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Material properties of smectic layers and the formation of modulated and cubic smectic phases

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Résumé. — On propose des modèles pour la phase smectique modulée (\tilde{A}) et pour les cubiques smectiques (D, et une phase sans nom). Ces modèles sont basés sur les propriétés d'une couche smectique isolée : élasticité de courbure et énergies des parois d'inversion de polarisation. On en déduit des critères pour la transformation de phases smectiques ordinaires (A, C) en phases modulées (\tilde{A}) ou cubiques.

Abstract. — Models are proposed for a modulated smectic phase (\tilde{A}) and the cubic smectics (D and a nameless phase) that are based on the material properties of the single smectic layer such as curvature elasticity and boundary (or inversion wall) energies. They furnish criteria for the transformation of regular smectics (A, C) into these phases.

A number of so-called smectic phases have been discovered lying in the phase diagrams of thermotropic liquid crystals next to the classical smectic states A and C. We are interested here in those which consist, or seem to consist, of fluid smectic layers (neither crystalline nor hexatic) forming two- or three-dimensional superlattices. The modulated smectics, also called ribbon phases, represent the former class. They were found by the Bordeaux group [1, 2] with molecules possessing three benzene rings and one strongly polar end group (CN or NO₂). Their characteristic feature is a monolayer polarization alternating from layer to layer and in a direction parallel to the layers. Three types of ribbon phases have been distinguished. They differ by their 2d lattices which were reported to be centred rectangular (\tilde{A}), oblique (C), and simple rectangular (A_{cre}). The cubic smectics, D [3, 4] and a nameless one [5], were detected by the Halle group. We conjecture that one or both of them are made of a single multiply connected smectic layer forming the 3d lattice. To date, only three compounds are known to exhibit thermotropic cubic smectic phases.

The present note is an attempt to understand modulated and cubic smectic phases in terms of the material properties of the single smectic layer. We are motivated by the obvious success of such an approach in the case of amphiphile-water systems [6], among them phospholipid bilayers in water [7]. Accordingly, we will mostly apply existing ideas to the thermotropic cubic smectic phases. At first, however, we will propose a

new model for the ribbon phases, concentrating on \tilde{A} which is the most common and best established type.

Smooth, i.e. unmodulated, smectic A sometimes falls apart into three phases of equal symmetry which may all occur in a binary phase diagram if the constituent molecules possess a strongly polar end group: the monolayer phase A_1 , the bilayer phase A_2 , and the partially bilayer phase A_d [2, 8, 9]. Monolayer and bilayer are commensurate where A_1 and A_2 meet in a second-order phase transition, the thickness of the latter being twice that of the former. The bilayer comprises two oppositely polarized monolayers. The partial bilayer is intermediate in thickness and properties between the bilayer and the monolayer. The ribbon phases have mostly been found between A_1 at higher and A_2 at lower temperatures.

Prost and coworkers [10-12] developed a mean-field theory for smooth smectics and their phase transitions. It is based on the idea of two incommensurate periods competing with each other. One is the thickness of the nonpolar monolayer and the other that of a bilayer less than twice as thick as the monolayer. The theory was extended, also by Prost *et al.* [11, 13], to modulated smectic phases. Commensuration is now achieved by mentally tilting the bilayer until its apparent period as measured along the monolayer normal doubles that of the monolayer. The (mean) molecular orientation is thought to remain uniform and, in all A phases, orthogonal to the monolayers. The theory can account for A and C and their location in binary phase

diagrams. However, there seems to be no physical reason why this kind of commensuration should reduce the free energy, as has to be postulated in order to predict modulated phases.

Let us try an alternative explanation for smectic A. The proposed structure is sketched in figure 1. It differs from the usual picture mainly by an alternating curvature of the polarized monolayers, resulting in nonuniformity and tilt, both small, of the (mean) molecular alignment. As compared to the smooth bilayer phase A_2 we have two important additional energies.

One of the energies is linked to the curvature of the monolayers. The bending elastic energy per unit area of a fluid layer may be expressed by [7, 14, 15]

$$g = \frac{1}{2} \kappa (c_1 + c_2 - c_s)^2 + \bar{\kappa} c_1 c_2 \quad (1)$$

where c_1 and c_2 are the principal curvatures, c_s a spontaneous curvature, κ the bending rigidity, and $\bar{\kappa}$ the modulus of Gaussian curvature $c_1 c_2$. There is only one nonzero principal curvature in a ribbon phase, so (1) reduces to

$$g = \frac{1}{2} \kappa (c_1 - c_s)^2. \quad (2)$$

A spontaneous curvature can arise from the polarization of the monolayers. Their polarization should be stabilized by some pairwise overlap of the monolayers on the sides of the strongly polar end groups. Both signs of the spontaneous curvature seem possible because of the contrary action of steric repulsion and electrostatic attraction in the regions of overlap. Figure 1 depicts the case of net repulsion which is more probable considering the shape of the molecules known to form \tilde{A} . The other energy to be taken into account is associated with the reversal of polarization within a

monolayer which is supposed to be abrupt, as suggested by recent freeze-fracture experiments [16]. The change requires a boundary (or wall) energy γ per unit length of boundary between oppositely polarized areas of the monolayer.

The negative free energy of polarization and overlap need not be known since it is assumed to be the same as in the smooth bilayer phase. However, figure 1 indicates that the overlap of the monolayers decreases as the tilt angle of the molecules increases. The accompanying gradual increase of the free energy of the bilayer is difficult to deal with. For simplicity, we take this energy to be constant up to a fixed limiting angle φ_0 , and there to jump up to zero. If φ_0 is small enough, one may equally neglect the tilt energies of the nonoverlapping regions of the layers.

The free energy Δg per unit area of monolayer due to the breakup of the smooth phase into ribbons may be written as

$$\Delta g = \frac{1}{2} \kappa \left(\frac{4 \varphi_0}{a} - c_s \right)^2 - \frac{1}{2} \kappa c_s^2 + 2 \frac{\gamma}{a} \quad (3)$$

where a is the period of modulation parallel to the layers. Minimization with respect to a yields

$$a = \frac{4 \varphi_0^2 \kappa}{\kappa \varphi_0 c_s - \gamma/2}. \quad (4)$$

Physical solutions $a > 0$ of this equation are characterized by $\varphi_0 c_s > \gamma/2 \kappa$ provided $\kappa > 0$ and $\gamma > 0$. Insertion of (3) in (4) leads after some manipulations to

$$\Delta g = -\frac{1}{2} \kappa \left(\frac{2 \varphi_0}{a} \right)^2. \quad (5)$$

Accordingly, smooth smectic A_2 breaks up into ribbons whenever equation (4) has a physical solution. The criterion for the stability of A may be rewritten as

$$|c_s| > \frac{\gamma}{2 \kappa |\varphi_0|}. \quad (6)$$

For an estimate we assume the following values

$$\begin{aligned} \kappa &= 3 \times 10^{-13} \text{ erg} \\ \gamma &= 3 \times 10^{-7} \text{ dyn} \\ |\varphi_0| &= 10^0 = 0.175 \text{ rad} \end{aligned}$$

where the first two are the products of the layer thickness (3 nm) with a curvature elastic modulus typical of liquid crystals (10^{-6} dyn) and a very low interfacial energy (1 erg cm^{-2}), respectively. $|\varphi_0|$ is chosen small enough to be compatible with the above model. With these numbers the criterion (6) becomes $|c_s| > 2.9 \times 10^6 \text{ cm}^{-1}$, which means that the radius of spontaneous curvature must be ten times the layer

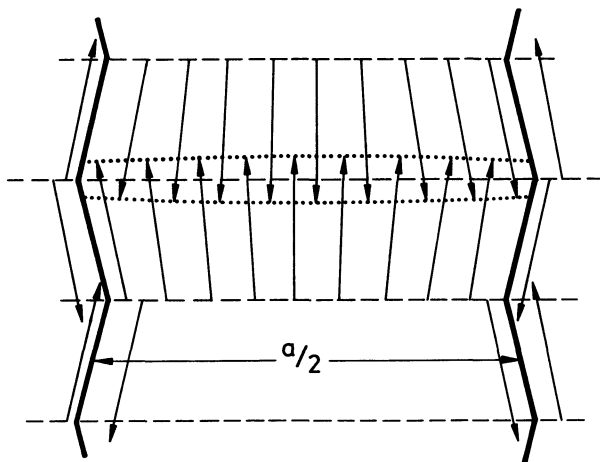
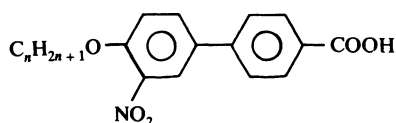


Fig. 1. — Model of smectic A. The arrows represent molecules, their heads the polar end groups. a is the period of modulation. The heavy lines indicate in-layer boundaries between up and down polarizations.

thickness or less. Actual radii of spontaneous curvature may be expected to be larger by up to an order of magnitude (on the basis of packing considerations, i.e. crowding of polar end groups as suggested by Fig. 1). Despite the crudeness of the model the estimate suggests that modulated smectics of the type envisaged here can occur.

In any wall model, the phase transition from A to A₂ can be understood as the disappearance of the inversion boundaries. The ribbons were found to widen as the temperature was lowered towards the transition [17]. Our model predicts, indeed, a divergence of the period *a*. However, the model must fail above a certain width unless one adds to (3) a term for the energy of molecular tilt which is no longer negligible. More troubling in the context of our model is the reported intervention of a simple rectangular phase A_{cre} between centred rectangular \tilde{A} and smooth A₂ [2, 17]. The range of A crenellated is very narrow, generally only a few °C. In our model it would imply a pairing of the inversion walls (at \tilde{A} to A_{cre}) and their mutual annihilation (at A_{cre} to A₂). Being unable to account for such a pairing, we are led to wonder whether A_{cre} is a separate phase of unknown origin or, in conflict with present evidence [17], part of \tilde{A} and a consequence of complex statistical mechanics of strongly fluctuating inversion walls. Phase transitions of systems of fluctuating domain walls are currently of considerable theoretical interest [18, 19]. We refrain from speculating on the details of \tilde{C} , found between A₁ and \tilde{A} or A₄ and A₂ [2, 20]. There seems to be no room for it in our model unless it is brought about by a genuine tendency, as in smectic C, towards molecular tilt which is suppressed again at lower temperatures.

The cubic smectic phase D has so far been found [3, 4] only with two homologous compounds, namely the alkyloxynitrophenyl-carboxylic acids



with *n* = 16 and 18. For *n* = 16 it is situated in temperature between C and A, for *n* = 18 between C and nematic. Carboxylic acids are known to form very stable dimers [4]. Accordingly, one may expect smectic bilayers. In comparison to bilayers in water, these bilayers of thermotropic smectics are inverted, i.e. their more polar parts are in the middle of the bilayer. Also, they are not embedded in a fluid. (Oil would be needed here.) The nameless cubic phase [5] was obtained in the bialkyl-oxybenzoylhydrazine



with *n* = 10. The monolayer of this material has the character of an inverted amphiphilic bilayer, like the dimeric bilayer of the previous compound. However, the two thermotropic smectic layers are connected, i.e. they cannot be split up into monolayers, in contrast to most amphiphilic bilayers. X-ray diffraction patterns were taken from both cubic phases. They are compatible with the space groups Ia3d for smectic D [21] and Pn3m for nameless cubic [5]. (X-ray structural analysis of superlattices is notoriously difficult so that confirmations would be desirable.)

Interestingly, the same space groups were established for amphiphile-water systems. Phospholipid bilayers (among them lecithin bilayers) in water were found to form infinitely connected cubic lattices such that two interwoven water bodies are separated by a single bilayer [7]. The space group is Pn3m, with the water channels representing two interpenetrating diamond lattices as sketched in figure 2. Glycerol monooleate, another well-known amphiphile, displays two cubic phases [22, 23], apart from a lamellar (i.e. smectic A) one, depending on water concentration and temperature of the sample. They were assigned to the space groups Pn3m and Ia3d. Again, the idea is that two interwoven networks of water channels are separated by a single bilayer of amphiphile, as sketched for Ia3d in figure 3. In one case (diamond) the channels are linked four by four, in the other three by three. The bilayer connections, which are « passages » for water, and their lattice are easy to imagine for Pn3m. Drawings [6] and pictures obtained by optical microscopy [7, 24] may be found in the literature, a very simple diagram is shown in figure 4. The network of water channels of space group Ia3d can also be interpreted as a lattice of passages, but visualization is more difficult.

We expect in thermotropic cubic smectics the hydrocarbon chain ends of the molecules or dimers to assume the role that water plays in their lyotropic amphiphilic counterparts. A prerequisite for such a function is that the molecules or dimers are able to span the distance between the center lines of neighboring

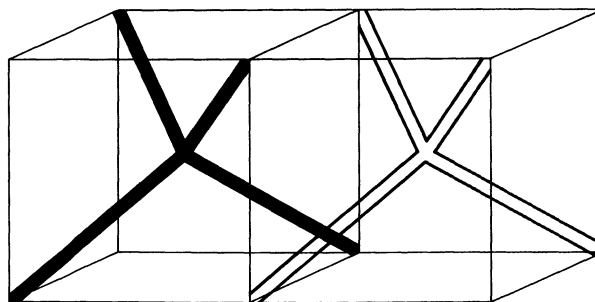


Fig. 2. — Two unit cells of Pn3m. The two systems of channels forming two diamond lattices are distinguished by black and white. Actual channels are relatively wider. (They consist of water in amphiphilic systems, presumably of hydrocarbon chain ends in the nameless cubic smectic phase.)

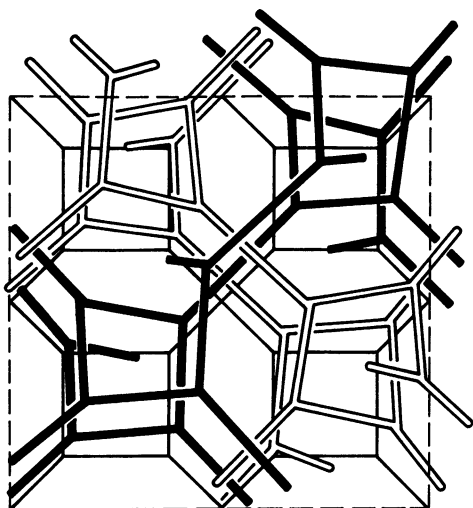


Fig. 3. — Two unit cells of Ia3d on top of each other in perspective view. The two systems of channels are distinguished by black and white. Actual channels are relatively wider. (They consist of water in amphiphilic systems, presumably of hydrocarbon chain ends in smectic D.) Adapted from reference [6].

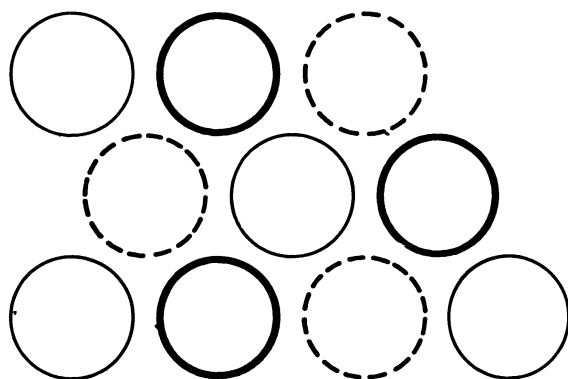


Fig. 4. — View along a principal diagonal of Pn3m, indicating the passages (e.g. of water) parallel to the direction of viewing. Three levels are shown, differing by line strength.

channels belonging to different oil (instead of water) systems. In the case of smectic D, the measured [21] lattice parameter of 102 Å implies, for Ia3d, a channel spacing about half as large. This compares well with the length of the stretched dimer which is about 60 Å. The lattice parameter of the nameless cubic phase [5] was found to be 52 Å. The spacing between the center lines of the channels of Pn3m is about the same, but the length of the stretched molecule is roughly 45 Å. The gap might be bridged if the cores of adjacent parallel molecules are staggered with respect to each other along the molecular axis. A tendency for a relative shift may, in fact, be anticipated as the nameless cubic smectic phase lies next to C, but far from smectic A.

Before applying the concept of bilayer bending to thermotropic cubic smectics, let us summarize some of the difficulties we have to be aware of. Most of them result from the fact that there is no free filling material like water or oil. Therefore, the bilayer has to be strained, e.g. dilated or compressed, to fill all space. Moreover, the hydrocarbon chains of adjacent bilayers will overlap to some extent, so that speaking of the material properties of the single layer is an idealization. Other problems may arise from the « connectedness » of the two sides of the bilayer, but they are not typical since connected amphiphilic layers in water made of bipolar molecules are also known [25].

Passages and their lattices can be thermodynamically stable if the elastic modulus of Gaussian curvature, $\bar{\kappa}$, of equation (1) is sufficiently positive [7, 15]. The simplest structure of this kind is the well-known Schwarz minimal surface of space group Im3m [6, 26]. As minimal surfaces are characterized by $c_1 + c_2 = 0$, which entails $c_1 c_2 \leq 0$, their preference over the lamellar state requires only $\bar{\kappa} > 0$. It seems unknown to date whether there exists a minimal surface separating the two networks of channels in Ia3d and Pn3m. If there is none, $\bar{\kappa}$ must exceed some positive value to permit the conversion from lamellar to cubic. The situation is further complicated (and $\bar{\kappa}$ must probably be even larger) if the bending is so strong that Hooke's law and thus equation (1) are no longer exactly valid.

A positive $\bar{\kappa}$ may be anticipated for the compounds displaying smectic D. This is because the dimers making up the bilayer are much thicker in the middle than at their ends represented by fluid hydrocarbon chains. The chains may be expected to have a negative order parameter $P = \frac{3}{2} \left(\langle \cos^2 \vartheta \rangle - \frac{1}{3} \right)$, ϑ being the angle between chain and layer normal. (The effect should be especially pronounced in the C phase if the centre portion of the dimers is tilted, but continuous tilt in a cubic phase may be impossible. Note that no smectic D is found if NO₂ is replaced by less polar side groups [4]). The modulus of Gaussian curvature equals the second moment of the stress profile of the (flat) bilayer [7, 15], i.e.

$$\bar{\kappa} = \int z^2 t(z) dz \quad (7)$$

where z is a coordinate normal to the layer and t the bulk normal stress, i.e. a force per unit area. If $P < 0$ there should be pull ($t > 0$) in the chain regions balanced by push in the central region. Accordingly, $\bar{\kappa}$ is likely to be positive as required for the formation of passages. It is rather difficult to predict the sign of $\bar{\kappa}$ for the smectic layers giving the nameless cubic phase. Their centres are not as thick as those of the dimers of smectic D. Molecular tilt may be necessary, and is conceivable as the phase neighbours smectic C only. On the other hand, tilt is unwelcome as

it further decreases the layer thickness (see above). A staggered array of untilted molecular centres might be a suitable compromise.

The models we propose for modulated and cubic smectic phases are, of course, speculative. They remain to be checked experimentally, e.g. by looking for the predicted tilt angle φ_0 and by further structural studies of the cubic phases. Nevertheless, we think that theories employing the material properties of the single smectic layer may be useful, despite their inherent short-

comings. They are halfway between continuum theories considering the bulk and molecular theories which can be worked out only by computer. From a practical point of view, they could be helpful in material engineering, that is in devising the molecules needed to obtain certain phases.

Note added in proof: X-ray diffraction data have just been obtained with a new smectic D material by Etherington *et al.* [27] who propose space group Pm3.

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