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## Smectic A-Smectic B interface : faceting and surface free energy measurement

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**Résumé.** — Nous avons observé la forme d'équilibre d'un monodomaine de Smectique B en contact avec une phase Smectique A et comment un joint de grain déforme l'interface Smectique A-Smectique B en présence d'un gradient de température. Le matériau choisi est le 40,8 (butyloxybenzilidène octylaniline). En utilisant la construction de Wulff et le modèle T.L.K., nous calculons à la fois l'énergie libre d'une facette parallèle aux couches et l'énergie libre d'une marche. Nous montrons également l'existence de faces d'orientations interdites. En accord avec les prédictions d'Herring nous observons qu'une telle face est toujours instable vis-à-vis de la formation d'une structure brisée en zig-zag.

**Abstract.** — We have observed the equilibrium shape of a Smectic B monodomain in contact with a Smectic A phase and how a grain boundary deforms the Smectic B-Smectic A interface in the presence of a temperature gradient. The chosen material is the 40.8 (butyloxybenzilidene octylaniline). By using the Wulff construction and the T.L.K. model, we calculate both the surface free energy of a facet parallel to the layers and the free energy of a ledge. The existence of faces of forbidden orientations is also shown. In accord with the theoretical predictions of Herring, we observe that such a face is always unstable with respect to the formation of a hill-and-valley structure.

### 1. Introduction.

In this article, we are interested in the static properties of the Smectic A-Smectic B interface. Let us remember that Smectic A is a lamellar phase with fluid layers whereas Smectic B is a plastic hexagonal close packed crystal with layers stacked ABAB...

The chosen material is 40.8 (butyloxybenzilidene octylaniline) which has the following phases :

K---Sm . B	---	Sm . A	---	N---I
33	49.5	64	79	

Here, K is the crystal phase, N the nematic and I the isotropic liquid. The transition temperatures are given in °C.

In a recent article [1], we showed the behavior of the Sm A-Sm B interface in directional growth and the first observations of cells and dendrites in this system. Despite a small latent heat ( $L = 0.5$  kcal/mole [2]) the cellular bifurcation was found subcritical (contrary to what happens with the Nematic-Isotropic interface [3]). We also observed that the cells were pointed with a tendency to be faceted. In order to understand these properties, a thorough knowledge of surface tension and its anisotropy is essential.

Also the Smectic B phase of 40.8 is interesting in its own right because of its very large structural anisotropy. Because the spacing «  $a$  » of molecules in each layer is  $5 \text{ \AA}$ , while the spacing «  $b$  » between layers is  $30 \text{ \AA}$  [4], the elastic and plastic properties are very anisotropic [5]. We find even the surface properties to be very anisotropic resulting in facets parallel to the layers.

## 2. The experiment.

The 40.8 has been prepared by one of us (C.G.). It was purified by recrystallizing from solution four times. At the temperatures used in our experiments (always less than  $55 \text{ }^\circ\text{C}$ ) the samples did not noticeably decompose. We measured  $T_{\text{Liquidus}} = 49.6 \text{ }^\circ\text{C}$  and  $T_{\text{Solidus}} = 49.2 \text{ }^\circ\text{C}$ . Experiments at fixed temperatures have been made in an hot stage controlled to about  $0.01 \text{ }^\circ\text{C}$ . Other experiments in the presence of a temperature gradient have been performed in an apparatus similar to the one we described in reference [1]. The sample straddles the space between two ovens. They are separated by a gap of  $4 \text{ mm}$  and their temperatures are individually controlled to about  $0.05 \text{ }^\circ\text{C}$ . Temperature gradients are measured with a Cu-Constantan thermocouple. The samples are prepared between two glass plates (respectively  $1 \text{ mm}$  and  $0.5 \text{ mm}$  thick). In order to obtain a planar alignment of the molecules on the glass (smectic layers normal to the glass), a  $300 \text{ \AA}$  thick layer of polyimide ZII-2650 (Merck Corp.) was deposited on the plates. In order to get maximum hardness, we baked them during 1 hour at  $300 \text{ }^\circ\text{C}$ . This layer was then rubbed in a single direction in order to orientate the smectic layers (here in the direction perpendicular to the scratches). In order to know the thickness of our sample, we used spacers (metallic wires whose diameter varies from  $8$  to  $50 \text{ }\mu\text{m}$ ). Most of our experiments have been performed with  $15 \text{ }\mu\text{m}$  thick samples. Observations have been made in phase contrast through a polarizing microscope (Leitz Laborlux 12 POL).

## 3. Germs at equilibrium : determination of the Wulff's diagram.

**3.1 EXPERIMENTAL RESULTS.** — By cooling down the sample a few tenths of  $^\circ\text{C}$  below its liquidus temperature, we observe the nucleation and the rapid growth of numerous germs of smectic B phase. In order to select a single germ we increase again the temperature till all the germs disappear except one. Then we decrease the temperature very slowly ( $0.01 \text{ }^\circ\text{C}/\text{min}$ ) in order to let this germ grow. Its growth is stopped as its size lies between  $20$  and  $30 \text{ }\mu\text{m}$ , by increasing again the temperature. The germ is then in unstable equilibrium but it is possible to keep it unchanged during at least one day. Repeated experiments show that all the germs of this size evolve towards a single shape that we believe, for this reason, very close to equilibrium. Such a germ is shown in figure 1. It is faceted parallel to the smectic layers and is slightly pointed at its ends. Its shape anisotropy is close to 3. Finally the matching between the facet and the vicinal surface is smooth without any discontinuity of the slope. We did not observe any change with thicker samples which means that meniscus effects are negligible.

**3.2 WULFF CONSTRUCTION.** — One knows that the equilibrium shape of a crystal comes from the minimisation of its surface free energy at fixed volume. This minimisation leads to a

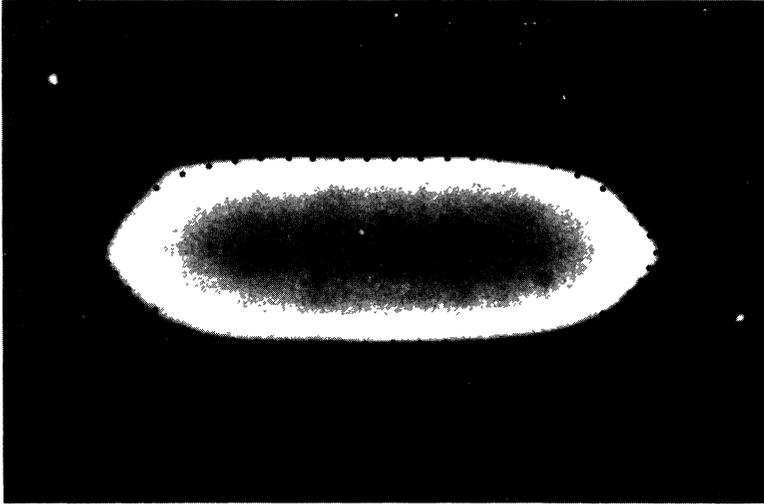


Fig. 1. — Smectic B monodomain in equilibrium with the Smectic A phase. In this picture, the layers are perpendicular to the glass plates and parallel to the facets. The plotted points represent the shape calculated from equation (2) using the Wulff construction. Here  $A = 3.05$  and  $E = 1.8$ .

simple geometrical construction (Wulff, 1901) [6]. Let  $\mathbf{n}$  be the unit vector normal to the surface of the crystal and  $\gamma(\mathbf{n})$  the surface free energy per unit area for this direction. Let  $\Sigma(\mathbf{n})$  be the surface of polar equation  $\rho = \gamma(\mathbf{n})$ . At equilibrium, the surface of the crystal is the convex envelop of a set of half straight lines issued from the points of  $\Sigma$  and perpendicular to  $\mathbf{n}$  (Fig. 2). The presence of a facet parallel to the layers indicates that the  $\gamma$ -plot has a cusped minimum in the direction normal to the layers.

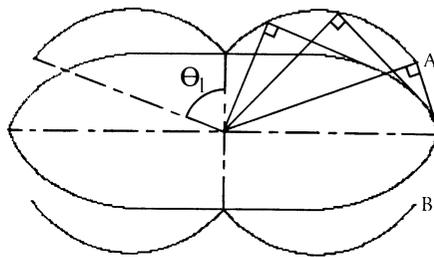


Fig. 2. — Wulff construction : equilibrium crystal shape and  $\gamma$ -plot. The parts of the  $\gamma$ -plot which do not contribute to the equilibrium shape ( $\theta > \theta_l$ ) are not shown. The tangent planes corresponding to the points A and B on the Wulff plot meet at an angle, forming an edge in the crystal shape.

Thus the Wulff construction allows us to get in a simple way the shape of the  $\gamma$ -plot from the observed equilibrium shape. The result of this construction is shown in figure 1. In this figure we used to fit the shape of the germ and analytical representation of  $\gamma(\mathbf{n})$  deduced from a generalization of the TLK model. This model is commented in the following subsection.

**3.3 TLK MODEL.** — In this model, first introduced by Kossel [7] and Stranski [8], the basic idea is to represent any crystalline surface by planar surfaces (terraces) separated by atomic ledges which contain themselves a certain density of kinks (Fig. 3). Let us call  $\theta$  the angle between  $\mathbf{n}$  and the normal to the layers and  $b$  the height of a ledge ( $b = 30 \text{ \AA}$ ). The mean distance between two steps is :

$$\ell = b / |\tan \theta| . \quad (1)$$

Let  $\gamma_0$  be the energy of the facet and  $e$  the free energy per unit length of a ledge. We obtain :

$$\gamma(\theta) = \gamma_0 |\cos \theta| + (e/b) |\sin \theta| . \quad (2)$$

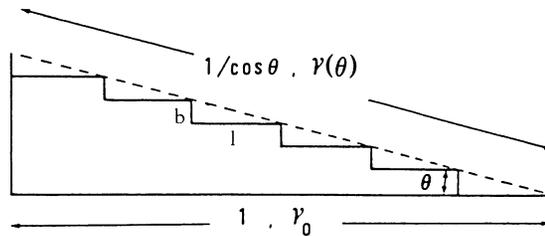


Fig. 3. — T.L.K. model. A face of angle  $\theta$  (with respect to the smectic layers i.e. the facet) consists of a succession of terraces separated by ledges of height  $b$ . At  $T \neq 0$ , thermal excitations generate kinks on the steps (or ledges) whose free energy per unit length remains well-defined and nonzero as long as  $T < T_r$  ( $T_r$  is the roughening temperature).

This model does not take into account the fact that we are dealing with a Smectic-Smectic transition. It is well known that the layer spacing is slightly different in the two phases :  $b(\text{Sm. A}) \approx 28.1 \text{ \AA}$  and  $b(\text{Sm. B}) \approx 28.6 \text{ \AA}$  [4]. In order to take into account this parameter shift  $\Delta b$ , we must introduce epitaxial dislocations whose density is simply given by  $\Delta b |\sin \theta| / b^2$  for a face of angle  $\theta$  with respect to the layers. Let  $K$  be the energy of such a dislocation. The free energy per unit surface can be rewritten in the most general form :

$$\gamma(\theta) = \gamma_0 |\cos \theta| + (1/b)(e + K \Delta b / b) |\sin \theta| . \quad (3)$$

On the other hand, at  $T \neq 0$ ,  $e$  is not constant and depends on the ledge density and then on  $\theta$ . By taking into account only the entropic repulsions between steps, Gruber and Mullins [9] show that the specific energy of a ledge may be written in the form :

$$e = e_0 - \nu(T) kT \cos[\pi |\tan \theta| / (1 + 2 |\tan \theta|)] \quad (4)$$

$e_0$  is the ledge energy at  $T = 0$ . The  $\nu(T) kT$  term corresponds to the entropy of an isolated step. It depends upon the kink formation energy and the temperature. It is difficult to calculate theoretically. Nevertheless, Burton and Cabrera gives for  $\nu(T)$  the following expression :

$$\nu(T) = (2/a) \exp(-\Phi/2 kT) / [1 + 2 \exp(-\Phi/2 kT)] \quad (5)$$

where  $\Phi$  is the interaction energy between two molecules in a Sm. B layer. In this calculation, only nearest-neighbor interactions have been taken into account.

Finally, the  $\theta$  dependence in equation (4) expresses the entropic repulsion between ledges.

This model disregards any other interactions than the entropic ones, in particular the elastic interactions. This can be justified in a smectic B phase. We have previously shown [5] that two basal dislocations which are not exactly in the same slip plane interact very little because of the very large anisotropy of the elastic constants. We conclude that it will be the same for two ledges and that the entropic repulsions should dominate.

In conclusion we believe very reasonable to write  $\gamma(\theta)$  in the form :

$$\gamma(\theta) = \gamma_0 [ |\cos \theta| + A |\sin \theta| - E |\sin \theta| \cos(\pi |\tan \theta| / (1 + 2 |\tan \theta|))] \tag{6}$$

$A = (e_0 + K \Delta b / b) / b \gamma_0$  characterizes the anisotropy of the free energy at zero temperature. It is easy to see that  $A$  is also the shape anisotropy of the germ (to a first approximation).

$E = \nu(T) kT / b \gamma_0$  is the entropic term upon which the shape of the rounded regions of the germ will depend.

Using this model, we have been able to fit very well the shape of the germ that we observed experimentally (Fig. 1). A good agreement between theory and experiment is found by taking :

$$A = 3 \pm 0.2 \quad \text{and} \quad E = 1.8 \pm 0.2 .$$

Let us notice two important points :

— the ends of the germ are pointed and present an angular point. The orientations of angle  $\theta$  lying between  $\theta_l \approx 75^\circ$  and  $\theta_{max} = 90^\circ$  do not appear on the equilibrium shape. The consequences of this observation will be discussed in the section 5 ;

— the Wulff construction does not allow to calculate  $\gamma_0$ . In order to do that we use an other method that we discuss in the following section.

**4.  $\gamma_0$  measurement using the grain boundary method.**

A classical method to measure the surface free energy is to put the sample into a temperature gradient and to look at the shape of the interface constrained by the presence of a grain boundary. The interface equation is given by the Gibbs-Thomson relation. Assuming that the facet is perpendicular to the temperature gradient, this equation may be written as (Fig. 4) :

$$y = \frac{h^2}{2} \frac{\left( \gamma^* + \frac{d^2 \gamma^*}{d\theta^2} \right)_{\theta = \tan^{-1}(dy/dx)} \frac{d^2 y}{dx^2}}{\left[ 1 + \left( \frac{dy}{dx} \right)^2 \right]^{3/2}} \tag{7}$$

with  $\gamma^* = \gamma / \gamma_0$  and  $h = (2 \gamma_0 T^* / GL)^{1/2}$ .  $T^*$  is the Sm A-Sm B phase transition temperature of the pure compound ( $T^* = 49.8^\circ\text{C}$ ) and  $L = 0.5$  kcal/mole the corresponding latent heat.  $h$  is a characteristic length of the problem.

The boundary conditions are :

$$y(x = \pm \infty) = 0 \quad \text{and} \quad dy/dx(x = 0) = p . \tag{8}$$

The slope  $p = \cot \alpha$  depends upon the grain boundary energy  $E$  :

$$E = 2[\gamma(\alpha) \cos \alpha + d\gamma/d\theta|_{\theta = \alpha} \sin \alpha] . \tag{9}$$

$p$  can be obtained from experimental data. Figure 5 shows an example and the best fit with the theoretical shape (after adjustment of the magnification). Here  $p = 1.6$  and

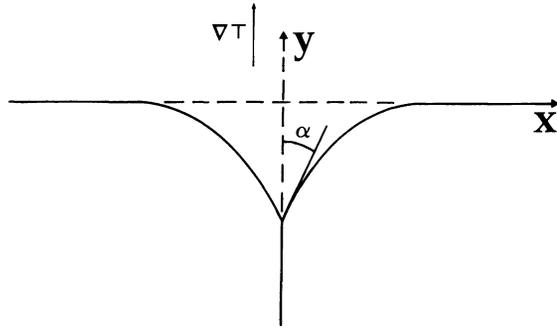


Fig. 4. — A grain boundary groove in the Sm. A-Sm. B interface. In a linear temperature gradient, the local interface curvature is a function of the distance from  $x$ -axis via the Gibbs-Thomson relation (Eq. (7)).



Fig. 5. — A grain boundary groove in a temperature gradient of 3.5 K/cm. The plotted points have been numerically calculated from equation (7) with  $p = 1.6$  and  $E = 1.8$ . Here the layers are parallel to the interface (far from the groove) i.e. perpendicular to the temperature gradient.

$G = 3.5$  K/cm. The numerical resolution of equation (7) with  $E = 1.8$  leads to the groove depth  $H$ . We found :

$$H(p = 1.6) = 0.92 h . \quad (10)$$

Experimentally we found  $H \approx 5 \mu\text{m}$  whence  $\gamma_0 = 0.092 \text{ erg/cm}^2$ . This very small value of  $\gamma_0$  is compatible with the very small value of the shear modulus ( $C_{44} = 10^6 \text{ erg/cm}^3$  [5]) and confirms that the layers are energetically very weakly coupled. It may be remarked that the stacking fault energy is of the order of  $10^{-2} \text{ erg/cm}^2$  [5b] and we also notice that  $C_{44} a \approx 0.05 \text{ erg/cm}^2$  which is of the same order of magnitude as  $\gamma_0$ .

From the values of  $A$  and  $E$  we get  $e_0 + K \Delta b/b \approx 8.3 \times 10^{-8} \text{ erg/cm}$  and  $\nu(T) kT \approx 5 \times 10^{-8} \text{ erg/cm}$ . Let us note that the epitaxial contribution is certainly not

negligible. Knowing that the energy of a dislocation is close to  $10^{-6}$  erg/cm (of the same order of magnitude as the curvature constant of a layer) we get  $K \Delta b/b \approx 1.7 \times 10^{-8}$  erg/cm. Thus, dislocations may play an important role in the large value of the observed anisotropy. Finally we calculate from equation (5) the interaction energy between two molecules in a layer :  $\Phi \approx 7 kT \approx 3 \times 10^{-13}$  erg. As expected, this is of the same order of magnitude as

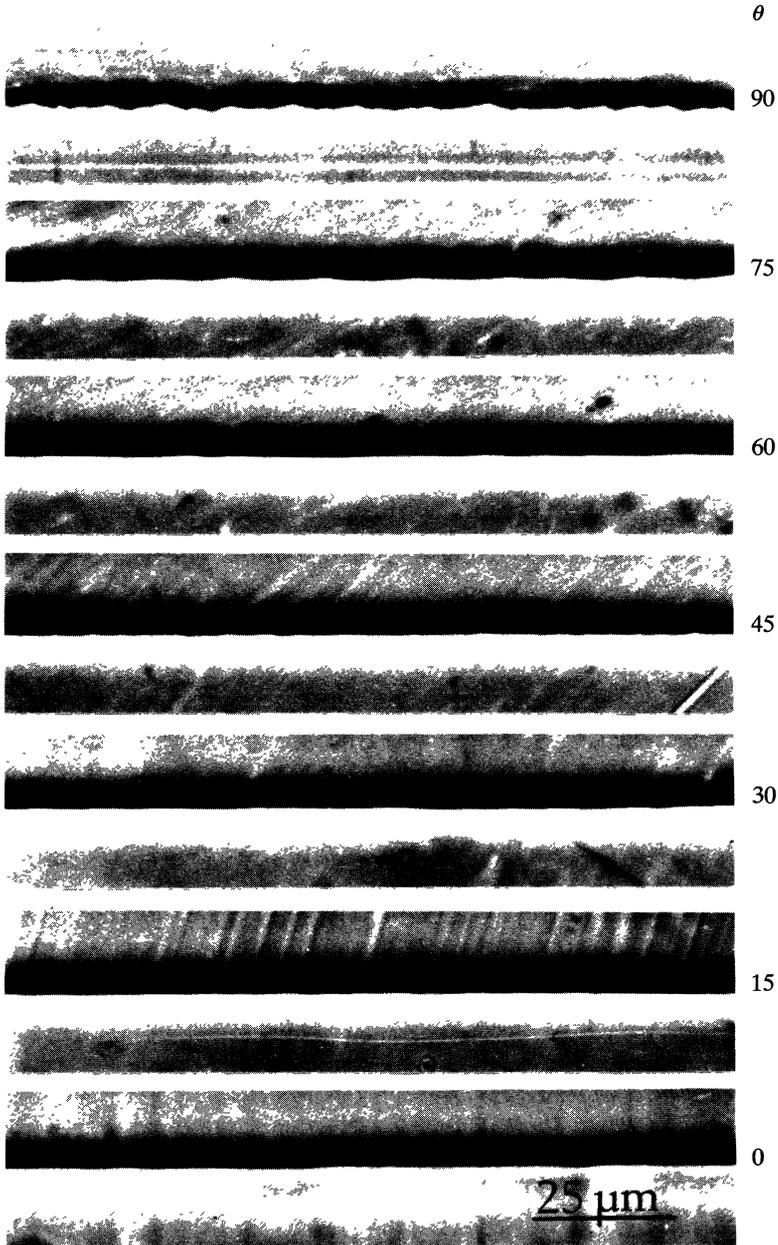


Fig. 6. — Thermal faceting of the Sm. A-Sm. B interface in a temperature gradient of 10 K/cm. The angle  $\theta$  is indicated on each photograph. For  $\theta = 90^\circ$  a hill-and-valley formation is quite visible. For  $\theta = 75^\circ$  this broken structure is just visible : its amplitude does not exceed  $1 \mu\text{m}$ . For smaller angles the front is very smooth.

$C\Omega \approx 4 \times 10^{-13}$  erg ( $C \approx 5 \times 10^8$  erg/cm<sup>3</sup> is the elastic modulus of the hexagonal lattice and  $\Omega \approx 7.5 \times 10^{-22}$  cm<sup>3</sup> the molecular volume).

### 5. Hill-and-valley structure for surfaces of angle $\theta$ greater than $\theta_\ell$ .

We have seen that the equilibrium shape of the germ did not exhibit faces of angle  $\theta > \theta_\ell$ . These angles are forbidden. What happens if we try to build such a face ? Herring [11] has shown that, in this case, there is always a hill-and-valley structure of smaller energy. In order to confirm this theoretical prediction we put samples of different angles in a weak temperature gradient (here  $G \approx 20$  K/cm). In our experiment the angle  $\theta$  is simply equal to the angle between the scratches on the plates and the temperature gradient. We observed that for small angles (typically less than  $\theta_\ell$ ) the interface is smooth and planar whereas for greater angles it appears to be irregular (Fig. 6). An hill-and-valley structure appears in accordance with the theoretical predictions of Herring. Its amplitude is maximum when  $\theta = 90^\circ$  i.e. when the layers are parallel to the temperature gradient. In fact it is precisely in this geometry that we had previously performed our growth experiments. We believe that such an initial structure may play an important role when the cellular instability develops. In the same way the existence of forbidden angles explains (at least qualitatively) why our cells and dendrites were always very pointed.

It would be interesting in the future to study whether it is possible to see some changes in this hill-and-valley structure when the Smectic B phase is growing and, also, how it destabilizes above the critical threshold of Mullins and Sekerka. We are now working on this problem.

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