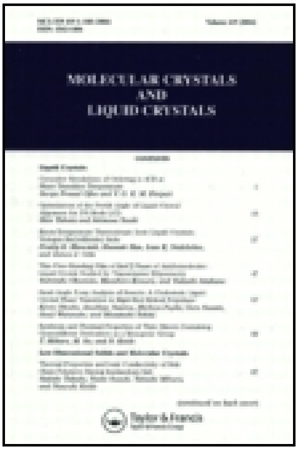

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On the Shapes of Lamellar Droplets in Sponge Phase

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On the Shapes of Lamellar Droplets in Sponge Phase

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We present a qualitative study of the macroscopic properties of the interface between the lamellar and the sponge phase and a brief account of the shape of droplets of lamellar phase in sponge phase. Similar to G. Friedel's "bâtonnets", but much simpler, those droplets are the result of a competition between interfacial tension, smectic elasticity and growth mechanisms.

Keywords: lamellar; sponge; shape; defects; focal conic domain; wall defects

Nuclei (droplets) of a thermotropic SmA phase growing from the isotropic liquid phase have been first studied in detail by G.Friedel[1]. These droplets ("bâtonnets") display numerous focal conic domains (FCDs) [2, 3], which impedes a detailed description of the first steps of growth and the conditions of nucleation of the FCDs.

The aim of this paper is to explain some steps of the nucleation of the droplets that can be observed in a great variety of ***lyotropic*** systems, where a similar lamellar-isotropic transition can be found, namely the lamellar-to-sponge transition [4]. The L_α lamellar phase is a stack of bilayers of surfactants and cosurfactants in solvent, whereas in the L_3 sponge phase an infinite and multi-connected membrane divides the solvent into two equivalent subvolumes. Thus the L_α and L_3 phases differ only in the topology of the membrane. The interface between L_α and L_3 phases presents some interesting characteristics. Previous observations of transient droplets have shown that the L_α phase meets the interface at a non-trivial angle[5, 6]. This angle originates in a phenomenon of epitaxy, explained by the continuity of the membrane through the interface, which results in the matching of the characteristic distances d_α and d_3 of the lamellar and the sponge phase [6, 7].

We firstly analyse the shape of the droplets of sponge phase at equilibrium, from which we obtain some features of the surface tension. Then we describe the shapes of droplets of L_α phase in L_3 phase and show how the boundary conditions and the smectic elasticity are satisfied by the creation of different defects, according to the size of the bâtonnets (we will use this term since it conotes the anisotropic droplets of a smectic phase into an isotropic one).

SAMPLES PREPARATION

Our choice of the Cetylpyridinium chloride CPCl/hexanol/brine system has been favoured by the precise knowledge of the L_α and L_3 phases in this system. Studies have been performed on the microscopic structure of both phases, on their phase diagram and on the defects of L_α phase[4, 8, 9]. Moreover, the temperature transition domain between the L_α and the L_3 phases is large [10] and it is possible to observe stable lamellar droplets for a few hours.

The ionic surfactant CPCl, the cosurfactant hexanol and salt NaCl have been obtained from SIGMA and used without further purification. The samples were prepared at different points of the phase diagram close to the domain of coexistence of L_α and L_3 phases (wt ratio hexanol/CpCl =h/c between 1.06 and 1.11, volume fraction of the membrane ϕ between 0.1 and 0.3), either in the sponge phase (h/c≈1.115) or in the domain of coexistence at RT, by mixing the appropriate amount of surfactants, brine (1% wt NaCl) and hexanol in glass vials. The samples were then centrifuged and held at rest a few days in order to obtain a complete homogenization. Glass capillaries of different shapes and thicknesses were then filled with the samples, sealed to prevent evaporation and observed under a polarizing microscope equipped with a heating stage (Mettler Hot Stage ±0.1°C), a movie camera and a movie recorder.

EQUILIBRIUM SHAPE OF L_3 DROPLETS

A quantitative study of interfacial effects requires samples with a high degree of order. This situation is not easily achieved with the L_α phase, which relaxes with numerous defects. On the other hand, the classic use of thin samples [11] is inadequate since they give an homeotropic orientation and thus no information with regard to the direction perpendicular to the layers. However it is possible to obtain reproducible L_3 phase droplets by employing cylindrical capillaries in which the lamellar phase organizes itself in a leek-like way [6] (orientation parallel to the glass boundary). This is certainly the simplest geometry in which the lamellar phase is least perturbed by defects.

We prepared a lamellar-sponge sample in which a small quantity of sponge phase is present in cylindrical capillaries of different radii (0.15mm to 0.5mm). We have focused on the trapped droplets located along the axis, which have an axial symmetry (Fig. 1). The equilibrium shape of those droplets is obtained in a few hours and remains stable for weeks. This geometry does not yield the classic Wulff construction. Nevertheless it can be shown that the deformation of the lamellae in the bulk can be neglected and that the cylindrical symmetry makes possible a construction analogous to the Wulff construction[12].

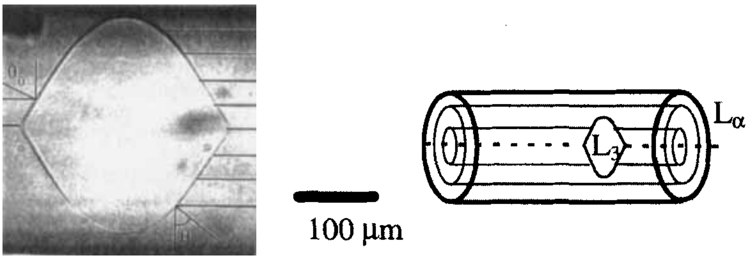

FIGURE 1 Shape of sponge droplet in a perfectly orientated lamellar phase (ϕ=0.15, $\theta_0 \approx 55°$).

The main results are as follows. First, the conical parts of the droplet define a facet ($\theta=\theta_0$ where θ_0 is close from the tilt-angle previously observed in lamellar droplets [5, 6]: $\theta_0 \approx 55°$ for ϕ=0.15 and $\theta_0 \approx 70°$ for ϕ=0.3). Forbidden orientations ($\theta>\theta_0$) are not observed and the facets end with a singularity point. The facets match tangentially with the regions $\theta<\theta_0$.

SHAPE OF THE LAMELLAR DROPLETS

Free Growth Experiments

The nucleation of smectic bâtonnets is usually obtained by decreasing the temperature from the isotropic phase. In our experiments, the bâtonnets are obtained by heating the sponge phase. We prepared samples close to the domain of coexistence at room temperature ($\phi \approx 0.3$, h/c $\approx$1.113 for which the L_α-L_3 domain can be found between $T_i \approx 39°C$ and $T_f \approx 83°C$). Thin rectangular capillaries (thickness: 200, 300 or 400μm) are observed in the heating stage under microscope. The sample is stabilized in the sponge phase at T_i and a temperature jump ΔT is applied. Bâtonnets grow from the sponge with a shape which strongly depends on ΔT. We distinguish two types of growth.

When ΔT is smaller than $\approx 1\,°C$, the complex shapes are due to mechanisms which will not be discussed here and which mix growth itself and nucleation of macroscopic defects. At rest, the droplets exhibit the following properties (see Fig. 2). On average, the layers are perpendicular to the axis of revolution and the droplets only possess a few macroscopic defects, unlike thermotropic bâtonnets. The shapes present often an axial symmetry: therefore the equilibrium is immediately obtained inside the layers (liquid state of the surfactant and cosurfactant) whereas in the direction perpendicular to the layers, the thermodynamical equilibrium is not reached and the shapes are strongly out-of-equilibrium.

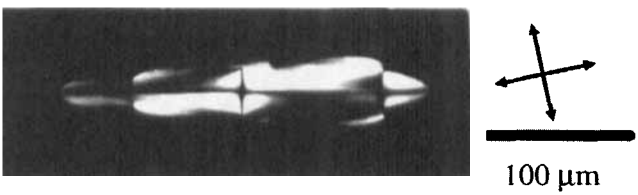

FIGURE 2 A lamellar bâtonnet in sponge phase (only one FCD can be seen: central cross).

Dendritic Growth

It is easier to describe the second type of growth (ΔT greater than $\approx 1\,°C$) since the growth kinetics is fast enough to separate the two phenomena: the growth and the nucleation of defects relaxing the interface energy. In a first step, the growing bâtonnet forms a stack of parallel membrane perpendicular to the growth direction. The bâtonnet reaches several hundred μm and does not display side branches. During the growth (or after it has ceased for the greater ΔT: a few seconds for$\Delta T \approx 5°C$), the interface destabilizes and an hill-and-valley structure forming sharp edges (Fig. 3) appears.

During this experiment, the smectic elasticity plays no role. Thus the growth is the same than a crystal growth in its melt. The growth mechanism observed here, known as needle-crystal growth or dendritic growth in solid crystal physics has been reported in different thermotropic systems [13-16].

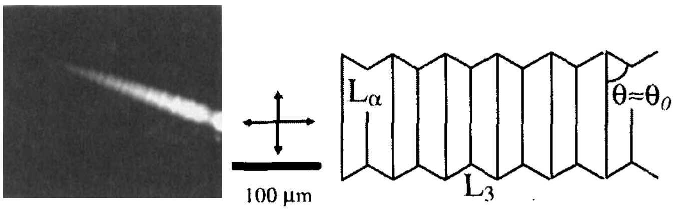

FIGURE 3 (Left)Dendritic growth of the lamellar phase in the sponge phase (right) Organisation of the layers and interface instability

The instability which develops at the interface is not the usual side-branching of the dendritic growth. It seems to have the following origin: the growth mechanisms yield an interface perpendicular to the layers ($\theta \approx 90°$); this interface is highly unfavourable since this orientation does not appear in the equilibrium shapes (see above). Herring[17] has shown that such an orientation is always unstable and an hill-and-valley instability appears. Note that this instability has already been observed in the study of SmA-SmB interface[18].

Long-time Formation of a Texture of Defects

The relaxation of the surface energy involves focal conic domains when the characteristic sizes are greater than typically 30-40μm. The smallest droplets which can be observed do no exhibit FCDs but rather curvature walls. For example, the previous bâtonnets (see Fig. 3) destabilize after the growth ($\approx$10s to a few minutes) (Fig. 4). The change of shape involves elastic deformation and local flow but no global flow perpendicular to the layers. The flat layers curve to form a conical stack and a line of curvature is created along the symmetry axis. The region near the apex bends into a spherical stack of layers and a surface of discontinuity of the director separates the two stacks.

Since the number of layers remains constant during the deformation, this wall defect preserves the continuity of the layers. Such walls defects have been observed in different modulated phases (lamellar diblock copolymer)[19]. Here they appear to keep the parallelism of the layers in the bulk. Thus wall defects play the same role for small droplets than FCDs for large bâtonnets. The appearance of either wall defects or FCDs is related to the specific shape of the droplets and their size. In a further publication[12] we will show that the curvatures walls are prefered in small size droplets (typical size smaller than ≈40μm), but they can be also found in the presence of FCDs.

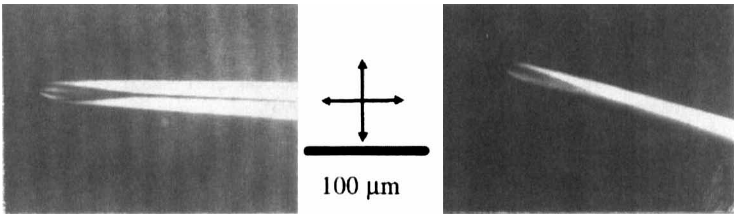

FIGURE 4 Relaxation of the surface energy of the droplet of Fig. 3 and creation of curvature line CL and wall CW.

CONCLUSION

The lamellar bâtonnets in sponge phase exhibit rich morphological transitions due to the smectic elasticity and the interface properties. The previous experiments show that the shapes of lamellar droplets (bâtonnets) are not equilibrium shapes: for example, the orientation of the layers perpendicular to the axis of the droplet is a result of the growth mechanisms and is not related to equilibrium shapes. On the other hand, the layers behave like 2D liquids, which explains the revolution symmetry of the droplets. The nature of the defects which appear to relax the interface energy changes with the size of the droplets: FCDs are present and follow the rules already observed in SmA systems, but the smallest droplets display only wall defects, which has never been previously documented in the thermotropic and lyotropic smectics.

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