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Escape from incommensurability : the two-dimensionally ordered $S_{\tilde{A}}$ antiphase

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Résumé. — L'étude de l'énergie libre des smectiques A frustrés permet la compréhension théorique de l'antiphase $S_{\tilde{A}}$ récemment découverte, comme échappatoire bidimensionnel aux phases incommensurables. La description que nous obtenons correspond aux données expérimentales obtenues par rayons X. Le diagramme de phase $S_{\tilde{A}}$, $S_{A'}$ bicouche, S_{Ai} incommensurable, $S_{\tilde{A}}$ est aussi obtenu.

Abstract. — The study of the frustrated S_A free energy allows the theoretical understanding of the recently discovered $S_{\tilde{A}}$ antiphase, as two dimensional escape to incommensurate phases. The picture obtained agrees with X-ray experimental evidence. We further give the phase diagram between bilayer $S_{A'}$, incommensurate S_{Ai} , and antiphase $S_{\tilde{A}}$.

Introduction. — The physics of mesophases of highly dipolar molecules has been recently described as a competition between two lengths, namely that of the molecule and that of the pair of antiparallel dipoles which are known to exist in such liquid crystals [1]. With this point of view, the same free energy has the potentiality of describing either a nematic reentrant behaviour, when the ratio of these lengths is close to one, or a smectic A-smectic A transition when this ratio is nearly two. Moreover, the same picture can be used to describe commensurate-incommensurate phase transitions. This theoretical conjecture has the advantage of unifying otherwise uncorrelated experimental results [2-4].

More recently, a new smectic phase called $S_{\tilde{A}}$ has been discovered by Sigaud *et al.* [5] : X-ray evidence shows that it corresponds to a smectic in which the monolayer order is unperturbed, and the bilayer order oscillates from one equivalent lock-in position to another periodically in a direction parallel to the planes (Fig. 1b). For that reason, the name smectic antiphase has been proposed [5]. In this paper, this phase is shown to be induced by the competition between the two microscopic lengths and appears as an alternative to the incommensurate phase. Depending on the values of the Landau parameters, one can get either a bilayer $S_{A'}$, an incommensurate S_{Ai} , or the new $S_{\tilde{A}}$ phase : the corresponding phase diagram is given.

1. Formulation of the model. — The $S_{\tilde{A}}$ phase appears in a binary mixture of strongly polar mole-

Fig. 1. — a) The incommensurability $2k_1 \neq k_2$ (left) does not prevent phase matching (right) in a two dimensional vector space. b) Schematic view of the structure resulting from this matching. The solid lines represent the (unperturbed) monolayer order, the dotted lines the bilayer order. The two possible lock-in positions of the dipolar part of the molecules (straight segment) are made clear on the figure. The cosine dependence of P along x implies that, midway between two such positions, an equal number of heads and tails (wavy lines) coexist.

cules. In this case, the ratio of the dipolar and the molecular lengths is about 1.8 in the high temperature S_A phase.

As in reference [1], we introduce two order parameters : $P_z(\mathbf{r})$ the antiferroelectric order parameter and $\rho(\mathbf{r})$ the density modulation ; their optimum periodicities being respectively k_1 and k_2 with :

$$\frac{k_2}{k_1} \simeq 1.8.$$

The coupling between them favours the lock-in of their phases. Because of the incommensurability of k_1 and k_2 , this energy competes with the elastic terms. Assuming the amplitudes of the order parameters to be homogeneous in space and allowing their phases to be a function of z only (z is the direction perpendicular to the layers), one obtains a well-known one dimensional commensurability problem [6, 7, 1]. In this case, the most stable phase is either a commensurate or an incommensurate phase, in which a phase defects condensation leads to partial locking of P_z and ρ .

However, in two or three dimensional systems, the lock-in can be obtained by an escape from one-dimensionality as shown on figure 1a. As proved in the following, this situation corresponds to that of the S_A phase. It is therefore necessary to consider a 2d or a 3d problem to describe such a phase.

2. The free energy of the model. — We consider for simplicity a 2d model only. We assume that the wavevector of $\rho(\mathbf{r})$ is along the z direction. As in the first model [1], we do not consider the amplitude fluctuations of ρ and P . We have therefore :

$$\rho(\mathbf{r}) = \rho_0 e^{i(k_2 z + \beta)}.$$

In the following, β will be taken constant in space (see concluding remarks for a quick discussion of this approximation). Then we will take β equal to zero (choice of the origin of the phases).

To describe easily the lock-in in the two cases of figure 1, we introduce two antiferroelectric order parameters :

$$P_1(\mathbf{r}) = P \exp \left[i \left(\frac{k_2}{2} z + q_x x + \alpha_1 \right) \right]$$

$$P_2(\mathbf{r}) = P \exp \left[i \left(\frac{k_2}{2} z - q_x x + \alpha_2 \right) \right]$$

where the phases α_1 and α_2 and q_x will be calculated by minimization of the free energy.

The physical polarization is related to P_1 and P_2 by :

$$P_z(\mathbf{r}) = \frac{1}{2} \text{Re} (P_1 + P_2).$$

With this notation, the coupling energy between $\rho(\mathbf{r})$ and $P_z(\mathbf{r})$ is given simply, by a generalization of references [1, 8], as :

$$- 2 D P^2 \rho_0 \cos (\alpha_1 + \alpha_2).$$

The elastic energy can also be expressed as a function of α_1 and α_2 . First, we introduce terms indicating that the optimum periodicities of P_1 and P_2 have a modulus k_1 ; i.e.

$$\frac{1}{2 M_{\parallel}} P^2 [(|\mathbf{grad} \varphi_1| - k_1)^2 + (|\mathbf{grad} \varphi_2| - k_1)^2]$$

where φ_1 and φ_2 are the phases of P_1 and P_2 respectively.

Assuming that q_x and $d\alpha_i/dz$ are much smaller than $k_2/2$, we obtain at the relevant (first) order :

$$|\mathbf{grad} \varphi_i| - k_1 = \left(\frac{k_2}{2} - k_1 \right) + \frac{q_x^2}{k_2} + \frac{d\alpha_i}{dz}.$$

The elastic term can then be expressed in this approximation as :

$$\frac{P^2}{2 M_{\parallel}} \left[\left(\frac{d\alpha_1}{dz} + \frac{q_x^2}{k_2} + \frac{k_2}{2} - k_1 \right)^2 + \left(\frac{d\alpha_2}{dz} + \frac{q_x^2}{k_2} + \frac{k_2}{2} - k_1 \right)^2 \right].$$

On the other hand, tilting the P_1 and P_2 wavevectors costs energy ; to the same order of approximation this gives :

$$\frac{P^2}{2 M_{\perp}} \left[\left| \frac{\partial \varphi_1}{\partial x} \right|^2 + \left| \frac{\partial \varphi_2}{\partial x} \right|^2 \right] = \frac{P^2 q_x^2}{M_{\perp}}.$$

Note that $M_{\parallel}$ and $M_{\perp}$ are, *a priori*, functions of ρ (see concluding remarks). Finally, the total free energy density becomes :

$$F = \frac{P^2}{2 M_{\parallel}} \left[\left(\frac{d\alpha_1}{dz} + \frac{q_x^2}{k_2} + \frac{k_2}{2} - k_1 \right)^2 + \left(\frac{d\alpha_2}{dz} + \frac{q_x^2}{k_2} + \frac{k_2}{2} - k_1 \right)^2 \right] + \frac{P^2 q_x^2}{M_{\perp}} - 2 D P^2 \rho_0 \cos (\alpha_1 + \alpha_2).$$

As usual, the equilibrium phases will be obtained by the minimization procedure, with respect to the variables of the problem (α_1 , α_2 and q_x).

In fact, the minimization with respect to $\alpha_1 - \alpha_2$ is straightforward and leads to : $\alpha_1 - \alpha_2 = \text{constant}$.

Thus, F can be rewritten (with $\alpha_1 + \alpha_2 = 2 \gamma$) :

$$F = \frac{P^2}{M_{\parallel}} \left[\frac{d\gamma}{dz} + \frac{q_x^2}{k_2} + \frac{k_2}{2} - k_1 \right]^2 + \frac{P^2 q_x^2}{M_{\perp}} - 2 D P^2 \rho_0 \cos 2 \gamma.$$

Clearly, for $M_{\perp}$ very large,

$$\gamma = 0 \quad \text{and} \quad q_x = \sqrt{k_2 \left(\frac{k_2}{2} - k_1 \right)}$$

will minimize the free energy : this is the simplest case of the S_A antiphase which corresponds to figure 1.

On the other hand, for vanishing $M_{\perp}$, we recover the commensurate-incommensurate 1d problem described in reference [1]. In the next section, we give the details of the corresponding phase diagram.

3. The deduced phase diagram. — With the notation :

$$q_0 = k_1 - \frac{k_2}{2} - \frac{q_x^2}{k_2}$$

$$\tilde{\gamma} = \frac{\pi}{2} + \gamma$$

$$\xi = \frac{1}{\sqrt{4 D \rho_0 M_{\parallel}}},$$

the free energy F can be written :

$$\frac{F}{P^2} = 4 D \rho_0 \left[\xi^2 \left(\frac{d\tilde{\gamma}}{dz} - q_0 \right)^2 - 2 \sin^2 \tilde{\gamma} \right] + \left[2 D \rho_0 + \frac{q_x^2}{M_{\perp}} \right].$$

The first term has exactly the same form as the free energy used by de Gennes to describe the nematic-cholesteric transition [6]. Using his results gives after minimization with respect to $\tilde{\gamma}$:

$$\frac{F}{P^2} = 4 D \rho_0 \left(\xi^2 q_0^2 - \frac{1}{k^2} \right) + 2 D \rho_0 + \frac{q_x^2}{M_{\perp}}$$

or in reduced notation $\left(x_0 = \frac{k_1 - k_2/2}{k_2} \right)$:

$$\frac{\xi^2 M_{\parallel} F}{P^2} = (k_2 \xi)^2 \left[x_0 - \left(\frac{q_x}{k_2} \right)^2 \right] - \frac{1}{k^2} + \frac{1}{2} + \frac{M_{\parallel}}{M_{\perp}} \left(\frac{q_x}{k_2} \right)^2 (k_2 \xi)^2.$$

Here k is given by :

$$\bullet \frac{\pi}{2} q_0 \xi = \frac{\pi}{2} (k_2 \xi) \left[x_0 - \left(\frac{q_x}{k_2} \right)^2 \right] = \frac{E(k)}{k} \quad \text{when}$$

this equation has a solution (i.e. : $q_0 \xi > 2/\pi$, which implies $0 \leq k \leq 1$).

$$\bullet k = 1 \text{ otherwise.}$$

$E(k)$ is the complete elliptic integral of second kind.

In the first case, the solution $\gamma(z)$ implies the existence along z of a new periodicity incommensurate with k_2 (periodic stack of discommensuration near threshold). The corresponding phases will be called incommensurate. In the second case, γ is constant in space. This gives a commensurate phase along z .

It remains to minimize F with respect to q_x (q_x/k_2 in reduced units), without forgetting that k is a function of q_x . The resulting plots of F versus q_x are given figure 2, where the existence domains are deduced from the absolute minimum of F . As is clear from the

Fig. 2. — The phase diagram obtained :

- Heavy continuous line : first order $S_{\tilde{A}}-S_{A_i}$ transition.
- Heavy dotted lines : second order $S_{\tilde{A}}-S_{A_i}$ and $S_{A_i}-S_{A_i}$ transitions.
- Light dotted lines : limits of domains in which the free energy $F(q_x)$ assumes a typical shape given explicitly on the figure (the dotted lines are associated with the incommensurate and the continuous lines with the commensurate solutions; the heavy point locates the absolute minimum of energy).
- B coordinates : $k_2 \xi = 2 \pi x_0^{-1}$, $M_{\perp}/M_{\parallel} = (2 x_0)^{-1}$.

reduced form, the results depend on $M_{\perp}/M_{\parallel}$ and $k_2 \xi$ (at constant x_0).

We obtain :

- an incommensurate phase with $q_x \neq 0$,
- a commensurate phase with $q_x = 0$,
- an antiphase with $q_x \neq 0$.

4. Concluding remarks. — The first two phases have already been described in the study of one dimensional models [1, 8]. The commensurate phase with $q_x = 0$ is merely a bilayer smectic A, whereas the incommensurate phase has been recognized as a possible candidate for ferroelectricity [1, 9].

The appearance of the $q_x \neq 0$ antiphase necessitates a non-zero value of $M_{\perp}$. The associated polarization is :

$$P = \frac{1}{2} \text{Re} (P_1 + P_2) = P_0 \cos(q_x x) \cos\left(\frac{k_2 z}{2} + \alpha_0\right).$$

From this relation it is clear that along a given plane ($z = \text{constant}$) the sign of the polarization oscillates

from plus to minus as shown on figure 1b. This phase can therefore be identified with the $S_{\tilde{A}}$ antiphase recently discovered by Sigaud *et al.* [5].

The transitions $S_{A'}-S_{Ai}$ and $S_{\tilde{A}}-S_{A'}$ are both second order, whereas the $S_{\tilde{A}}-S_{Ai}$ transition is always first order. Note in particular that the $S_{\tilde{A}}$ phase is obtained from the bilayer $S_{A'}$ by a continuous growth of q_x . It should be noted that the proximity of the nematic-smectic A transition could modify our results : with a Rodbell Beam type of coupling, it could render the $S_{A'}-S_{Ai}$ and $S_{\tilde{A}}-S_{A'}$ transitions first order.

Further research is possible :

- The shape of the free energy *versus* q_x , shown on figure 2, suggests that in some parts of the phase diagram, incommensurate fluctuations in the $S_{\tilde{A}}$ phase and, reciprocally, $S_{\tilde{A}}$ fluctuations in the S_{Ai} could be observed.

- To compare our results with the experimental diagram, the temperature dependence of the different parameters must be specified. In fact, due to the proximity of the nematic- $S_{A'}$ transition, the most pronounced dependence is carried by $\rho_0(T)$. At first sight, this implies $\xi = f(T)$ only, which implies the absence of the observed $S_{\tilde{A}}-S_{A'}$ transition [5]. However, if we relax the assumption of an incompressible monolayer order, we obtain T -dependence in both $M_{\parallel}$ and $M_{\perp}$ [10]. It then becomes possible to reach the $S_{A'}$ phase.

Additional improvements could include a varying P amplitude, but this would not change the qualitative features of our results.

The relative stability of the $S_{\tilde{A}}$ (2nd order) with that of a « crystalline » 3d antiphase can be questioned and will be the subject of further work.

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