected that the discreteness of the molecules would allow for an electric field outside the dipolar layer. If, for instance, we model the B sheet as a square lattice of dipoles then the interlayer coupling is ferroelectric. The energy difference per molecule between the two orientations is :

$$W \simeq - \frac{8 \pi p_0^2}{\epsilon d^3} \left(\frac{d}{a} \right) \exp(-2 \pi d/a). \quad (2.5)$$

With $d \simeq 34 \text{ \AA}$ as the layer-layer spacing, this gives $W \sim k_B T \exp(-42)$, so there is, according to this « capacitor » argument, no meaningful dipolar inter-layer coupling for a uniform infinite sheet of dipoles.

Next, we turn to the van der Waals coupling. Let H_{CAAC} be the Hamaker constant for the van der Waals coupling between two layers of C groups separated by a medium of A groups and define H_{CAAB} and H_{BAAB} in the same fashion. All Hamaker constants are of order $k_B T$. The energy difference W_{\parallel} per unit area and per layer between parallel and anti-parallel orientations is then to leading order :

$$\begin{aligned} W_{\parallel} \simeq & - \frac{H_{BAAB}}{24 \pi} \left\{ \frac{1}{(2 d_{A_1})^2} - \frac{2}{(2 d_{A_1} + d_B)^2} + \frac{1}{(2 d_{A_1} + 2 d_B)^2} \right\} \\ & - \frac{H_{CAAC}}{24 \pi} \left\{ \frac{1}{(2 d_{A_2})^2} - \frac{2}{(2 d_{A_2} + d_C)^2} + \frac{1}{(2 d_{A_2} + 2 d_C)^2} \right\} \\ & + \frac{H_{BAAC}}{12 \pi} \left\{ \frac{1}{(d_{A_1} + d_{A_2})^2} - \frac{1}{(d_{A_1} + d_{A_2} + d_B)^2} - \frac{1}{(d_{A_1} + d_{A_2} + d_C)^2} \right\} \\ & + \frac{1}{(d_{A_1} + d_{A_2} + d_C + d_B)^2}. \end{aligned} \quad (2.6)$$

Here d_{A_1} , d_{A_2} , d_B and d_C are the lengths of respectively the A group attached to the B group, of the A group attached to the C group, and of the B and C groups.

If we first assume d_{A_1} to be small compared to d_{A_2} , d_B and d_C , then to leading order :

$$\begin{aligned} W_{\parallel} & \simeq - \frac{H_{BAAB}}{96 \pi d_{A_1}^2} \\ & \simeq - \frac{(\sqrt{A_{BB}} - \sqrt{A_{AA}})^2}{96 \pi d_{A_1}^2} \end{aligned}$$

We decomposed here H_{BAAB} into A_{BB} and A_{AA} which are the Hamaker constants associated with the van der Waals interaction of B (resp A) with B (resp A) through vacuum. Clearly, W_{\parallel} is always negative, and thus favors antiferroelectricity as mentioned in section 1. The van der Waals energy per molecule is however only of order $10^{-2} k_B T$ or less for the present case. If we compute W_{\parallel} for the case $d_A = d_{A_2} = d_{A_1}$, (and taking d_A to be the chain length of

8 carbon atoms) then W_{fl} drops down to $10^{-4} k_B T$ per molecule! Compounds with $d_{A_1} = d_{A_2}$ have recently been synthesized [7]. The van der Waals energy contribution of a hypothetical A-B-C ferroelectric would clearly be much larger. The dielectric contrast between the A and C groups would again favor antiferroelectricity but now with a characteristic energy of $k_B T$ per molecule.

These estimates produce values much smaller than the characteristic energy scale of the dipolar interaction. The van der Waals energy thus can only be important if the « capacitor » argument truly rules out dipolar coupling. This is in general not so as we shall see. Consider, for instance, what happens if we have impurities present. Assume a single « foreign » molecule, with no dipole, inside a dipolar layer. The electrical field outside the two-dimensional liquid of dipoles is then exactly that of the missing dipole except it has opposite sign. Two impurities in neighboring layers then feel an attractive force and form a bound-state.

To show this, note that two impurity dipoles in adjacent layers with a lateral separation r have an interaction energy :

$$E(r) = \pm \frac{p_0^2}{\epsilon} \left[\frac{1}{(d^2 + r^2)^{3/2}} - \frac{3d^2}{(d^2 + r^2)^{5/2}} \right] \quad (2.7)$$

where the + sign holds if the two layers have the same polarization and the - sign if the two layers have opposite polarization. In the first case — with ferroelectric order — $E(r)$ has a minimum at $r = 0$ so the binding energy $E_B = -2 p_0^2 / \epsilon d^3$. For the second case — with antiferroelectric order, the minimum of $E(r)$ is at $r = 2d$ with a binding energy $E_B = -\frac{1}{5^{5/2}} (2 p_0^2 / \epsilon d^3)$, which is much weaker. Since $2 p_0^2 / \epsilon d^3$ is of order $k_B T$, it follows that with more than one impurity per 10^2 molecules this « stapling » effect would overwhelm the van der Waals energy and favor ferroelectric ordering from layer to layer so F^+ / F^- mixtures should be able to avoid the « capacitor plate » effect. In the next section we will investigate the competition between dipolar and van der Waals coupling on a larger scale.

3. Rigid layer model.

As discussed in the previous section, there are three types of competing interactions in the F^+ / F^- mixtures :

- i) amphiphilic interactions which tend to promote polar order in a single layer ;
- ii) dipolar interactions which favor antiferroelectric order within a single layer. In the presence of amphiphilic interactions they tend to tilt the molecules with respect to the layer normal and they favor ferroelectric interlayer order ;
- iii) van der Waals long range forces, which promote anti-ferroelectric interlayer order.

In this section, we present a Landau theory, which allows us to investigate the phase-behavior resulting from the competition. Our first problem is the identification of the order parameter. At the macroscopic level, this should be the longitudinal ferroelectric polarization. We must relate this polarization to the population of A-B-C-A and A-C-B-A sequences in an F^+ / F^- mixture.

3.1 SINGLE-LAYER FREE ENERGY. — We start by assigning an order parameter $m_j(\mathbf{x}_\perp)$ to each layer j . To define m_j we consider (F^- , F^+) molecules as « spin-up » if they have the A-B-C-A or A-B'-C-A orientation and « spin-down » if they have the opposite one (i.e. A-C-B-A, A-C-B'-A). Let $n_j^+(\mathbf{r}_\perp)$ be the number of spin-up molecules per unit area and $n_j^-(\mathbf{r}_\perp)$ the number of spin down molecules per unit area in layer j at point \mathbf{r}_\perp . The order parameter

$m_j(\mathbf{r}_\perp)$ is defined as :

$$m_j(\mathbf{r}_\perp) = n^+(\mathbf{r}_\perp) - n^-(\mathbf{r}_\perp). \quad (3.1)$$

Note that m_j is not equal to the ferroelectric polarization. Let ϕ be the average fraction of F^+ molecules. The (two-dimensional) polarization is then :

$$\begin{aligned} \mathbf{P}_j(\mathbf{r}_\perp) &= P_0 \phi_j m_j(\mathbf{r}_\perp) \hat{z} - P_0(1 - \phi_j) m_j(\mathbf{r}_\perp) \hat{z} \\ &= P_0(2\phi_j - 1) m_j(\mathbf{r}_\perp) \hat{z} \end{aligned} \quad (3.2)$$

with P_0 the average normal component of the dipole moment of an F^+/F^- molecule. Note that if $\phi = 1/2$, (i.e. 50 % F^+ /50 % F^-) the polarization is absent even if all « spins » are up.

We will describe the two-dimensional ordering of the molecules in the layers by a Landau energy F_j .

$$F_j = \int d^2r \frac{1}{2} \left\{ c_\perp (\nabla_\perp m_j)^2 + r m_j^2 + \frac{1}{2} u m_j^4 \right\}. \quad (3.3)$$

We exclude the long-range dipolar coupling in F_j as it will be absorbed in the interlayer interactions. The ordering transition occurs at $r = 0$, as usual in Landau theories, with $m_j \propto (-r/u)^{1/2}$ for $r < 0$, while c_\perp sets the length scale $\xi_\perp = \sqrt{|c_\perp/r|}$ over which m_j fluctuations are correlated. No odd powers of m_j are allowed since a given state $m_j(\mathbf{r})$ must have the same energies as the state $m_j(\mathbf{r})$ with all molecules inverted.

3.2 LAYER-LAYER INTERACTION. — The dipolar coupling is most easily expressed in Fourier space, with

$$m_j(\mathbf{q}_\perp) = \int d^2r_\perp e^{i\mathbf{q}_\perp \cdot \mathbf{r}_\perp} m_j(\mathbf{r}_\perp). \quad (3.4)$$

The dipolar energy is then

$$F_d = \int \frac{d^2q_\perp}{(2\pi)^2} \left\{ \sum_j \frac{\pi}{2\epsilon} (q_\perp^c - q_\perp) |P_j(q_\perp)|^2 - \frac{\pi}{\epsilon} \sum_{j \neq j'} P_j(q_\perp) P_{j'}(-q_\perp) q_\perp e^{-q_\perp |j-j'|d} \right\}. \quad (3.5)$$

Note that F_d is the full dipolar energy including the intra-layer coupling. The first sum in equation (3.5) corresponds to the intra-layer dipole-dipole repulsion. Recall that locally tilting the molecules over the magical angle greatly diminishes this repulsion: this reduction is expressed in our calculation by choosing the cut-off wave vector q_\perp^c of the order of a_\perp^{-1} , with a_\perp the transverse tilt coherence length. The second sum is the interlayer dipolar coupling. It expresses the « stapling » effect: for $q_\perp \rightarrow 0$, dipolar interactions vanish, but at any intermediate scale it favors local parallel alignment of P_j in adjacent layers.

We still have to take account of the van der Waals contribution. It can be expressed in terms of adjacent layers coupling :

$$F^{vw} = \frac{V}{2} \int d^2r_\perp \sum_j m_j(\mathbf{r}_\perp) m_{j+1}(\mathbf{r}_\perp). \quad (3.6)$$

We saw that van der Waals interactions favor anti-ferroelectric order, so V must be positive.

From the arguments developed in section 2. We also saw that the van der Waals interaction energy (per unit area) between two (fully ordered) layers with $d_{A_1} \ll d_{A_2}$ is of order

$$\frac{H}{96\pi d_{A_1}^2}$$

which should equal $\frac{V}{2} \frac{1}{a^4}$ (if we set $|m_j| = |m_{j+1}| = 1/a^2$), hence $V \simeq Ha^4/48\pi d_{A_1}^2$. For conventional liquid crystals the energy scale of the van der Waals interaction is much larger because of the factor $(a/d_{A_1})^2$. For $d_{A_1} = d_{A_2}$, the discrepancy is even greater.

The complete free energy is now :

$$F = \sum_j F_j + F_d + F^{VW} \quad (3.7)$$

To analyze F , it is useful to introduce the *complete* Fourier transform :

$$m(\mathbf{q}) = \sum_j m_j(\mathbf{q}_\perp) e^{iq_z d} \quad (3.8)$$

In terms of $m(\mathbf{q})$:

$$F = \frac{d}{2} \int \frac{d^3\mathbf{q}}{(2\pi)^3} |m(\mathbf{q})|^2 \left\{ r + \frac{2\pi}{\varepsilon} \bar{P}_0^2 q_\perp^c + V \cos q_z d + c_\perp q_\perp^2 - \frac{2\pi \bar{P}_0^2}{\varepsilon} q_\perp \frac{(1 - e^{-2q_\perp d})}{(1 - 2 \cos q_z d e^{-q_\perp d} + e^{-2q_\perp d})} \right\} + O(m^4) \quad (3.9)$$

in which $\bar{P}_0 = P_0(2\phi - 1)$. To analyze the nature of the ordering near $r = 0$, we first neglect the $O(m^4)$ term in equation (3.9). We can then classify the nature of the low-temperature phase by minimizing the mode spectrum $\varepsilon(\mathbf{q})$ with respect to q . The mode spectrum is defined here as :

$$F = \frac{d}{2} \int \frac{d^3\mathbf{q}}{(2\pi)^3} |m(\mathbf{q})|^2 \left[\varepsilon(\mathbf{q}) + r + \frac{2\pi}{\varepsilon} \bar{P}_0^2 q_\perp^c \right]. \quad (3.10)$$

The mode with the lowest $\varepsilon(\mathbf{q})$ will have the highest transition temperature. It is easily shown that the minimization of $\varepsilon(\mathbf{q})$ either demands $q_z \simeq 0$ or $q_z = \pm \pi/d$. We will discuss these two cases separately.

3.2.1 Anti-ferroelectric interlayer order. — For $q_z = \pm \pi/d$, we have anti-ferroelectric order between layers. The mode energy is

$$\varepsilon(\mathbf{q}_\perp) = \frac{-2\pi \bar{P}_0^2}{\varepsilon} q_\perp \frac{(1 - e^{-q_\perp d})}{(1 + e^{-q_\perp d})} + c_\perp q_\perp^2 - V. \quad (3.11)$$

i) If $c_\perp > \frac{\pi \bar{P}_0^2 d}{\varepsilon}$ the minimum is found for $q_\perp = 0$. This corresponds to the smectic bilayer structure S_{A_2} (Fig. 2a) [8].

ii) If $c_\perp < \frac{\pi \bar{P}_0^2 d}{\varepsilon}$, the minimum is obtained for non-zero q_\perp and the structure corresponds

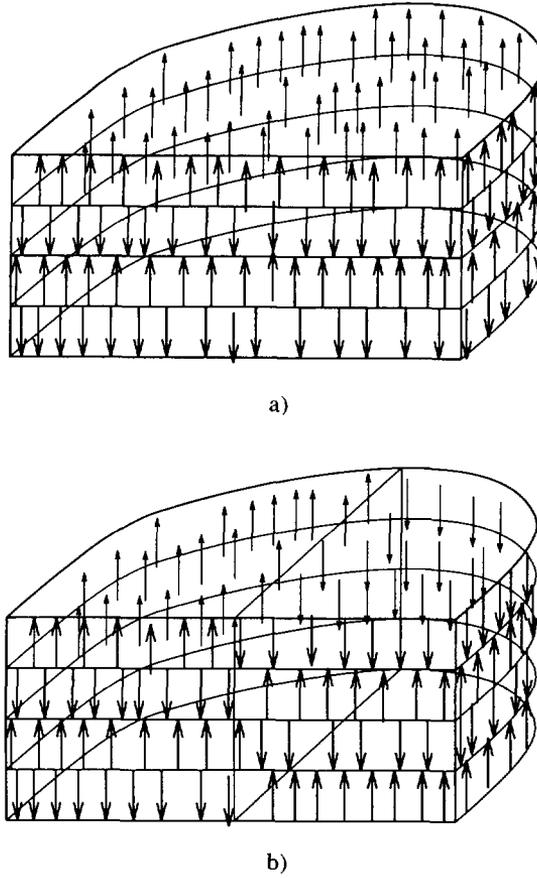


Fig. 2. — a) Schematic representation of the anti-ferroelectric bilayer smectic A phase (S_{A_2}). b) Schematic representation of the antiphase $S_{\bar{A}}$. Note the antiferroelectric order both in the plane of the layers and from plane to plane.

to the $S_{\bar{A}}$ antiphase structure [8], and anti-ferroelectric both from layer to layer and inside the layers (Fig. 2b).

iii) If $c_{\perp} = \frac{\pi \bar{P}_0^2 d}{\epsilon}$, we find a Lifshitz point near $r = 0$. For $c_{\perp} \approx 2\pi \bar{P}_0^2 d / \epsilon$ the optimum wave vector in the antiphase $S_{\bar{A}}$ obeys

$$q_{\perp}^2 \approx \frac{6}{d^2} \left(\frac{\bar{P}_0^2 - P_{0c}^2}{\bar{P}_0^2} \right) \quad (3.12)$$

with $P_{0c}^2 = \frac{c_{\perp} \epsilon}{\pi d}$. According to (3.12), when \bar{P}_0 is of the order of P_{0c} , the period of the $S_{\bar{A}}$ antiphase parallel to the layers is of the order of a few d 's which agrees well with experimental studies of the $S_{\bar{A}}$ phase [9].

3.2.2 *Ferroelectric interlayer order.* — For $q_z = 0$ we have ferroelectric interlayer order. We must minimize the spectrum

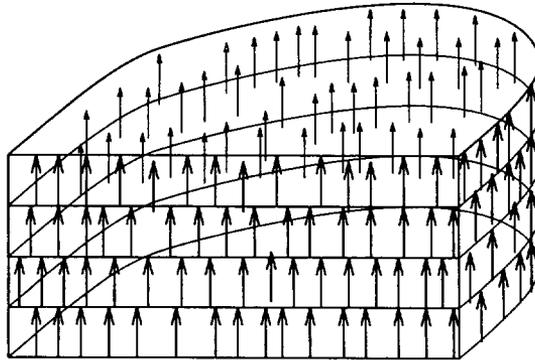
$$\varepsilon(\mathbf{q}_\perp) = \frac{-2\pi\bar{P}_0^2}{\varepsilon} q_\perp \frac{(1 + e^{-q_\perp d})}{(1 - e^{-q_\perp d})} + c_\perp q_\perp^2 + V \quad (3.13)$$

with again three cases :

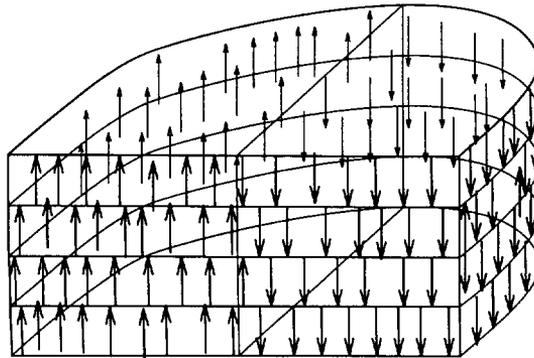
i) If $c_\perp > \frac{2\pi\bar{P}_0^2 d}{3\varepsilon}$ then $q_\perp = 0$ is the minimum. The corresponding phase is a longitudinal ferroelectric (Fig. 3a). We will denote it by S_{AF} .

ii) If $c_\perp < \frac{2\pi\bar{P}_0^2 d}{3\varepsilon}$ the minimum is obtained for non-zero q_\perp . The structure is that of a « stripe » phase, with an interlayer ferroelectric, and an intralayer anti-ferroelectric arrangement (Fig. 3b).

iii) If $c_\perp = \frac{2\pi\bar{P}_0^2 d}{3\varepsilon}$ we again have a Lifshitz point. In its vicinity, on the modulated side, the



a)



b)

Fig. 3. — a) Simple view of the ferroelectric smectic A. b) Schematic representation of the stripe phase.

optimum wave vector obeys :

$$q_{\perp}^{*2} \cong \frac{30}{d^2} \left(\frac{\bar{P}_0^2 - P_{0c}^2}{\bar{P}_0^2} \right) \quad (3.14)$$

with $P_{0c}^2 = \frac{3 c_{\perp} \varepsilon}{2 \pi d}$ so, again, the period should be of the order of a layer thickness or more.

Can we now decide whether ferro (B) or anti-ferro (A) interlayer ordering is realized ? First, for $c_{\perp} < \frac{2 \pi \bar{P}_0^2 d}{3 \varepsilon}$, when the mode energy always is lowest for $q_{\perp} \neq 0$, the dipolar energy

favors the (B) case while the van der Waals energy favors (A). If $\frac{\bar{P}_0^2}{\varepsilon d} \geq V$, we should expect (B)

and if $\frac{\bar{P}_0^2}{\varepsilon d} \leq V$ we expect (A). From the earlier estimates of the energy scales (Sect. 2)

$\left(\frac{\bar{P}_0^2}{\varepsilon d} \sim k_B T \text{ and } V \ll k_B T \right)$ ferroelectric interlayer order is expected unless $\phi \cong 1/2$ where

$\bar{P}_0 \cong 0$ and anti-ferroelectric interlayer order should be seen. For $c_{\perp} > \frac{2 \pi \bar{P}_0^2 d}{3 \varepsilon}$, the S_{A_2} anti-phase structure (A case) has a mode energy $\varepsilon(\mathbf{q}_{\perp} = 0) \cong -V$. However, for the $q_z = 0$ S_{A_f} phase (B case), $\varepsilon(\mathbf{q}_{\perp})$ is really *singular* in the limit $\mathbf{q}_{\perp} \rightarrow 0$ (see Eq. (3.13)) and a separate discussion is required.

3.2.3 Longitudinal S_{A_f} ferroelectric phase. — To gain insight into the singular behavior of $\varepsilon(\mathbf{q})$ in the small \mathbf{q} limit, we expand equation (3.13) for small \mathbf{q} :

$$\varepsilon(\mathbf{q}) \cong -\frac{4 \pi \bar{P}_0^2}{\varepsilon d} \left\{ 1 - \frac{q_z^2}{q_z^2 + q_{\perp}^2} \right\} + \left(\frac{c_{\perp}}{2} - \frac{\pi}{\varepsilon} \bar{P}_0^2 \frac{d}{3} \right) q_{\perp}^2 - \frac{1}{2} V q_z^2 d^2 + V \quad (q_z d \ll 1). \quad (3.15)$$

If we would naively first set $q_{\perp} = 0$ and then $q_z = 0$ we would find only the van der Waals term V , in agreement with the « capacitor » argument of section 1. This is however incorrect. Minimize $\varepsilon(\mathbf{q})$ with respect to q_{\perp} . This leads to :

$$q_{\perp}^2 \cong \sqrt{\frac{8 \pi \bar{P}_0^2}{\varepsilon d \tilde{c}}} q_z \quad (3.16)$$

and, to lowest order,

$$\varepsilon(q_z) = -\frac{4 \pi \bar{P}_0^2}{\varepsilon d} + 2 \sqrt{\frac{\tilde{c} 2 \pi \bar{P}_0^2}{\varepsilon d}} |q_z| + V \quad (3.17)$$

where

$$\tilde{c} = \frac{c_{\perp}}{2} - \frac{\pi}{3 \varepsilon} \bar{P}_0^2 d. \quad (3.18)$$

Minimizing $\varepsilon(q_z)$ next with respect to q_z shows that for $\tilde{c} > 0$ and for $\bar{P}_0^2/\varepsilon d \geq V$ we must choose q_z as small as possible. For a sample consisting of a slab of thickness D , this means that

$q_z \sim \pi/D$. With q_\perp given by equation (3.16), our longitudinal ferroelectric S_{A_F} does not really have a macroscopic ferroelectric polarization. The polarization in the plane has a modulation length $\ell_\perp = \frac{2\pi}{q_\perp}$

$$\ell_\perp \approx \sqrt{2\pi D} \left(\frac{\varepsilon d \tilde{c}}{8\pi \bar{P}_0^2} \right)^{1/4} \quad (3.19)$$

This size is the geometrical mean of a macroscopic and a microscopic length. For sample thicknesses of about 100 microns, like those of reference [3], one expects ℓ_\perp to be of micron size. If the $Sm X'$ phase corresponds to the S_{A_F} phase, then the interpretation of their observations should be reinvestigated, since only the difference between « up » and « down » domains could have been observed. The true polarization \bar{P}_0 could thus be orders of magnitude larger than the measured one.

In summary, for $c_\perp < 2\pi \bar{P}_0^2 d/3\varepsilon$ and for $\bar{P}_0^2/\varepsilon d \geq V$, we expect a phase with in plane modulation of the polarization on a length-scale of order the layer spacing and inter-layer ferroelectric order, while for $c_\perp < 2\pi \bar{P}_0^2/3\varepsilon$ we expect a phase with in plane modulation on a « mesoscopic » length-scale of order ℓ_\perp and inter-layer ferroelectric order.

Having found the optimal $|\mathbf{q}_\perp|$ wave vector does, however, not mean that we completely know the precise nature of the low temperature phase. One could, for instance, imagine structures which are the superposition of a series of modulations, all with the same $|\mathbf{q}_\perp|$. This would be controlled by the non-linear $O(m^4)$ term in equation 3.9. By analogy with dipolar-coupled magnetic thin films (as discussed for instance by Garel and Doniach [10]) we expect competition between two basic structures : a stripe phase — with a single wave vector — and a « bubble » phase (Fig. 4) with

$$\mathbf{q}_{1\perp} + \mathbf{q}_{2\perp} + \mathbf{q}_{3\perp} = 0 \quad |\mathbf{q}_{1\perp}| = |\mathbf{q}_{2\perp}| = |\mathbf{q}_{3\perp}|.$$

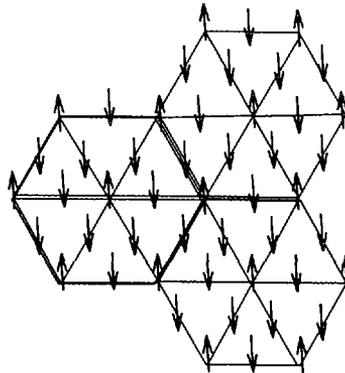


Fig. 4. — Bubble phase.

For the case $q_z = 0$ and $c_\perp < \frac{2\pi \bar{P}_0^2 d}{3\varepsilon}$, this « bubble » structure would seem to have no macroscopic ferro-electric polarization. However, in the Fourier expansion of $m^4(\mathbf{r})$, one

encounters a term $m(\mathbf{q} = 0) [m(\mathbf{q}_{1\perp}, q_z = 0) m(\mathbf{q}_{2\perp}, q_z = 0), m(\mathbf{q}_{3\perp}, q_z = 0)]$ with $\mathbf{q}_{1\perp} + \mathbf{q}_{2\perp} + \mathbf{q}_{3\perp} = 0$. In the « bubble » phase, this term imposes $m(\mathbf{q} = 0) \neq 0$. This type of longitudinal ferroelectricity is quite different from the S_{AF} phase. In that case, we were dealing with a longitudinal ferroelectric with *liquid* in-plane order while the present « bubble » ferroelectric really is a ferroelectric *crystal*. If the coefficient u of the m^4 term in equation (3.11) is wave vector independent then the « stripes » have always a lower energy than the « bubbles » in the absence of external fields (as shown in the Appendix). However, for u wave vector dependent, a « bubble » phase may be possible.

4. Macroscopic properties of S_{AF} .

We now consider the part of the phase diagram of section 3 where we indeed have a paraelectric ferroelectric transition (i.e. an $S_A - S_{AF}$ transition at a temperature T_F). What will be the macroscopic response of the new phase? More precisely, if we study the X-ray diffraction line shape very close to a Bragg spot or probe the S_{AF} ferroelectric sample with sound waves, how will the response differ from that of an ordinary smectic? « Macroscopic » actually means here that we are interested in length-scales large compared to the layer spacing d but still small compared to the domain size ℓ_\perp described in the preceding section.

It is well-known that for smectics, the macroscopic properties are largely controlled by layer compression fluctuations and by layer undulations. We thus must relax the rigid layer constraint of section 3. Let $u(\mathbf{r})$ be the vertical displacement of the layers. If we demand that the polarization $\mathbf{P}(\mathbf{r})$ is anchored to the layer normal then

$$\mathbf{P}(\mathbf{r}) = P(\mathbf{r}) (\hat{z}, -\nabla u). \quad (4.1)$$

If we are not too close to T_F we can assume $P(\mathbf{r}) = \langle P \rangle + \delta P(\mathbf{r})$ with $\langle P \rangle$ the spontaneous macroscopic polarization ($\equiv \langle m \rangle \bar{P}_0$) and $\delta P \ll \langle P \rangle$. The fluctuation free energy for $T < T_F$ is then

$$\Delta F = \int \frac{d^3r}{(2\pi)^3} \left\{ \frac{1}{2} \left[B \left(\frac{\partial u}{\partial z} \right)^2 + K_1 (\nabla_\perp^2 u)^2 \right] + \left(e_\perp (\nabla_\perp^2 u) + e_\parallel \left(\frac{\partial^2 u}{\partial z^2} \right) \right) \delta P \right. \\ \left. + \frac{1}{2} \left(\frac{1}{4\pi \varepsilon_\parallel} \delta P^2 + c_\perp (\nabla_\perp \delta P)^2 \right) \right\} + \int d^3r \int d^3r' \frac{(\nabla \cdot \mathbf{P})_r (\nabla \cdot \mathbf{P})_{r'}}{[|\tilde{\varepsilon}| \tilde{\varepsilon}_{ij}^{-1}(\mathbf{r} - \mathbf{r}')_i (\mathbf{r} - \mathbf{r}')_j]^{1/2}}. \quad (4.2)$$

The first term in equation (4.2) is the standard energy cost of layer fluctuations in a smectic with compressional modulus B and Frank bending energy K_1 . The second term describes the flexoelectric effect: a curved layer has a polarization proportional to $\nabla_\perp^2 u$ and a compressed layer a polarization proportional to $\frac{\partial^2 u}{\partial z^2}$ since both terms break inversion symmetry. They couple to P and describe the tendency to instability for a ferroelectric smectic described in section 1. The third term is the fluctuation energy of a $d = 2$ ferroelectric with $\varepsilon_\parallel \rightarrow \infty$ at the critical point. The last term is the Coulomb energy due to charge fluctuations $\nabla \cdot \mathbf{P}$ in an anisotropic medium with dielectric tensor

$$\varepsilon_{ij} = \begin{pmatrix} \varepsilon_\perp & 0 & 0 \\ 0 & \varepsilon_\perp & 0 \\ 0 & 0 & \varepsilon_\parallel \end{pmatrix}$$

assuming that there are no free charges.

Far below T_F , we can neglect « amplitude » fluctuations, i.e. we can set $\delta P = 0$. The remaining layer undulations have a fluctuation energy

$$\Delta F = \int \frac{d^3q}{(2\pi)^3} \frac{1}{2} \left\{ Bq_z^2 + q_\perp^4 \left(K_1 + \frac{\langle P \rangle^2}{\varepsilon_\parallel q_z^2 + \varepsilon_\perp q_\perp^2} \right) \right\} |u_q|^2 \quad (4.3)$$

with u_q the Fourier transform of $u(\mathbf{r})$. The Coulomb energy thus produces an effective \mathbf{q} dependent K_1 bending energy :

$$K_1^{\text{eff}}(\mathbf{q}) = K_1 + \frac{\langle P \rangle^2}{\varepsilon_\parallel q_z^2 + \varepsilon_\perp q_\perp^2} \quad (4.4)$$

which diverges as $q \rightarrow 0$. Physically, a layer undulation produces a charge fluctuation and the Coulomb repulsion then enhances the stiffness K_1 . This has obviously a *stabilizing* effect on the smectic state. The cross-over length

$$\lambda \equiv (\varepsilon K_1 / \langle P \rangle^2)^{1/2} \quad (4.5)$$

where this effect becomes important is of order 10^2 \AA if we assume that every molecule has a dipole with a 5 \AA charge separation, if we set $\varepsilon \sim 10$, and if we take $K_1 \approx 10^{-6} \text{ erg/cm}$.

The equipartition theorem predicts :

$$\langle |u_q|^2 \rangle = \frac{k_B T}{Bq_z^2 + K_1^{\text{eff}}(q) q_\perp^4} \quad (4.6)$$

This renormalization has important consequences for X-ray diffraction. In the absence of the Coulomb interaction, $K_1^{\text{eff}} = K_1$, and $\int d^3q \langle |u_q|^2 \rangle$ diverges logarithmically. The Bragg peak intensity is proportional to $e^{-\langle u^2 \rangle / d^2}$ and is thus zero. However, in our case this logarithmic divergence is cutoff at $q_\perp = 1/\lambda$:

$$\langle u^2 \rangle \propto \frac{k_B T}{\sqrt{K_1 B}} \ln \left(\frac{(\varepsilon K_1)^{1/2}}{a_0 \langle P \rangle} \right) \quad (4.7)$$

with a_0 a microscopic cutoff. We even could use X-ray studies to measure the true microscopic value of $\langle P \rangle$ since the Bragg peak intensity $I_G \propto e^{-G^2 \langle u^2 \rangle}$ at $(G = n2\pi/d)$ is :

$$I_G \sim \left[\frac{(\varepsilon K_1)^{1/2}}{a_0 \langle P \rangle} \right]^{\frac{k_B T G^2}{\sqrt{K_1 B}}} \quad (4.8)$$

and thus has a power-law dependence on $\langle P \rangle$!

Another interesting consequence of equation (4.3) concerns the propagation of second sound along the layers. For ordinary smectics this is an overdamped mode with a relaxation rate $\Gamma_q \sim \frac{K_1 q_\perp^2}{\eta}$ with η the viscosity. In the present case, second sound would obey an equation of motion

$$\rho \ddot{u}_{q_\perp} + \eta q_\perp^2 \dot{u}_{q_\perp} = -q_\perp^4 \left(K_1 + \frac{\langle P \rangle^2}{\varepsilon_\perp q_\perp^2} \right) u_{q_\perp} \quad (4.9)$$

with ρ the mass density. The associated mode dispersion is then

$$\omega_q \approx \begin{cases} \frac{iK_1 q_\perp^2}{\eta} & q_\perp \gg 1/\lambda \\ \frac{q_\perp \sqrt{\frac{4\rho \langle P \rangle^2}{\varepsilon_\perp} - \eta q_\perp^2 + i\eta q_\perp^2}}{2\rho} & q_\perp \ll 1/\lambda \end{cases} \quad (4.10)$$

so for $q_\perp \ll 1/\lambda$ and for $q_\perp \leq \left[\frac{4\rho \langle P \rangle^2}{\varepsilon_\perp \eta} \right]^{1/2}$ we would have a *propagating* mode. The second constraint is severe. It requires that $q_\perp \leq \frac{1}{\lambda} \left\{ \frac{\rho K_1}{\eta} \right\}^{1/2}$. For $K_1 \sim 10^{-6}$ erg/cm, $\eta = 1$ poise, and $\lambda = 10^2 \text{ \AA}$, q_\perp^{-1} must exceed 10^5 \AA . This restricts the new mode propagation to macroscopic wavelengths, but it should be achievable experimentally. Note however that we assumed that there was no electrostatic screening. In the presence of free ions, the effect would be absent unless the Debye length significantly exceeds $\lambda(\eta/\rho K_1)^{1/2}$.

As we increase ε_\parallel and approach T_F , amplitude fluctuations in $\delta\rho$ become more important. If we integrate over the $\delta\rho$ fluctuations we find :

$$\Delta F = \int d^3q \left\{ \frac{1}{2} B q_z^2 + K_1^{\text{eff}}(q) q_\perp^4 - \frac{\left[(e_\perp q_\perp^2 + e_\parallel q_z^2)^2 + \frac{4 q_z^2 q_\perp^4 \langle P \rangle^2}{(\varepsilon_\parallel q_z^2 + \varepsilon_\perp q_\perp^2)^2} \right]}{2 \left[\frac{1}{4\pi\varepsilon_\parallel} + c_\perp q_\perp^2 + \frac{q_z^2}{\varepsilon_\parallel q_z^2 + \varepsilon_\perp q_\perp^2} \right]} \right\} |u_q|^2 \quad (4.11)$$

In the small q limit, we can absorb the flexoelectric term in a renormalization of K_1 :

$$K_1^R = K_1 - 2\pi\varepsilon_\parallel e_\perp^2. \quad (4.12)$$

As we approach the critical point $\varepsilon_\parallel \rightarrow \infty$, this renormalization drives K_1^R to zero and triggers a bending instability. This is exactly the destabilizing splay of ferroelectricity discussed in section 1. It means that we cannot have a simple Ising-like second-order transition at $q_\perp = 0$. If we look at the mode spectrum for $q_z = 0$:

$$\varepsilon(q_\perp) = \frac{1}{2} K_1 q_\perp^4 + \frac{\langle P \rangle^2}{\varepsilon_\perp} q_\perp^2 - \frac{1}{2} \frac{e_\perp^2 q_\perp^4}{\left(\frac{1}{4\pi\varepsilon_\parallel} + c_\perp q_\perp^2 \right)} \quad (4.13)$$

then for $\varepsilon_\parallel^{-1} = 0$ and $\langle P \rangle = 0$ (the critical point), the minimum of $\varepsilon(q_\perp)$ is at

$$q_\perp^* = \left(\frac{e_\perp^2}{2c_\perp K_1} \right)^{1/2} \quad (4.14)$$

In the critical region, we thus expect to first find an anti-ferroelectric phase with in-plane modulation before we reach the true S_{AF} phase. However, as we enter the $\langle P \rangle \neq 0$ phase deeper, this modulation should disappear once K_1^R again becomes positive. The reason is, that away from the critical point, ε_\parallel and e_\perp should have values in the S_{AF} phase comparable to that

of ordinary smectics for which K_1^R indeed is positive. Thus, in the case of a (near) continuous onset of longitudinal ferroelectric order we should expect to encounter a modulated phase in the critical region due to the ferroelectric « splay » effect. In the case of large first-order transition, the instability may be suppressed.

5. Conclusion.

Our study for longitudinal ferroelectric ordering has produced a variety of structures. By varying temperature and/or the mixing composition of the F^+ and F^- molecules, we ought to encounter a rich sequence of phases. Suppose, for instance, that we varied the F^+ concentration ϕ , and thus \bar{P}_0 , in the low temperature region. Since $\bar{P}_0^2 \propto (2\phi - 1)^2$, we would first decrease \bar{P}_0^2 — till $\phi = 1/2$ where $\bar{P}_0^2 = 0$ — and subsequently increase it. If, for $\phi = 0$, $\bar{P}_0^2(\phi = 0) d/\varepsilon \geq c_\perp$ and if $\bar{P}_0^2(\phi = 0)/\varepsilon d \gg V$, then we should first find the « stripe » phase anti-ferroelectric with in-plane modulation. As we increase the F^+ concentration, the « stripe » phase should transform to the S_{AF} ferroelectric when $\bar{P}_0^2(\phi) d/\varepsilon$ drops below c_\perp . As we keep adding F^+ molecules, $\bar{P}_0^2(\phi)/\varepsilon d$ should eventually drop below V near $\phi \simeq 1/2$ and we should encounter the S_{A_2} double-period anti-ferroelectric. Increasing ϕ beyond $1/2$ should invert the sequence. The resulting phase sequence is

$$\text{Stripe} \rightarrow S_{AF} \rightarrow S_{A_2} \rightarrow S_{AF} \rightarrow \text{Stripe}$$

$$\xrightarrow{\phi}$$

Even more complicated phase-sequences are possible if the « bubble » and $S_{\bar{A}}$ phases are allowed.

If we increase the temperature in the S_{AF} longitudinal ferroelectric we find, assuming a (near) continuous transition

$$S_{AF} \rightarrow \text{Stripe} \rightarrow S_A$$

$$\xrightarrow{T}$$

The complete topology of the $\phi - T$ phase diagram is thus likely to be quite complex, since the stripe phase near $T \sim T_F$ could be connected in the $\phi - T$ phase diagram to the stripe phase near $\phi \sim 0$ and $\phi \sim 1$.

According to the recent X-ray work of Ostrovski *et al.* [4] the ordered phase (SmX) of the pure compounds F or F' is indeed a stripe phase but slightly more complicated than the one we describe here. The structure is very close to that of figure 3b, but the layers are shifted by half a period from one domain to that of the neighboring one, (leading to extinction of the (001) Bragg peak). Our model does not allow this structure (although it could be included). In view of the small measured coherence lengths, we feel that more experimental work is needed to determine definitively the actual structure.

The predicted S_{AF} ferroelectric phase, may well correspond to the (SmX') 75/25 mixture. If so, it must have a complex structure since according to our results it should consist of lateral mesoscopic domains. Since these domains are not coupled to any simple optical property they may not be easily detected but it would be important to reveal their existence. Indeed, if they constitute an intrinsic part of the physics of the SmX phase, then the polarizations measured up to now are probably only a small part of their actual value (as they are due to residual imbalance between ferroelectric domains). One can think of several ways of measuring this true polarization :

- investigating the size dependence of the measured polarization. For layers parallel to the sample holder, it should depend on the sample lateral size L_{\perp} and oscillate between zero and $\pm \ell_{\perp}/L_{\perp}$;
- sweeping a microelectrode over an oriented ferroelectric sandwich (the domain size should be of micron size for a 100 μm thick slab) ;
- studying the field-induced transition from the domain S_{AF} structure to a true homogeneous ferroelectric. If we use equation (3.16) to estimate the electrical field required to force $q_{\perp} \Rightarrow 0$, then this demands $E \geq P_0/\epsilon a^2 d$. This is a very large field since it really supresses the ferroelectric inter-layer coupling. However, near T_F the effect may be observable ;
- performing X-ray intensity measurements. This would probably give the most reliable values of $\langle P \rangle$, according to section 4.

Pretransitional studies of the divergence of the dielectric constant ϵ_{\parallel} and the flexoelectric coefficients are also of great interest. The coupling between the order parameter (the polarization) and the « soft » undulation mode should lead to the analog of Fisher-renormalized critical behavior in deformable magnets. The critical properties of undulation modes coupled to an order parameter which breaks inversion symmetry (i.e. the ΔF of Eq. (4.2) in the absence of Coulomb interaction) were in fact studied by Golubovic and Wang [11]. The long-range dipolar coupling may, however, affect their results. We refer to their paper for a discussion.

Acknowledgments.

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Appendix A.

In this appendix we compare in mean-field theory the relative stability of the ferroelectric smectic A phase with an order parameter $m(\mathbf{x}_{\perp}, z) = m_0$, the stripe phase with an order parameter $m(\mathbf{r}_{\perp}, z) = m_s \sqrt{2} \cos \mathbf{q}_{\perp} \cdot \mathbf{r}$, and the « bubble » phase (three-dimensional ferroelectric crystal) with an order parameter :

$$m(\mathbf{r}_{\perp}, z) = m_0 + \sum_{i=1}^3 m_B \sqrt{\frac{2}{3}} \cos(\mathbf{q}_i \cdot \mathbf{r}_{\perp})$$

$$\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3 = 0 \quad |q_1| = |q_2| = |q_3| .$$

The free energies computed from equation (3.9) are :

$$F_0 = \frac{1}{2} f_0 m_0^2 + \frac{u}{4} m_0^4 \quad (\text{A.1})$$

for the ferroelectric smectic A,

$$F_s = \frac{1}{2} f_{q_{\perp}} m_s^2 + \frac{3}{8} u m_s^4 \quad (\text{A.2})$$

for the stripe phase, and

$$F_B = \frac{1}{2} f_0 m_0^2 + \frac{u}{4} m_0^4 + \frac{1}{2} f_{q_\perp} m_B^2 + \frac{5}{8} u m_B^4 + \sqrt{\frac{2}{3}} u m_0 m_B^3 + \frac{3}{2} u m_0^2 m_B^2 \quad (\text{A.3})$$

for the « bubble » phase. Here, u is the coupling coefficient of the m^4 term in equation (3.11), and f_0 and f_{q_\perp} stand for the coefficients of the second order term taken at the relevant wave vector in equation (3.9).

Minimization of (A.1), (A.2) and (A.3) leads to

$$\begin{aligned} F_0 &= -\frac{f_0^2}{4u}; \\ F_s &= -\frac{f_{q_\perp}^2}{6u} \\ F_B &= \frac{-(F_0 \cos^2 \theta + f_{q_\perp} \sin^2 \theta)^2}{4u \left(\cos^4 \theta + \frac{5}{2} \sin^4 \theta + 6 \sin^2 \theta \cos^2 \theta + 4 \sqrt{\frac{2}{3}} \cos \theta \sin^3 \theta \right)} \end{aligned}$$

where we set $m_0 = m \cos \theta$, $m_B = m \sin \theta$ and minimized F_B for constant θ .

If we first ignore the bubble phase, then the (f_0, f_{q_\perp}) phase diagram is very simple. If $f_0 = 0$, with $f_{q_\perp} > 0$ we find a second-order phase transition to an S_A ferroelectric phase. If $f_{q_\perp} = 0$, with $f_0 > 0$ we find a (mean field) second-order phase transition to a stripe phase. Finally, if both $f_{q_\perp} < 0$ and $f_0 < 0$, we find at $f_0 = \sqrt{\frac{2}{3}} f_{q_\perp}$ a first-order ferroelectric-to-stripe phase transition.

In order to look for any stability domain of the bubble phase one has to compare successively, F_B to F_0 and F_s , for any possible θ . This is an algebraic exercise which does not present any difficulty. It turns out that F_B is always larger than either F_0 or F_s so that within this description scheme the « bubble » phase is never more stable than the others. There are, however, reasons to introduce q dependent fourth order coupling constants, e.g. due to concentration fluctuations, in which case it becomes possible to observe the crystalline ferroelectric « bubble » phase. A simple way of showing this possibility is to compare F_0 , F_s and F_B , on the first order $F_0 = F_s$ line. The free energies are then

$$\begin{aligned} F_0 &= \frac{1}{2} f_0 m_0^2 + \frac{\lambda u}{4} m_0^4 \\ F_s &= \frac{1}{2} f_{q_\perp} m_s^2 + \frac{3}{8} u m_s^4 \\ F_B &= \frac{1}{2} f_0 m_0^2 + \frac{\lambda u}{4} m_0^4 + \frac{1}{2} f_{q_\perp} m_B^2 + \frac{5}{8} u m_B^4 \\ &\quad + \sqrt{\frac{2}{3}} \nu u m_0 m_B^3 + \frac{3}{2} u \mu m^2 m_B^2 \end{aligned}$$

with $\lambda = \mu = \nu = 1$ corresponding to the case of a wave vector independent u .

Demanding that F_B be at least equal to F_0 and F_s on this line, leads to the conditions :

$$\begin{aligned} \text{tg } \theta &= -2 \sqrt{\frac{2}{3}} \nu \\ y &= -\frac{8}{3} \nu^2 + 6 \mu - \sqrt{6} = 0. \end{aligned}$$

When $y < 0$, this opens up a stability domain for the « bubble phase » between the stripe phase and the ferroelectric smectic A.

The same description applies to a discussion of the stability of the bilayer S_{A_2} , the antiphase $S_{\bar{A}}$ and a three dimensionally modulated phase $S_{\bar{B}}$. The corresponding order parameters would be :

$$\begin{aligned}
 S_{A_2} \cdot m(\mathbf{x}_{\perp}, z) &= \sqrt{2} m_0 \cos q_z z \\
 S_{\bar{A}} \cdot m(\mathbf{x}_{\perp}, z) &= 2 m_s \cos q_z z \cos q_{\perp} x \\
 S_{\bar{B}} \cdot m(\mathbf{x}_{\perp}, z) &= \sqrt{2} m_0 \cos q_z z + \sum_{i=1}^3 \frac{2}{\sqrt{3}} m_B \cos q_z z \cos \mathbf{q}_i \cdot \mathbf{x}_{\perp} \\
 \mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3 &= 0 \quad |q_1| = |q_2| = |q_3|.
 \end{aligned}$$

The corresponding free energies would be given by (A.1, A.2) and (A.3), provided u is replaced by $\tilde{u} = \frac{3}{2}u$. Again, for u constant the $S_{\bar{B}}$ phase is not stable. However, an appropriate q dependence of u could stabilize the $S_{\bar{B}}$ between the $S_{\bar{A}}$ and the S_{A_2} phases. This $S_{\bar{B}}$ phase may correspond to A. M. Levelut's « crenelated » structure [12] — in which case it should be a crystal.

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