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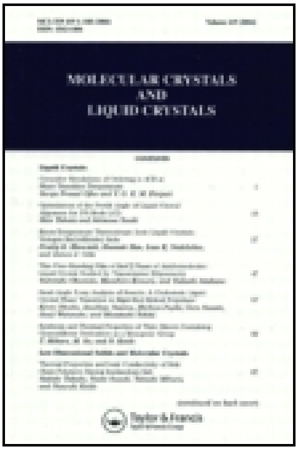

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Curvature Walls in Lyotropic Lamellar Phases

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Version of record first published: 24 Sep 2006

To cite this article: Christophe Blanc & Maurice Kleman (2000): The Curvature Walls in Lyotropic Lamellar Phases, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 351:1, 127-134

To link to this article: http://dx.doi.org/10.1080/10587250008023261

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Mol. Cryst. and Liq. Cryst., 2000, Vol. 351, pp. 127-134
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The Curvature Walls in Lyotropic Lamellar Phases

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We have studied the textures of lamellar phases of lyotropic systems in the sponge-lamellar domain of coexistence. The typical defects of the smectic systems (focal conics domains or "FCDs") are present, but our observations show also the existence of surfaces on which the director is discontinuous at optical scales. We have interpreted those surfaces as curvature walls. After having given their main geometric and energetic properties, we examine different cases (static and dynamic) which illustrate the importance of curvature walls in the formation of the lamellar textures.

Keywords: lamellar phase; sponge phase; wall defects; smectic texture

INTRODUCTION

The textures observed in smectic liquid crystals on an optical scale (>1μm), are usually described in terms of geometric properties of assemblies of parallel layers. These constructions naturally lead to the notion of macroscopic defects, *i.e. loci* where such a description is no longer valid (either due to the discontinuity of the layers or of the director orientation). A well-known example is the pioneering work of G. Friedel[1], who has been able to predict the layered organization of smectic *A* materials from his observation of focal conic domains (referred to as FCDs), whose marks are an ellipse and a hyperbola as singularity lines. A part of his work was dedicated to the nucleation of

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"bâtonnets" (nuclei) of Sm*A* phase in the isotropic phase. Although some features of the bâtonnets have been explained much later[2,3], his main conclusion was that the smectic organization could be seen as a geometric assembly of FCDs. This conclusion is still correct for the Sm*A* phases whose only defects are line defects (or point defects)[4]. Note however that in very thin samples (a few μm), other textures have been observed, *i.e.* the chevron texture[5] whose building defect has been modeled by a plane wall [6].

We have performed similar observations on the L_α lamellar phase of a lyotropic system, which is close to (or in coexistence with) the L_3 sponge phase. The lamellar and the sponge phases display the same local structure: a membrane made of two opposite monolayers of surfactants embedded in the solvent. The membranes are stacked with smectic order in the case of the lamellar phase whereas the isotropic sponge phase is usually described as a single disordered membrane which fills the sample, dividing the solvent into two equivalent subsystems[7].

In this paper, we report evidence that wall defects are not only present at rest in L_α textures (contrary to the observations of Sm*A* phases), but also play a major role in the appearance of lamellar textures as transient defects. A more detailed paper[8] will be published elsewhere and provides a quantitative study of the static part.

SURFACES OF DISCONTINUITY

Experiment

We report some optical observations of the L_α lamellar phase of the Cetylpyridinium Chloride (CPCl)/hexanol(h)/brine (1%NaCl) system in the domain of coexistence with the L_3 phase. This domain of coexistence and the nucleation of the lamellar phase in the L_3 phase is obtained either by varying the weight ratio h/CPCl (see the phase diagram in Reference [9]) or the temperature [10].

Samples of different brine volume fraction ϕ ($0.6<\phi<0.9$) were prepared in the L_3 phase, close to the domain of coexistence (h/CPCl≈1.12). The solutions were soaked into rectangular capillaries (thickness 200μm) and studied between crossed polars under a Leitz DMRXP microscope. The transition towards the L_α phase was studied

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in a hot stage (Mettler 82HT, accuracy 0.1°C) by means of a video camera and a video recorder.

Observations

Previous studies of the lamellar organization of simple shapes of lamellar phase droplets in sponge phase have indicated that the lamellar layers tend to be tilted at the interface[11]. In the concentrated region, the tilt angle ($\theta_0 \approx 70°$ for $\phi \approx 0.3$) is observed on most of the interface, which reveals a large anisotropy of the interface tension[12]. Therefore, like in the Sm*A* bâtonnets, in which most of the smectic layers are perpendicular to the interface ($\theta \approx 90°$), the L_α droplets can be seen as a stack of parallel layers which have to fulfill a strong boundary condition at the interface.

Our observations show that the inner L_α texture displays FCDs but, contrary to the case of Sm*A* phases, surface defects are also present and are characterized by the presence of a discontinuity of the director orientation (Figure 1). Those walls are seldom plane, but are curved surfaces (e.g. a cone in Figure 1).

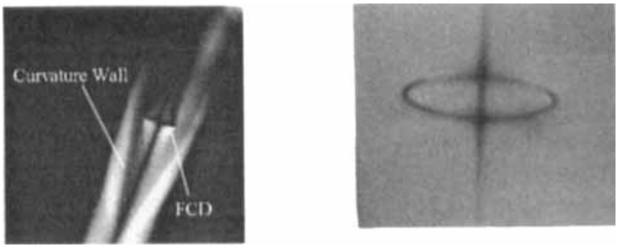

FIGURE 1 (left) In this part of a lamellar bâtonnet (size≈70μm), a FCD and a surface defect are both present. Similar defects are not observed in Sm-*A* samples in which only the FCDs are observed (right: diethyl-4-4'-azoxydibenzoate which was used in Friedel's observations).

Geometry and energetics

The main features of these wall defects are well understood in a semi-geometric model by considering three different scales (Figure 2). The first scale S_I (I) allows a continuous description of the layers ($S_I < 0.1\,\mu m$ which is the width of a wall for $\omega \approx 10°$: see below). Given two imposed orientations far from the wall ($-\omega$ and ω), the

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minimization of the total smectic energy (curvature and dilation) gives an energy by unit of area $E_s=2K(\tan\omega-\omega)\cos\omega/\lambda$[8] (which becomes $Es=2K\omega^3/3\lambda$[13] when $\omega<<1$) where K is the bulk curvature modulus and λ the smectic penetration length. It also gives the width of the domain of deformation $W\approx 2\lambda/\tan\omega \approx 2\lambda/\omega$. On the second scale $S_2\approx 1\,\mu m$ (II), the deformation of the layers is localized on a symmetric wall which separates two domains. The energy of the wall by unit of area is E_s. On the third scale $S_3>1\,\mu m$ (III), which is the scale of our observations, the wall defect is a curved surface between two different lamellar organizations, which are not usually flat. Its geometric construction is given by the following condition: locally its tangent plane is a plane curvature wall between the two lamellar organizations, therefore their bisector plane.

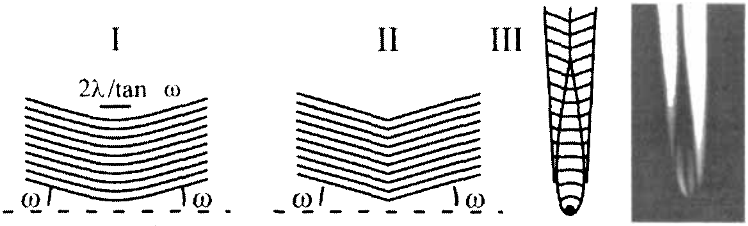

FIGURE 2 Curvature wall of a lamellar lyotropic phase, seen on different scales. The picture shows the surface defect observed between a spherical organization of the layers and a stack of conical layers (width≈30μm). The organization of the layers is sketched in III.

For example, the Figure 2-III represents one of the simplest curvature walls. It is observed between a hedgehog defect and a conical organization of the layers (see below the formation of such a bâtonnet).

TEXTURE OF THE LAMELLAR PHASE

Two other macroscopic defects are observed, point defects and FCDs. The fact that the energy of this latter varies as Kr (where r is a characteristic size of the ellipse) whereas the energy of a wall varies as $Kr^2\omega^3/\lambda$, yields several consequences, summarized below.

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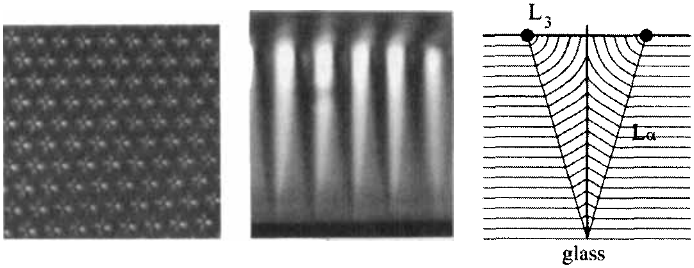
Hierarchy of defects with the size of the droplets

As in the Sm*A* bâtonnets, the nucleation of defects is caused by the anisotropy of interface tension; their presence has for consequence to locally favor the tilt of the layers at the interface[3]. Small droplets (typical size r <100 μm) exhibit only a few defects of typical size r (*e.g* Figure 1). Due to the different variations of energy with r, the curvature walls are found in small droplets whereas the FCDs are preferred in large droplets.

Combined defects

Due to the strong anisotropy of interface tension, a thin slab of L_α phase spontaneously anchored on a glass substrate and in contact with the L_3 phase is unstable toward the nucleation of defects tending to impose the tilt orientation of the layers at the interface. Such an instability gives rise to an hexagonal lattice of focal conic defects (Figure 3-a).



a) b) c)

FIGURE 3 This hexagonal lattice (a) of defects (diameter of the singularity circle ≈20μm) is obtained when the lamellar layers are in contact with both the sponge phase and the glass ((b): side view). The FCD alone cannot satisfy all the boundary conditions: a wall defect allows a strong parallel anchoring on the capillary glass(c).

Similar defects have also been observed during the Sm*A*-Isotropic transition but they involve a deformation of the Sm*A*-air interface rather than the creation of a wall defect (see the details in Reference[14]). The side view of the defects (Figure 3-b) show that the lamellar layers are parallel to the glass at its contact and that the FCD is bounded by a wall defect.

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CURVATURE WALLS AS TRANSIENT DEFECTS

The previous surface defects are stable and are observed at rest. There exist also transient curvature walls which appear during the nucleation and the reorganization of the lamellar layers. Those walls are of a great importance to achieve the final inner texture during the growth process.

For argument's sake, we will now detail the formation of the bâtonnets sketched in Fig 2-III. These bâtonnets are obtained by increasing the temperature of a sample of sponge phase by a few degrees; this process results in a rapid growth of the lamellar phase[15].

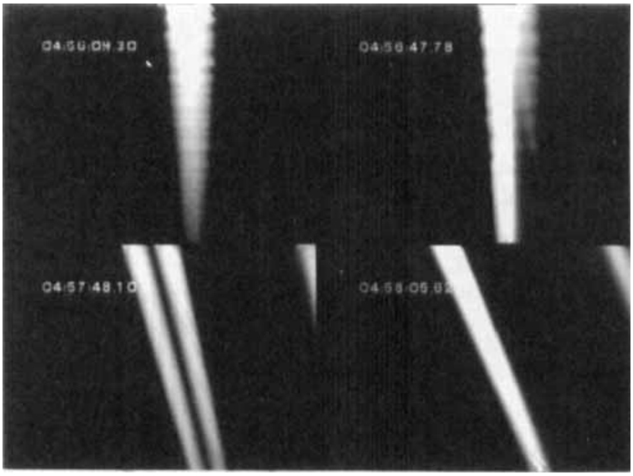

Figure 4 Evolution of the texture of a L_α bâtonnet (width ≈50μm). The initial flat layers are deformed in a conical shape by the advance of a surface defect (the sample has been rotated in the last two pictures).

The initial stacking geometry is due to the rapid formation (>10 $\mu m.s^{-1}$) of flat layers in a direction parallel to the director. A probable mechanism is a dendritic growth[15] favored either by the anisotropy of interface tension or the anisotropy of attachment kinetics. Using a video recorder (Figure 4) we have determined the stages of the formation (Figure 5). During the growth or quickly after it has finished, the flat

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lamellae are deformed in a stacking of conical layers (Figure 5-d). The final shape, obtained in a few minutes, is stable (at least for an hour) but slowly becomes more compact. The cause of the deformation is probably the interface energy since it decreases from Figure 5-a to Figure 5-d with the decrease of the interface area, while the contact angle θ_0 remains the same. In this way, the bâtonnet reaches a minimum of interface energy without flow in the direction perpendicular to the layers.

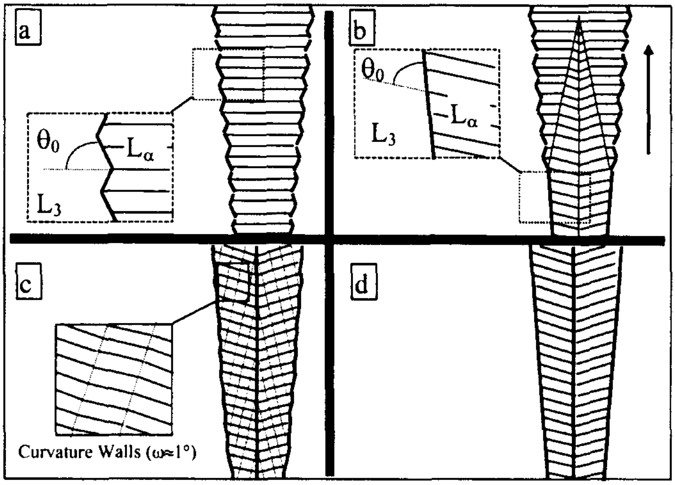

Figure 5 Simultaneous deformation of the lamellar layers and of the interface due to the advance of a curvature wall. The axial line can be seen as a degenerate curvature wall.

The deformation proceeds through the movement of a symmetric wall which separates the two stackings. This wall moves in the direction of the flat lamellae, changing them into a set of conical layers. Note that the perfect stacking of conical layers and the smooth interface is not instantaneously obtained, but transient striations are observed. Considering that all the initial layers (Figure 5-a) do not have the same area, we think that the striations are due to mechanical constraints at the interface. The striations disappear in a few minutes and the texture given in Figure 5-d is then obtained.

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CONCLUSION

This brief survey of the defects observed under microscope shows that the focal conic domains are not the only macroscopic defects of the L_α lamellar phases: wall defects are also present. These walls are rarely plane walls but curved surfaces which separates two stackings of parallel layers. The static textures are then explained in the geometric approximation by the combination of the wall defects and the FCDs. Finally transient wall defects are observed during the growth of the lamellar phase and explain the formation of the complex textures of the small droplets.

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