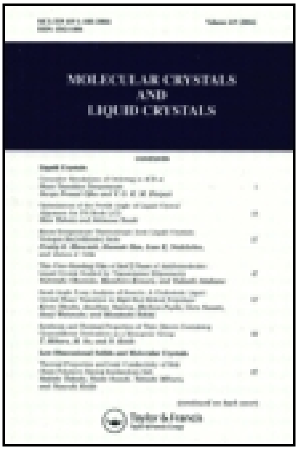

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New Faceting Phenomena in Lyotropic Liquid Crystals

P. Pieranski [a], C. Even [a], D. Rohe [a], L. Sittler [a], M. Bouchih [a], N. Ginestet [a], S. Popa-Nita [a], T. Plötzing [a] & J. Grenier [a]

[a] Laboratoire de Physique des Solides, UMR, Université Paris-Sud, Orsay, France

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P. Pieranski
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T. Plötzing
J. Grenier
Laboratoire de Physique des Solides, UMR, Université Paris-Sud,
Orsay, France

In lyotropic systems, four different isotropic phases may coexist with several cubic phases having different topologies and/or symmetries. We review here faceting phenomena, rising new conceptual issues, that have been recently found to occur at different cubic/isotropic interfaces: 1°- depending on their tension, these interfaces can be either rich or poor in facets or even completely rough, 2°- when facets coexist with rough surfaces, facets can grow due to the redistribution of the surfactant in the crystal, 3°- upon a temperature cycling, ratchet-like growth of facets, until an elimination of rough surfaces takes place, 4°- asymmetric crystal shapes are induced by temperature gradients, 5°-rough surfaces "melt" prior to facets that stay "dry".

Keywords: crystal shapes; lyotropic cubic phases; surface melting

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Address correspondence to P. Pieranski, Laboratoire de Physique des Solides, UMR 8502, Université Paris-Sud, Bât. 510, 91405 Orsay , France. E-mail: pawel@lpb.u-psud.fr

INTRODUCTION

Mostly serendipitous recent discoveries of several striking phenomena occurring at interfaces in lyotropic systems raised new interesting issues to the very old problem of crystal shapes. Here, we will present the first review on these phenomena with the aim to explain, *a posteriori*, what are the features of lyotropic systems that distinguish them from "classical" solid crystals and, by this means, make them so interesting from the point of view of crystal shapes.

Our first remark is an obvious one: in lyotropic systems, due to their at least binary composition, coexistence of phases is ubiquitous due to the Gibbs phase rule. Here, we will focus on the coexistence between cubic and isotropic phases because in this case the interfaces have the same symmetries as the "classical" crystal/liquid or crystal/vapour interfaces widely studied and discussed in past (an excellent introduction to the physics of crystal surfaces can be found in ref. [1]). Let us emphasize however that other lyotropic interfaces, even if not discussed here, are also interesting from the point of view of faceting phenomena. In particular, the lamellar/vapour interface displays the simplest possible configuration of facets shown in Figure 1. Here, a droplet of the lamellar phase ($C_{12}EO_6/H_2O$ mixture) sits on a glass plate and is surrounded by a humid atmosphere. The anisotropy of the lamellar/vapour interfacial energy leads to the occurrence of a unique facet on this drop. It can be inferred from the set of the interference fringes that this flat facet coexists with an almost spherical surface. This configuration is similar to the one observed and discussed previously by Oswald *et al.* [2,3].

CHOICE OF THE SYSTEM

Stimulated by the observation due to P. Sotta [4] of facetted air bubbles in the Ia3d phase of the $C_{12}EO_6/H_2O$ mixture, we worked mostly with C_mEO_n/H_2O mixtures but many other lyotropic systems are known to display similar cubic/isotropic coexistence domains [5–7]. Nevertheless, the C_mEO_n/H_2O mixtures have been preferred here because their well known phase diagrams offer multiple choices for the cubic/isotropic interface. For instance, it is known from the work of Lynch *et al.* [8] that in the $C_{12}EO_2/H_2O$ mixture, two cubic phases, Pn3m and Ia3d, can coexist with three different isotropic lyotropic phases: L1, L2, L3 (see Fig. 2b). This variety of cubic/isotropic interfaces is further enriched by the possibility of the coexistence of the cubic phases with the vapour phase (a humid atmosphere) like in the generic Sotta's experiment. We used this possibility in studies of shapes of Ia3d crystals in the $C_{12}EO_6$/mixture where the cubic

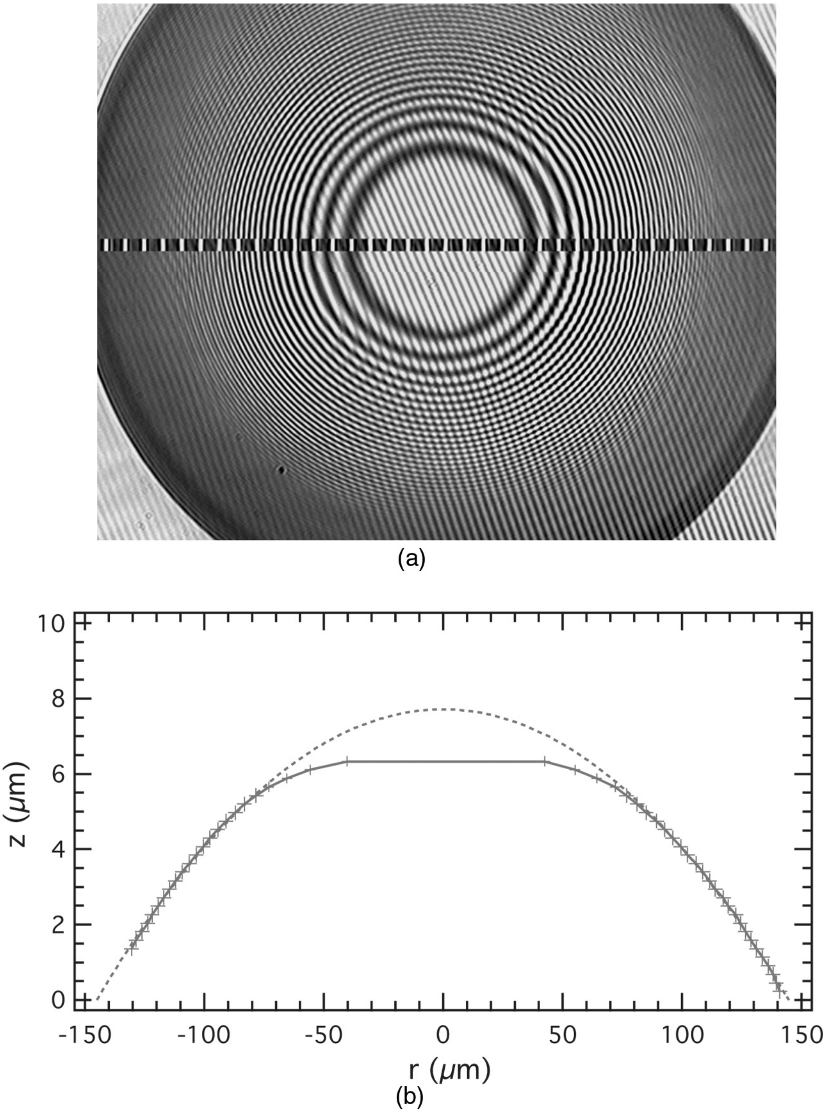


FIGURE 1 Shape of a droplet of the lamellar La phase surrounded by a humid atmosphere. a) Picture taken in a reflecting microscope upon a monochromatic illumination. Interference fringes reveal the presence of a facet on the top of the droplet. b) Shape z(r) of the droplet deduced from fringes in a. The dashed line correspond to a spherical shape fitting to sides of the droplet.

phase can coexist only with anisotropic lyotropic phases: the hexagonal and lamellar ones (see Fig. 2a).

EXPERIMENTAL METHODS

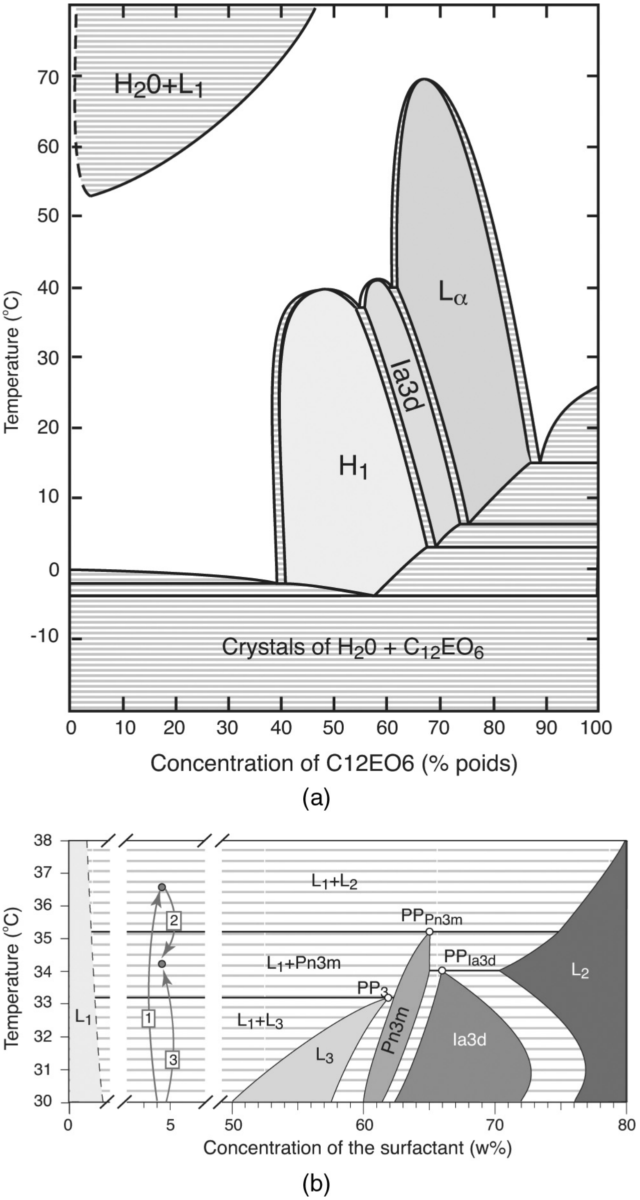
We learned from our experimental work that for successful studies of shapes of lyotropic interfaces, the necessary knowledge of phase diagrams must be completed by that of a few hints concerning experimental cells, preparation and handling of samples which are very different in the two cases considered here: 1° – cubic crystals surrounded the humid atmosphere, 2° – cubic crystals immersed in a lyotropic isotropic phase. A quite detailed description of our experimental methods with all necessary details can be found in ref. [9–11]. Here, we show only in Figure 3 the schemes of experimental cells devoted respectively to studies of shapes of the cubic/vapour (Fig. 3a) and cubic/isotropic liquid interfaces (Fig. 3b). It is worthwhile to emphasize that the size of the cubic crystals surrounded by the isotropic phase (or, in the complementary case, of the isotropic-in-cubic inclusions) should be small enough, typically $\approx 100\,\mu m$, for the chemical equilibrium between the coexisting phases could be reached in a reasonable time of a few minutes. Such a small size is also needed if one wants to avoid the influence of the gravity on crystal shapes.

RICH AND POOR FACETINGS

Our work on lyotropic interfaces started with the discovery of the devil's staircase–like faceting of Ia3d crystals ($C_{12}EO_6$/water mixture) surrounded by the humid atmosphere [9,10]. This astonishingly **rich faceting** is illustrated in Figure 4a by the picture of a small portion of the surface of a Ia3d crystal. Facets visible here can be indexed with the help of the theoretical scheme shown in the same figure. This scheme represents a view of an elementary triangular patch from the surface of a spherical Ia3d crystal. All other facets from the crystal surface can be obtained from this elementary patch by permutations and/or sign changes of Miller indices.

Why so many facets occur on this Ia3d/vapour interface? The answer to this question has been given by Nozières *et al.* [13]. Without entering into details of their theory which takes into account elastic repulsive interaction between steps and their rigidity, let us just quote the final formula of the roughening temperature above which thermal fluctuations destroy the order of steps composing vicinal facets:

$$k_B T_R = (2/\pi) c\, \gamma h_{hkl}^2$$



(a)

(b)

FIGURE 2 Phase diagrams: a) $C_{12}EO_6/H_2O$ mixture, b) $C_{12}EO_2/H_2O$ mixture [8].

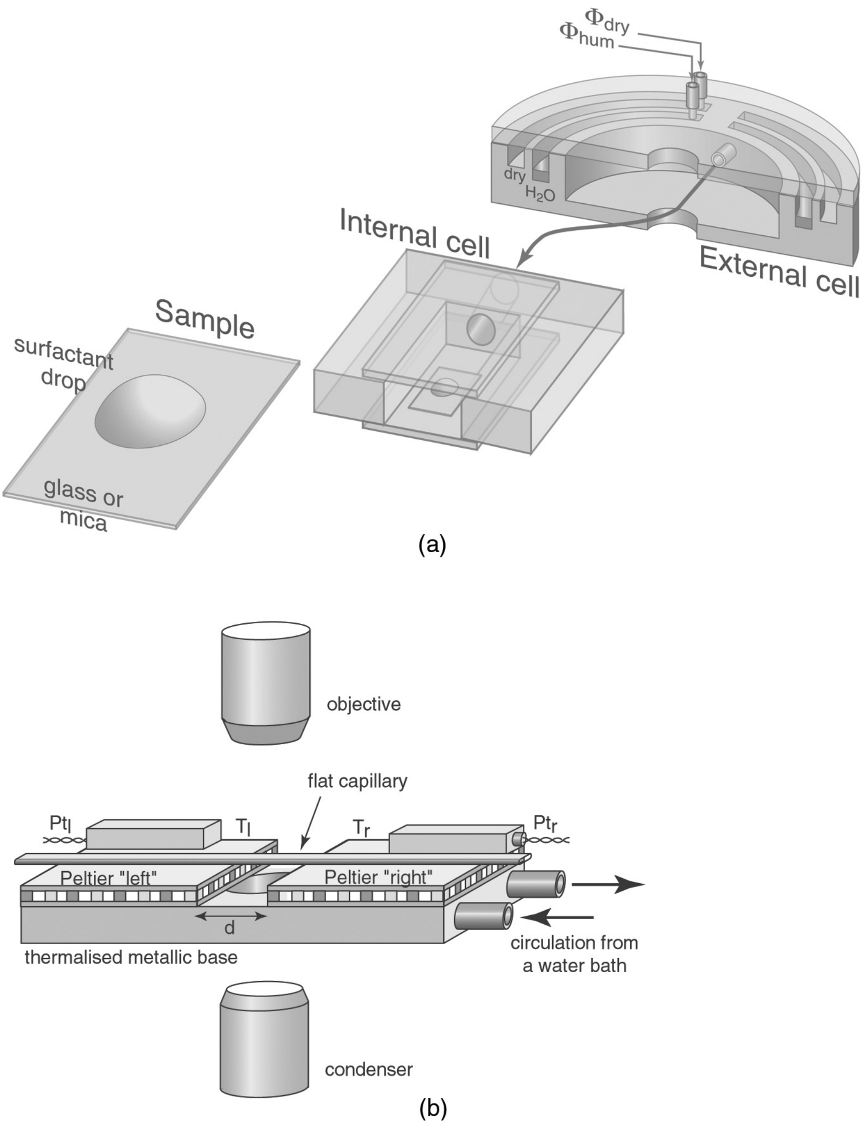


FIGURE 3 Schemes of set-ups developed for studies of: a) Ia3d crystals surrounded by a humid atmosphere [9,10], b) Pn3m crystals surrounded by the L1 phase [11,12].

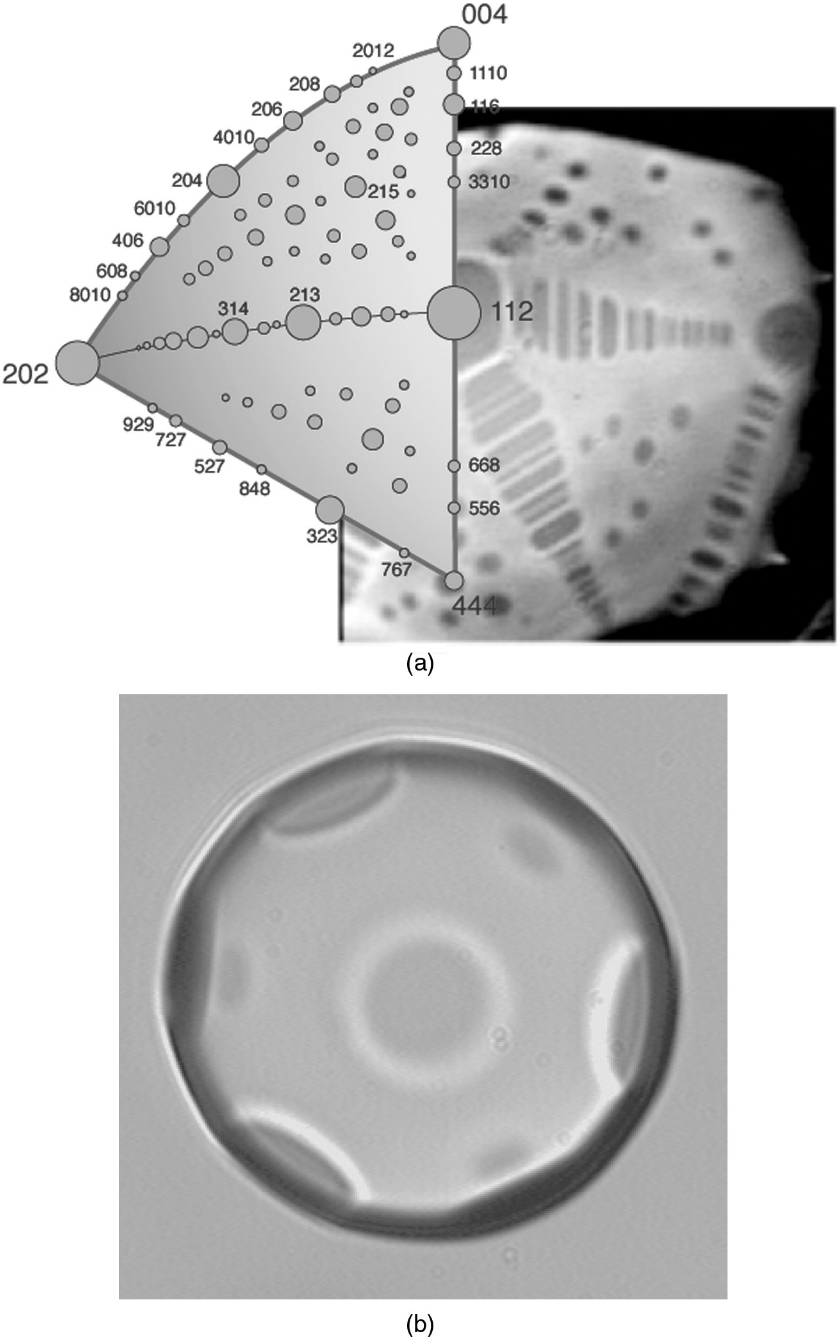


FIGURE 4 Rich and poor facetings of cubic lyotropic crystals. a) The devil's staircase–type faceting of Ia3d crystals surrounded by a humid atmosphere. b) Poor faceting of Pn3m crystals in coexistence with the L1 phase.

Here, c is a numerical factor of the order of 1, γ is the interfacial tension of principal facets and h_{hkl} is the height of elementary terraces on the (hkl) facet.

The interfacial tension of the Ia3d/vapour interface is of the order of 20 dyn/cm that is to say similar to that of "classical" crystal/vapour interfaces. On the contrary, the height of steps h_{hkl} is much larger because unit cells of cubic lyotropic phases are huge, about 100 Å in size. This explains why vicinal facets with large Miller indices have their roughening temperature higher than 300° K–the temperature of our experiments.

Does it mean that surfaces of the cubic lyotropic phases should always by so richly faceted? The size of unit cells is of the same order of magnitude in all cubic lyotropic phases. However, the interfacial tension can be much lower if instead of the humid atmosphere, the cubic crystal is surrounded by one of the three possible isotropic liquid lyotropic phases: L1, L2 and L3.

Stimulated by the work of Lynch *et al*. [8] we focused our attention on the $C_{12}EO_2$/water system which allows to realise all these three cubic/liquid interfaces (see the phase diagram in Fig. 2b). Our experiments [11] have shown that only the Pn3m/L1 interface is facetted while the other two, Pn3m/L3 and Ia3d/L2 are completely rough. Moreover, **the faceting of the Pn3m/L1 is poor**; at most, only two types of facets, (111) and rarely (100), occur at this interface (see Fig. 4b). This agrees with the theoretical expectations of the Nozières' *et al*. Let's note, with the aim to use this information below, that 1°- these facets coexist with rough surfaces and 2°- the junction between the facets and the rough surfaces is angular.

PSEUDOGROWTH OR GROWTH BY REDISTRIBUTION

In principle, one could continue to test the theory of the roughening transition by looking for effects of variations of the temperature. Unfortunately, in the case of the $C_{12}EO_2$ mixture, the temperature range of the Pn3m/L1 phase coexistence is very narrow; the two peritectic triple points, defining limits of the Pn3m/L1 coexistence range, are only separated by ≈2°K. Experiments revealed however that even very small temperature variations, inside this range, affect shapes of Pn3m crystals surrounded by the L1 phase. As an example we show in Figure 5 the evolution of a Pn3m crystal upon a slow triangular temperature cycling of the amplitude 0.5°K. The spatio-temporal cross-section extracted by computer from a movie picture proves that the size of the central (111) facet follows variations of the temperature.

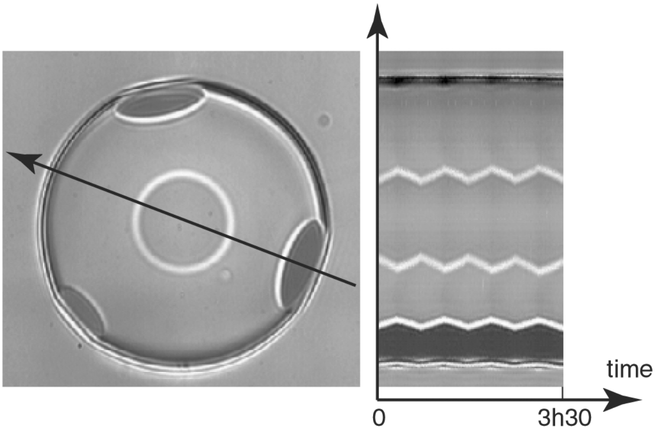


FIGURE 5 Evidence for the "growth-by-redistribution" phenomenon. Upon a triangular temperature cycling, the size of the (111) facet follows variations of the temperature. Left: picture taken with an optical microscope in trasmission mode. Right: spatio-temporal cross-section.

For instance, when T increases, the size of the facet grows **as if the crystal was growing**.

We have pointed out that this effect has no equivalence in classical solid crystal/liquid systems. Its mechanism is a consequence of the truly liquid-crystalline structure of cubic phases and we called it "pseudogrowth" or "**growth by redistribution**" for the following reason. Unit cells in cubic lyotropic phases are huge and "**liquid inside**" in the sense that molecules do not have fixed positions in them even if the volumes accessible to water and surfactant are separated. For this reason, the number n_s of surfactant molecules per unit cell is not fixed like in solid crystals but only known at average. Therefore, it has to be considered as a thermodynamic parameter that can vary as a function $n_s(T)$ of the temperature. In the $C_{12}EO_2$/water system, the surfactant is almost insoluble in the L1 phase so that in a given Pn3m crystal the total number of surfactant molecules N_s is fixed. As a consequence, the number of unit cells in the crystal $N_{uc} = N_s/n_s(T)$ varies with the temperature. If, for instance, n_s decreases with temperature, new unit cells have to be created and the surfactant, from the existing cells, redistributed in them. As the nucleation of new unit cells is easiest on rough surfaces of the crystal, the size of facets increases as shown in Figure 6.

The same phenomenon of the pseudo-growth occurs in the $C_{12}EO_6$/vapour system when the humidity of the gas surrounding Ia3d crystals varies.

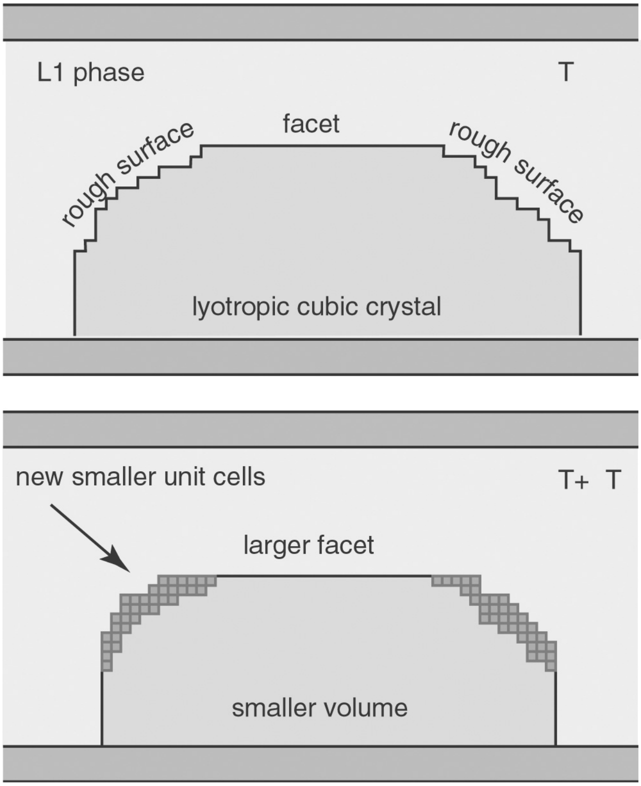


FIGURE 6 Schematic representation of the "growth-by-redistribution" phenomenon.

RATCHET-LIKE EFFECT

In the above explanation of the growth by redistribution phenomenon, the nucleation or suppression of unit cells is supposed to take place only on rough surfaces. In terms of the theory of faceting, one says that **facets are blocked** that is to say unable to change their distance D_{hkl}(in units h_{hkl}) from the crystal centre. The theory of faceting [1] stresses however that even if the nucleation of new terraces on a facet is prohibited, it is always possible to collapse existing terraces, starting from the edge of the facet. **This dissymmetry is at the origin of the so-called "ratchet-like" effect taking place when a Pn3m crystal surrounded by the L1 phase is submitted to a saw-tooth shaped temperature cycling**. During the positive slow temperature ramp, the size of facets increases due to the "growth by redistribution" mechanism. Upon the steep negative temperature ramp, a few terraces are collapsed on facets. As a result, the distance D_{hkl} decreases and, for the same volume of the crystal, facets increase in size at the end of each cycle. When such temperature cycles are repeated several times, the size of facets can grow until a complete elimination of the rough parts on the Pn3m/L1 interface. This phenomenon, discussed extensively in the ref. [12], is illustrated in Figure 7 by a series of pictures showing the same crystal at the end of several successive temperature cycles. The ratchet effect exists also in the case of crystals surrounded by the humid gas.

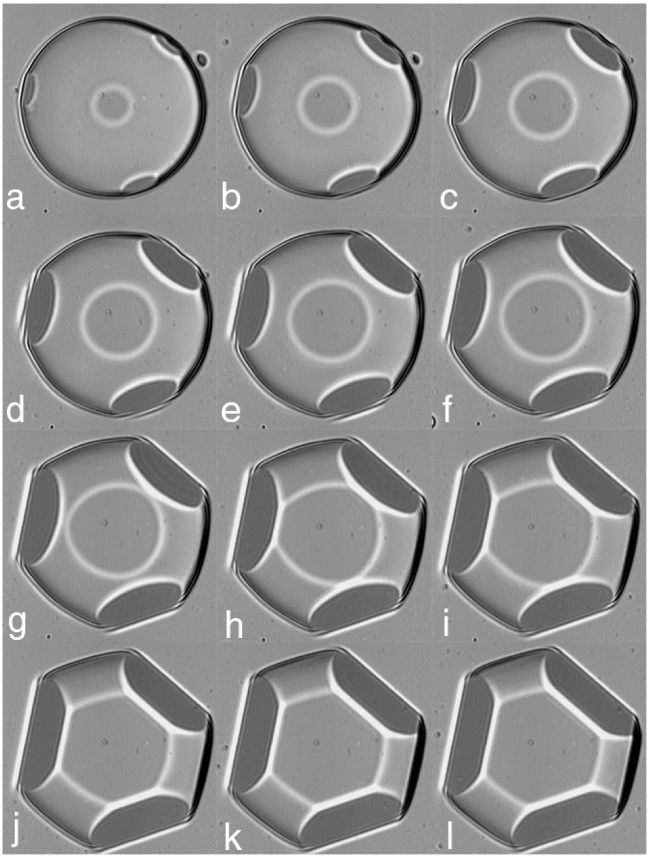


FIGURE 7 Experimental evidence for the "ratchet-like" growth of facets upon a saw-tooth temperature cycling. The series of picture showing shapes of crystals at the end of successive temperature cycles.

TEMPERATURE GRADIENT EFFECT

Experiments with Ia3d-in-vapour as well as with Pn3m-in-L1 crystals have shown that quite often sizes of facets of the same type (hkl) on the same crystal are different [14]. What is the reason of this symmetry breaking? In the search for the answer to this question, we have discovered that even very small temperature gradients can lead to a drastic dissymmetry of crystal shapes. In order to work to check quantitatively this effect, we worked with controlled temperature gradients in the cell shown in Figure 2b. This cell is equipped with independent temperature regulations for each of the two Peltier elements on which is positioned the flat capillary containing the sample. Typically, when a Pn3m-in-L1 crystal, about 100 μm in size, is submitted to a horizontal temperature gradient of 1.33°K/mm, its size changes progressively on the time scale of several hours as it is shown in Figure 8. Clearly, on its colder side the crystal is growing and at the same it is deconstructed on its warm side. This process involves obviously the transfer of the surfactant from the warm to the cold side of the crystal.

What is the path of this transfer? It cannot be through the L1 phase surrounding the crystal because $C_{12}EO_2$ surfactant is almost not soluble in it. The second possibility, the transfer through the crystal, is very plausible because lyotropic cubic phases are “liquid inside” so that the surfactant can flow by permeation, along the continuous surfactant bilayer, from one side of the crystal to the opposite side.

We are left with the question: “What drives this flow?”. In binary mixtures, the Soret effect is well known to occur. Now, cubic lyotropic crystals are nothing else but **organised binary mixtures** so that a kind of Soret effect should take place in them in the presence of a temperature gradient. This is the most plausible hypothesis at the present stage of our study.

ANISOTROPIC SURFACE MELTING

The last phenomenon which certainly deserves to be mentioned in this review concerns the so-called surface melting of crystals. The fact that the melting of crystals starts on their surfaces is well known. However, in the case when the crystal surface is made of facets coexisting with rough parts, one can ask “Does this surface melting starts simultaneously on facets and rough surfaces?” Electron and proton diffraction experiments with lead crystals have shown that rough surfaces melt first [15,16]. Theoretically, this phenomenon an **anisotropic surface melting** has been analysed by Nozières in ref. [1]. One of

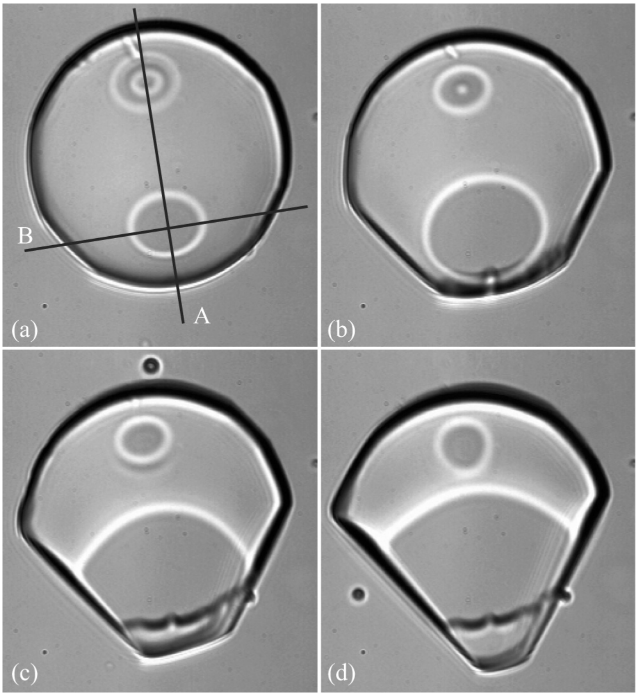


FIGURE 8 Changes of the shape of a crystal submitted to a temperature gradient of 1.33°K/mm. Images have been at intervals of 1 hour.

his conclusions is that rough surfaces can melt and facets stay dry only when, prior to the melting, the junction between facets and rough surfaces is angular. Another conclusion says that the size of a facets should decrease when the rough surface around it starts to melt. Finally, the theory of Nozières predicts the shape of the liquid lens between two facets. All these features are difficult to check in experiments with metal crystals.

Can lyotropic cubic crystals be used for such experiments? We know already that Pn3m crystals have facets coexisting with rough surfaces and the junction is angular, as required by the theory. Can Pn3m crystal melt? The answer is “yes” but, paradoxically, one has to cool them in order to make them melt. Indeed, in the case of the $C_{12}EO_2$/water system, the sponge L3 phase has the same topology as the Pn3m phase but is disordered. It can bee seen therefore as a melted Pn3m phase. Our previous experiments [11] have shown that when Pn3m-in-L1 crystals are cooled below the peritectic point PP3 of the sponge phase, a layer of the sponge phase forms at the Pn3m/L1 interface. More

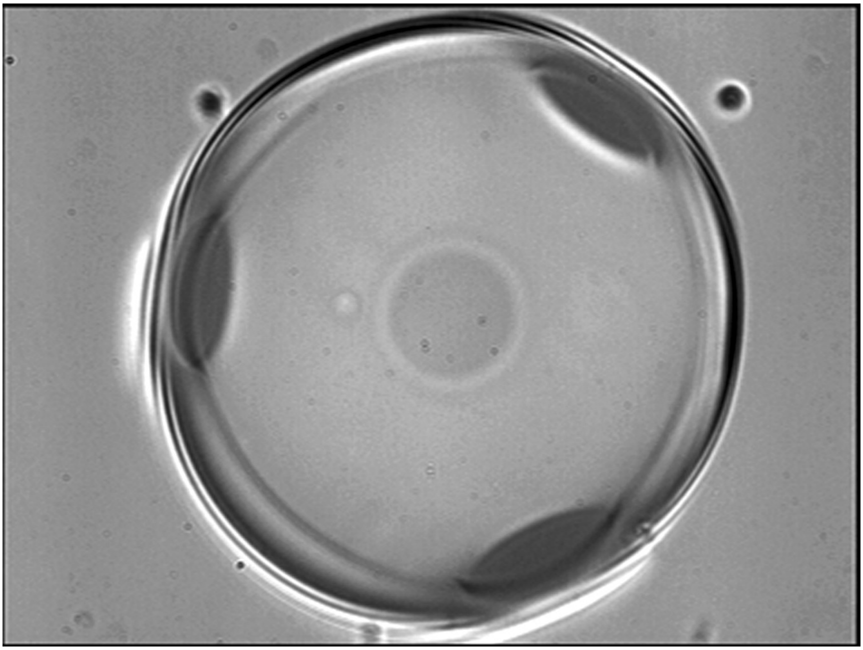


FIGURE 9 The experimental evidence for the anisotropic surface melting in a Pn3m-in-L1 crystal.

recently, we have observed that when the undercooling $\Delta T = T_{PP3}$ is very small, of the order of 0.01°K, a layer of the sponge phase wets rough surfaces but facets stay “dry”. Moreover, thanks to the perfect optical transparency of all three phases, the L3/Pn3m interface is visible as it shown in Figure 9. One can therefore follow thickening of the L3 layer and at the same time measure the size of facets. We have found, in agreement with Nozières’ prediction that the size of the facet decreases when the L3 layer is formed.

CONCLUSIONS

In the condensed review presented here, we focused on the most striking phenomena occurring at interfaces between cubic/isotropic interfaces in lyotropic systems. Other details can be found in references quoted here [9–12]. Our aim was to show that studies of interfaces in liquid crystals can contribute to a better understanding of universal issues concerning crystal surfaces in general. We hope in particular that the optical transparency of lyotropic systems will allow to shine new light on the astonishing anisotropic surface melting phenomenon.

Our studies rise also some other unique issues intimately connected with the "liquid inside" structure of cubic liquid crystals. The ratchet-like growth and the growth-by-redistribution phenomena are examples of such issues.

We think that the bicontinuous topology of certain lyotropic phases may also play some role in surface phenomena. One can ask for example: "How the prohibition of free edges of the unique bilayer can be respected at surfaces of the Pn3m or the sponge phases in the $C_{12}EO_2$/water system".

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