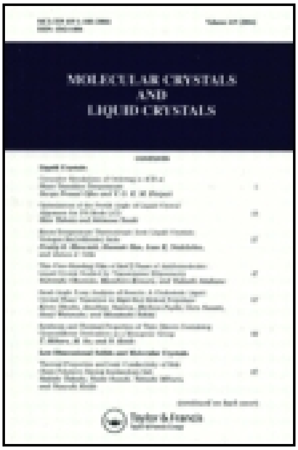

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Langmuir Monolayers and Liquid Crystals

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To cite this article: Charles M. Knobler (2001): Langmuir Monolayers and Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 364:1, 133-140

To link to this article: http://dx.doi.org/10.1080/10587250108024983

Mol. Cryst. and Liq. Cryst., 2001, Vol. 364, pp. 133-140
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Langmuir Monolayers and Liquid Crystals

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Over the past ten years, intensive studies of insoluble monolayers at the air/water interface (Langmuir monolayers) has revealed that there are close connections between the order in such films and that in smectic liquid crystals. By combining grazing incidence diffraction and imaging methods such as Brewster-angle microscopy, it has been shown that there are one-to-one correspondences between monolayer and liquid crystal phases. Monolayers have also been shown to have optical textures similar to those in smectics. The textures, which arise from an ordering of the molecular tilt azimuth, can be understood in terms of a Landau-de Gennes theory that is modified to take into account the broken symmetry at the interface. The tilt organization is most striking in ordered domains of a condensed phase surrounded by an isotropic phase. In such cases there is a coupling between the order within a domain and its shape, which has also been addressed by theory.

Keywords: Langmuir monolayers; textures: phase diagrams; smectic liquid crystals; hexatic phases; tilt order

INTRODUCTION

With the development over 80 years ago of methods for quantitative measurements of the surface pressure-area isotherms of insoluble monolayers at the air/water interface[1], it became evident that there were a variety of monolayer phases. Although these studies revealed that such films, which are now called Langmuir monolayers, are polymorphic, the character of the phases remained uncertain because no direct structural measurements could be performed. Nevertheless, many detailed phase diagrams were constructed from determinations of the densities of the monolayer phases, their compressibilities and their fluidity and from comparisons with the structures of three-dimensional phases[2,3]. Dervichian[4] proposed that some of these phases were mesomorphous, but noted that he did "...not necessarily imply that the state of the monolayer is identical to the state in a liquid crystal." The existence of liquid crystalline phases in monolayers of glycerides was inferred from measurements of their densities, which were lower than those of the three-dimensional crystalline phases and similar to those in lyotropic smectics[5].

With the advent of synchrotron sources, it became possible to determine the structures of monolayers by grazing incidence diffraction (GID) [6]. At essentially the same time, the imaging of monolayers by polarized fluorescence microscopy [7,8] and Brewster-angle microscopy (BAM) [9,10] revealed optical textures related to the organization of the molecular tilt azimuth. Peterson was the first to recognize that, in light of these results, strong analogies could be drawn between the molecular organization in monolayer phases and that in smectic liquid crystals (LC's) [11-13]. Subsequent studies have confirmed this insight and its utility in understanding the nature of monolayer phases and their properties.

In this review I will describe connections between monolayers and LC's, starting with a discussion of the phase diagrams. I will then turn to monolayer textures and their relation to textures in LC's and I will conclude by briefly discussing the problem of the morphology of monolayer domains.

MONOLAYER PHASE DIAGRAMS

Much of the detailed information about the phase behavior of monolayers has been drawn from measurements on the linear saturated fatty acids although there is a growing body of information about the corresponding esters. A schematic surface pressure – temperature (π,T) for the acids is shown in Fig. 1. There are two isotropic phases, a liquid (LE) and a gas (G). The high-pressure phases CS, C and LS are "untilted phases", i.e. the chain axes are perpendicular to the water surface. As the pressure is lowered there are transitions to "tilted" phases. Within these phases there is a continuous increase in tilt angle with decreasing pressure. Diffraction studies show that only two of the phases (CS, L_2'') are crystalline; the other condensed phases lack long-range translational order.

The tilted phases can be distinguished by their chain tilt azimuth. It is toward nearest neighbors (NN) in L_2 and L_2'' and toward next-nearest neighbors (NNN) in L_2' and Ov. Direct evidence of long-range chain backbone order (herringbone order) in the CS and L_2'' phases has been obtained from diffraction measurements [14] and limited backbone order in the S, L_2' and the low-temperature L_2 phase has been inferred from the direction of the unit cell distortion at zero

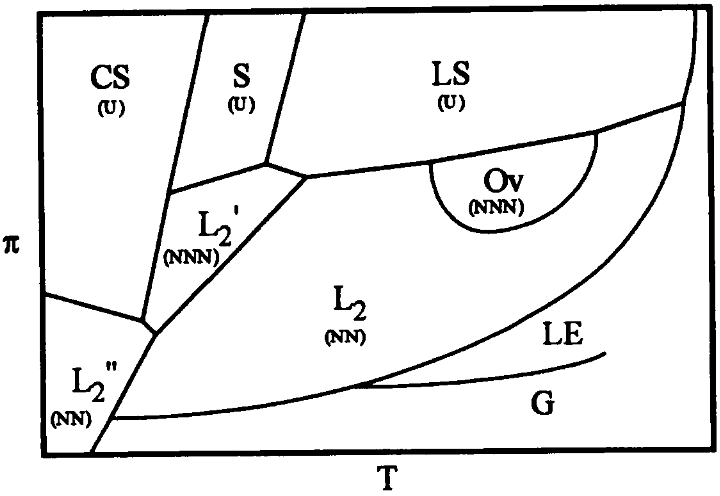

FIGURE 1 Schematic surface pressure-temperature phase diagram for monolayers of saturated fatty acids.

pressure [6]. (The L_2 phase is conventionally divided into two phases, L_{2d}, a rotator phase and L_{2h}, a phase with backbone order, but no clear transition between the two phases has been observed either by GID or BAM.)

The phase sequences have strong parallels with those in LC's. The LS and Ov phases and the L_2 phase at high temperature are rotator phases analogous to the hexatic smectics B, F and I, respectively. Although the lack of (quasi) long-range translational order in the monolayer phases is evident from the widths of the peaks, GID does not provide any information about the extent of the orientational order. It can be seen in the BAM textures, which are described below. As the temperature is lowered, there is an increase in backbone order. The two crystalline monolayer phases, CS and L_2", have long-range herringbone order and are similar to the crystalline smectic E and K phases, respectively. The backbone order in phases S, L_2' and L_2 at low temperature is intermediate between that of the rotator and crystalline phases and in this respect they are analogs of the crystalline B, G and J phases. In one case a small sliver of a phase in which the tilt direction is intermediate between NN and NNN has been detected at the boundary between the L_2' and L_2 phases [15]. This phase, designated I, would play the role of crystalline M; there has been no evidence of an intermediate tilt rotator phase corresponding to smectic L.

The phase diagrams for monolayers of other simple amphiphiles such as esters and alcohols are similar to those of the acids but lack one or more of the tilted mesophases [16].

TEXTURES

The monolayer textures observed with polarized fluorescence microscopy and BAM are closely similar to those in smectic liquid crystals [17]. Examples of common textures are shown in Fig. 2. All the tilted phases exhibit mosaic textures, Fig. 2a, in which the individual grains correspond to regions of uniform tilt azimuth or, in herringbone-ordered untilted phases, to regions of uniform backbone order [18]. Splay stripe textures and spirals in which there is a periodic rotation of the molecular azimuth, Fig. 2b, are observed in tilted phases at low temperatures [19]. These are analogous to stripes found in freely suspended films of chiral smectics and in surface phases [20].

A large variety of textures is found in domains of tilted phases surrounded by isotropic phases. Particularly striking are six-arm star defects [8], Fig. 2c, in which there are is a central topological defect and segments of uniform tilt direction separated by sharp walls that are 2π/6 disclinations. Also observed are boojums [21,22], Fig. 2d, in which the tilt azimuth changes continuously and the defect is at the domain boundary or there is a virtual defect in the surrounding phase. The star defects in monolayers are essentially identical to those found in freely suspended films of smectic I [23,8] and in smectic F domains surrounded by the isotropic liquid [17].

The textures in monolayers can be understood in terms of a Landau-de Gennes theory of tilted hexatic phases [24]. The simplest Landau free energy per unit area consistent with the symmetries of a nonchiral tilted hexatic monolayer is [8,25]

$$f = \frac{1}{2}K_6(\nabla\theta)^2 + \frac{1}{2}K_1(\nabla\cdot\hat{c})^2 + \frac{1}{2}K_3(\nabla\times\hat{c}) + V[6(\theta-\varphi)]$$
$$-\lambda_s\cos[6(\theta-\varphi)]\nabla\cdot\hat{c}$$

The first term is the deformation energy of a nonuniform 2-D hexatic with K_6 the hexatic rigidity and the second and third terms represent the deformation energy of a 2-D nematic with K_1 and K_3 the splay and

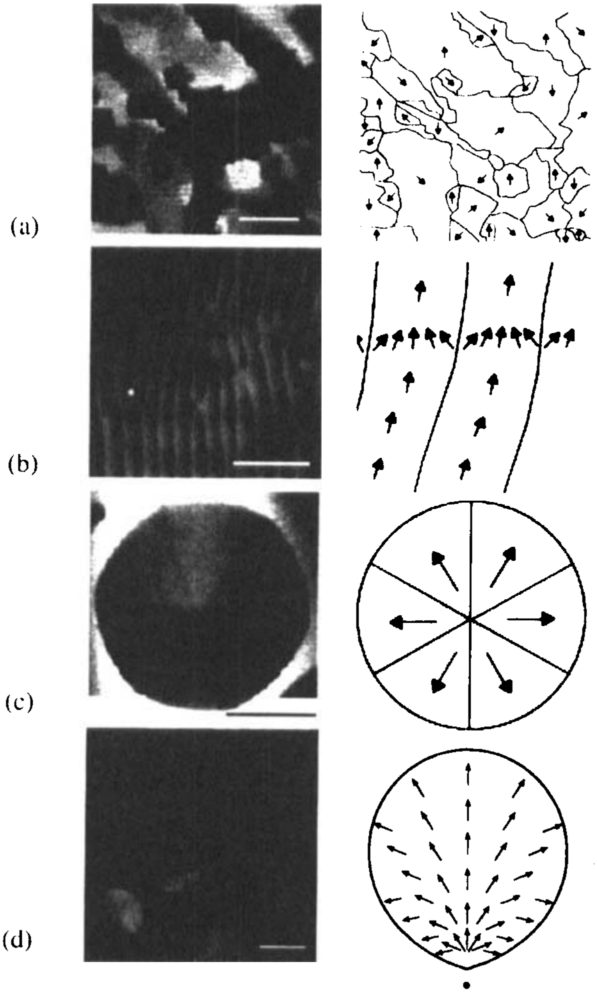

FIGURE 2 Textures observed in monolayer phases. Accompanying each texture is a sketch showing the underlying organization of the molecular tilt azimuth. The bars represent 100 μm (a) Mosaic texture; (b) Stripe texture; (c) Six-arm star defect; (d) Boojum.

bend rigidities, respectively. Here the director $\hat{c} = \cos\varphi(x), \sin\varphi(x)$ is the projection of the molecular axis onto the plane of the surface. There is a coupling between the tilt azimuth field $\varphi(x)$ and bond-angle field $\theta(x)$ specified by V. When the minima of V are at $m\ 2\pi/6$, the tilt is in the NN direction; it is in the NNN direction when the minima are at $m\ 2\pi/6 + \pi/6$. The last term, which involves λ_t, the head-tail asymmetry of the amphiphile, is not present in bulk phases.

In applying this free energy to domains surrounded by an isotropic phase one must also consider the anisotropy of the line tension at the boundary between the two phases. The tension can be written

$$\sigma(\phi) = \sigma_o + \sum_{n=1} a_n \cos n\phi$$

where σ_o is the isotropic part of the tension and ϕ is the angle between the director and the outward normal to the boundary. The preferred orientation of the tilt direction is usually outward. (Note that for amphiphiles anchored by their hydrophilic head groups at the water surface $\hat{c}(x) \neq -\hat{c}(x)$.)

With few exceptions, the textures observed in monolayer domains can be accounted for by the Landau-de Gennes theory. Unfortunately, unlike the case of LC's, there have been no independent determinations of the rigidities in monolayers so there have been no quantitative tests of the theory. Nevertheless, the theory provides insight into the competing interactions that determine the textures and their relation to the monolayer phases.

DOMAIN SHAPES

There is a coupling between the texture of a domain and its shape. This is evident in domains that have boojum textures, where there appears to be a cusp associated with the topological defect [22, 26]. Moreover, there are "inverse boojums", cusped droplets of the liquid or bubbles of gas surrounded by an anisotropic tilted phase [26, 27]. The dependence of the cusp angle Θ on the domain size has been measured by fluorescence microscopy [26] and, for small domains, by scanning force microscopy studies of monolayers transferred to solid supports by the Langmuir-Blodgett method [27]. The data are most conveniently shown as plots of the excluded angle $\Psi = \pi - \Theta$ against the reciprocal of the domain radius $1/R$. For small domains, $\Psi = 0$ (.e, the domains are circular), there is a threshold at which the cusp appears, Ψ rises to a maximum and then falls to a nonzero value at $1/R = 0$. There is no qualitative difference between boojums and inverse boojums.

In crystals, the surface energy is small compared to the energy associated with the organization of the bulk, so the morphology is determined by the bulk structure and can be calculated by the Wulff construction.. For 2-D mesophases, however, the energies associated with the organization of the tilt azimuth and the line energy of the boundary are comparable. As a result, theoretical treatments must deal with the texture and morphology self-consistently. The most ambitious work has been that of Rudnick and Loh [28,29], who have considered both boojums and inverse boojums. They examined the effects of both the line-tension anisotropy and the difference between the bend and splay energies on the textures and morphologies. They find that the boundary shape is more sensitive to the line-tension anisotropy than to differences in the elastic constants. The dependence of the shape on domain size is in good accord with the experimental measurements.

Acknowledgment
This work was supported by the US National Science Foundation.

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