

Interplay between Growth Mechanisms and Elasticity in Liquid Crystalline Nuclei

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A first order phase transition from an undercooled isotropic phase to an ordered phase usually yields complex morphologies, resulting from the competition between growth, diffusion and surface tension. We discuss the importance of similar mechanisms in the formation of soft lamellar phases appearing in an isotropic phase. Through the experimental study of the sponge-to-lamellar phase transition, we interpret the formation of batonnets and identify the relevant elementary mechanisms. Finally we discuss the role played by crystalline properties in the formation of smectic filaments.

§1. Introduction

Beautiful and complex figures are found when a crystal grows from its melt and this phenomenon has puzzled generations of scientists. For a long period, only a few features, such as the presence of symmetries, have been easily related to the microscopic structure. The anisotropy of the solid-liquid surface tension and the classic Wulf procedure¹⁾ were used at larger scale to explain the quasi-equilibrium shapes of monocrystals. It is however only in the last two decades that the non-linear equations of growth have been successfully handled to allow quantitative studies of the growth forms and their dynamics. First analytically²⁾ and then numerically, the formation of dendrites, the cells instability or other remarkable patterns³⁾ encountered in the solidification of solids have been approached more and more closely in the frame of the diffusion-limited theory. Today, the origin of the tip splitting or the nature of the dendritic growth is well understood. Various numerical methods (such as the powerful phase field simulations⁴⁾ . . .) are now available to simulate the rapid solidification of a crystal and to provide numerical solutions at large scale. These theoretical investigations have been constantly stimulated by meticulous experiments of the solidification of transparent crystals but also the growth of two-dimensional crystals formed by liquid crystals in thin cells.^{5),6)}

For soft materials, a first order phase transition from an isotropic phase to a mesophase also frequently yields complex morphologies. The growth patterns are however much more diversified and a rapid growth after a temperature quench does not necessarily yield classic dendritic patterns. From the early descriptions of smectic nuclei shape in the pioneering paper of Friedel⁷⁾ to more recent works on helical ribbon textures⁸⁾ observed in bent-core liquid crystals,⁹⁾ many studies have focused on the complex resulting shapes (a few examples are given in Fig. 1 for illustration). Some features are obviously related to the microscopic structure of the materials, like the chirality of forms in chiral liquid crystal phases. Complex patterns formed by simple materials such as the lyotropic lamellar phases or the thermotropic smectic *A*

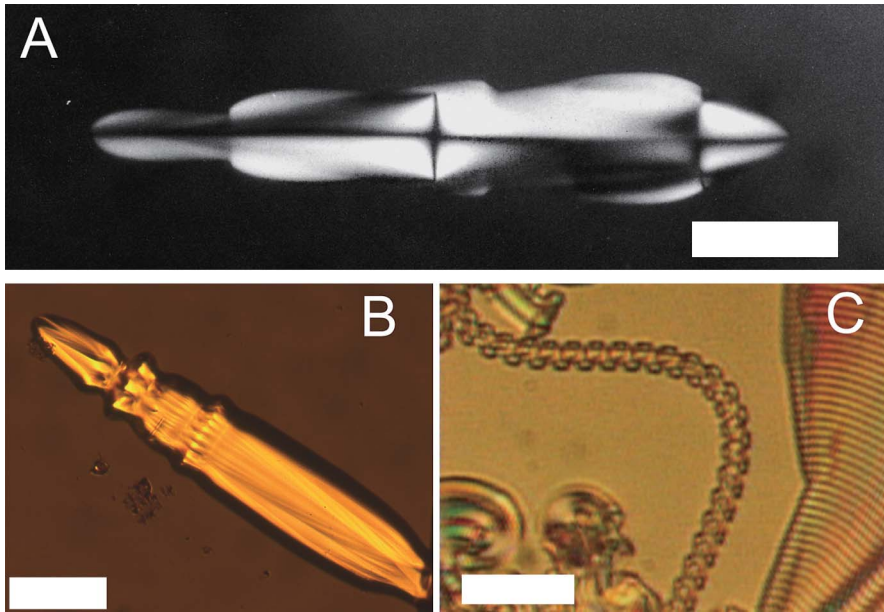


Fig. 1. Examples of growth patterns observed during the growth of (A) a lyotropic lamellar phase in a sponge phase,¹⁰⁾ (B) a thermotropic SmA phase in its isotropic phase,^{7),11)} and (C) a B7 mesophase⁸⁾ in the isotropic phase of a bent-core liquid crystal. Bar = 50 μm . Photomicrographs (A) and (B) are taken between crossed polarizers.

liquid crystals are however very puzzling. Up to now, these shapes have mostly been approached by the minimization of free energy with only a few dynamical ingredients. We will focus from now on the simplest lamellar materials and explore the influence of the dynamics on the formation of the growth patterns. After a short review (§2), we will consider the influence of the “softness” on the regular formation of dendritic patterns (§3) but also the peculiar role of the dynamics in the vicinity of the growth interface (§4).

§2. Anisotropy of surface tension and role of elasticity: a brief review

We consider the nucleation of a Smectic A (Sm- A)¹²⁾ phase in the isotropic phase of pure thermotropic liquid crystals but also the growth of surfactant-based L_α ¹³⁾ lamellar phases in the isotropic phase in the two-phase regions of amphiphilic systems. When appearing rapidly the nuclei of the lamellar phase commonly display two types of figures, either onion-like structures (spherical droplets with a single hedgehog defect) mixed with filaments^{15)–17)} or the classic batonnets (with a rod shape), which are anisotropic droplets with a complex texture made of assemblies of focal conic domains.^{7),11),18)}

The preferential formation of either onions and filaments or batonnets has been explained¹¹⁾ by the angular dependance of the interfacial tension between the isotropic

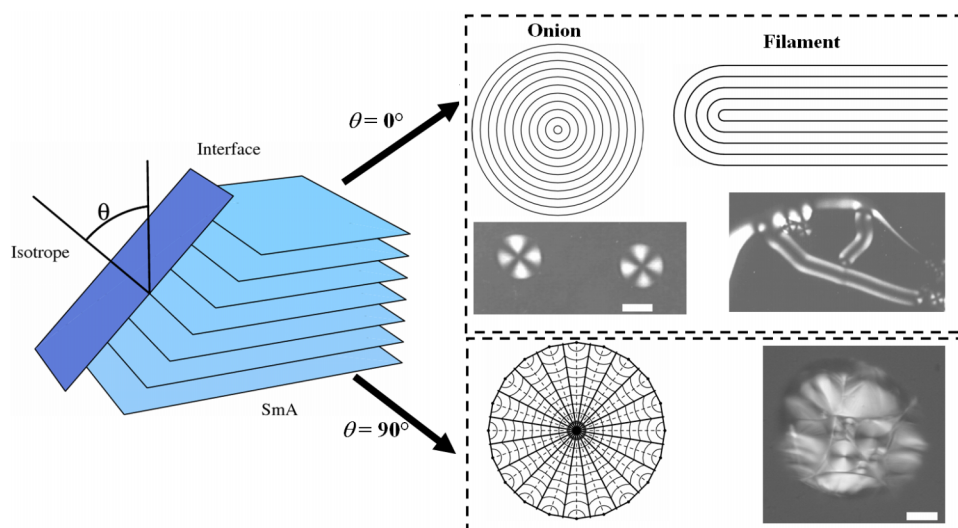


Fig. 2. Role of the anisotropy of surface tension in the texture of smectic phase droplet. Above: Simple geometries like spheres or filaments are compatible with a tangential orientation of the layers. Below: When the interfacial energy is minimal for a perpendicular anchoring macroscopic defects appear to relax the interface while keeping a spherical shape.^{7),11),18)}

phase and the lamellar phase. We introduce $\gamma(\theta)$, the value of the interfacial tension as a function of the angle θ between the normal of the nucleus interface and the normal of the layers (see Fig. 2). Due to the symmetry of the phases, this function possesses at least two extrema, at $\theta = 0^\circ$ and at $\theta = 90^\circ$. In the simplest cases, the layers orientation of lowest energy is either tangential ($\theta = 0^\circ$) or perpendicular ($\theta = 90^\circ$) to the interface. In a few systems, due to the microscopic structure of the isotropic phase the preferred orientation corresponds to an intermediate angle. This phenomenon has been observed when the isotropic phase has a well defined structure at mesoscopic scale. For example, the L_3 sponge phase¹³⁾ is a phase of disordered membranes which strongly orients the coexisting lamellar phase at an intermediate angle θ_e in the range $40^\circ - 70^\circ$.^{10),18)} Depending on the surfactant, the preferred $L_3 - L_\alpha$ contact angle is either $\theta = 0^\circ$ or $\theta = \theta_e$ with even some transitions observed in several systems.^{19),20)}

A quasi-static analysis would consist in minimizing the total free energy of a drop at constant volume to find its equilibrium shape and texture. The minimization problem is tricky and no general solution has been proposed in spite of significant advances in the treatment.²¹⁾ A dimension analysis however shows that the elastic energy¹²⁾ varies as KR where K is the bulk curvature modulus of the lamellar phase and R the typical droplet size whereas the interface energy changes as γR^2 . The asymptotic solution for $R \ll K/\gamma$ is therefore the same than for a rigid crystal. The layers are flat and the shape is given by the Wulff construction, which minimizes the interface energy. For large sizes ($R \gg K/\gamma$), the equilibrium droplet adopts a spherical shape whereas the layers deform so the preferred contact angle is satisfied all over the surface. For $\theta = 0^\circ$, the solution is obviously a spherical droplet with

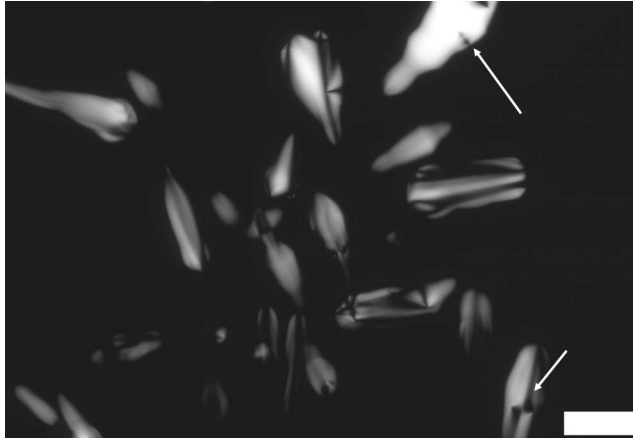


Fig. 3. Polarizing optical micrograph of droplets of various shapes and textures obtained by nucleating a L_α phase from the L_3 phase (the system is described in §3. The presence of embedded focal conic domains (arrows) and the variety of shapes and textures are typical features of batonnets observed in both lyotropic and thermotropic liquid crystals. Bar = 50 μm .

the onion texture (see Fig. 2). In Sm-A materials, the critical radius is usually sub-micrometric, which prevents any observations of the regime $R \ll K/\gamma$. For lyotropic systems, the transition between flat layers and the onion texture has been recently observed by the group of Tanaka.²²⁾ For large preferred contact angles, geometric considerations¹⁸⁾ show that the surface energy on a concave surface (like the inner surface of a sphere) is minimized only by the presence of numerous defects. The transition between flat and deformed textures has not been quantitatively analyzed in batonnets but a very similar phenomenon has been quantitatively studied in thin L_α slabs aligned on a solid surface and growing in the L_3 phase.^{23),24)}

The previous analysis explains the nuclei tendency to adopt simple textures when the contact angle is tangential or to form numerous defects at large contact angle. It however does not explain several striking features of batonnets, such as the presence of isolated focal conic domains embedded far from the interface or the variety of shapes and textures simultaneously observed (see Fig. 3). I will now show that studying the dynamical aspects is essential to understand these features. The simultaneous presence of onions and filaments in other systems and the origin of their formation will also be explained in the last section by an out-of-equilibrium approach.

§3. The growth of batonnets

Lamellar phases behave as two-dimensional crystals in thin cells with suitable anchoring layers. Several systems have thus been studied in depth either in directional solidification (see for example Refs. 5) and 25)) or in free growth experiments.^{6),26)} Measurements on the various observed instabilities have all been explained in the frame of the diffusion-limited solidification theory, for which the equilibrium shape of a crystal is observed at small undercoolings but is easily imbalanced by the diffusion

of heat or matter coming from the moving interface. This Mullins-Sekerka instability mainly yields stationary structures like dendrites growing at constant tip velocity.

For three dimensions lamellar nuclei, the relative importance of the classic growth mechanisms and the relaxation mechanisms discussed in the previous section has not been fully clarified. We have therefore closely studied the formation of batonnets during the $L_3 - L_\alpha$ phase transition of a lyotropic system. This latter phase transition is preferable to the Sm-A-Isotropic one because of a larger critical size K/γ in lyotropic systems, and, above all, because a preferred contact angle $\theta_e < 90^\circ$ on a concave surface can be satisfied by defects of finite size.¹⁸⁾

3.1. Experimental part

The quasi-ternary lyotropic system is obtained by mixing Hexadecyl pyridinium chloride (CPCl), brine (NaCl at 0.2 M) and hexanol. At room temperature a concentrated sponge phase (brine volume fraction about 0.7) is obtained in a narrow region of the phase diagram²⁷⁾ for a weight ratio between hexanol and CPCl of $h/c \approx 1.12$. Thin glass capillaries (thickness 100 μm) are filled by capillarity and then flame sealed to avoid chemical composition variations. The sample is observed under polarizing microscope in a temperature controlled hot-stage (Instec) cooled by a nitrogen circulation which ensures a temperature regulation about 0.1 $^\circ\text{C}$. The system allows a rapid temperature stabilization of the sample when the temperature is changed. The nucleation and the growth of L_α phase are obtained by a temperature quench from the two-phase region temperature boundary T_3 to a fixed targeted temperature T (the temperature step $T - T_3$ is noted ΔT below). The phase diagram shown in Fig. 4 is only weakly sensitive to the dilution. It therefore gives the chemical composition of the nucleating lamellar phase at the chosen temperature T . Images of the growth are recorded with a 60 fps firewire CCD camera and later analyzed.

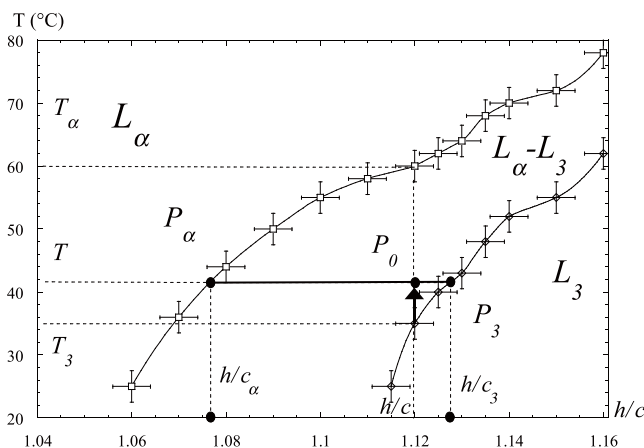


Fig. 4. Temperature phase diagram of the CPCl/brine/hexanol system as a function of h/c for a brine volume fraction of 0.7. When heated above T_3 , a sponge phase of composition P_0 demixes in a sponge phase of composition P_3 and L_α nuclei of composition P_α .

3.2. Results and discussion

For a ΔT -step of a few degrees only, batonnets grow in the sponge phase while they simultaneously reorganize with very complicated dynamics. Droplets of very different shapes and textures are then observed as shown in Fig. 3. Increasing the ΔT -step (which corresponds to larger “undercoolings” for a classic solidification) partly separates growth processes and reorganization. Figure 5 describes the growth dynamics of a batonnet after a single $+5^\circ\text{C}$ ΔT -step.

The distance covered by the tip as a function of time clearly shows bursts of stationary motions followed by slower periods of growth. A detailed analysis of these phenomena will be published elsewhere but this figure gives the qualitative features of dynamics for a large ΔT step. The change in the dynamics corresponds to morphological changes of the tip. As shown in the micrographs of Fig. 5 and in Fig. 6(A), the tip in the rapid growth texture is characterized by flat layers perpendicular to its direction of growth shown by an uniform illumination and complete extinctions between crossed polarizers. The stationary growth stops when the batonnet starts to reorganize. Several types of reorganization have been obtained from the birefringence figures. One of the simplest is given Fig. 6(B). It can be roughly described as the addition of a toroidal focal conic domain at the tip and the tilt of the layers in the cylindrical part.

The two factors that control the phase transition are the temperature and the chemical composition (hexanol and CPCI) in membranes. When entering in the

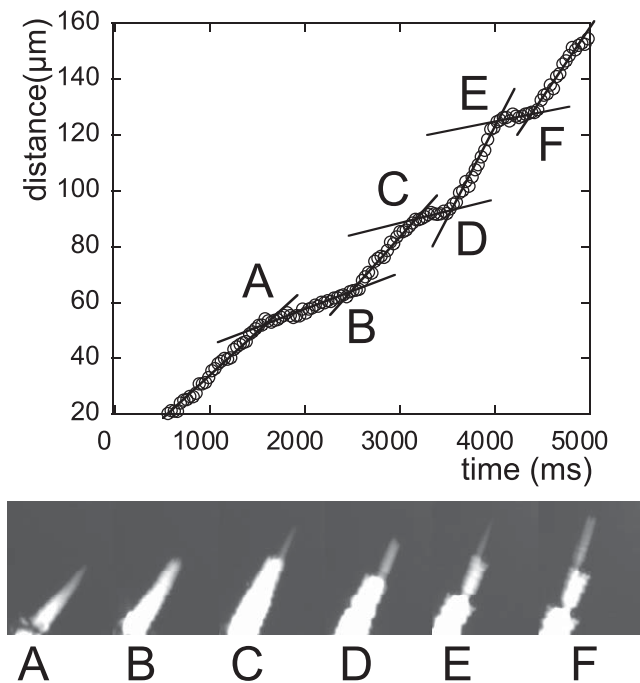


Fig. 5. Above: Distance covered by the tip of a batonnet with time after a temperature quench of 5°C . Straight lines have been added for the convenience of the reader. Below: Photographs of the tip are shown when dynamics changes occur.

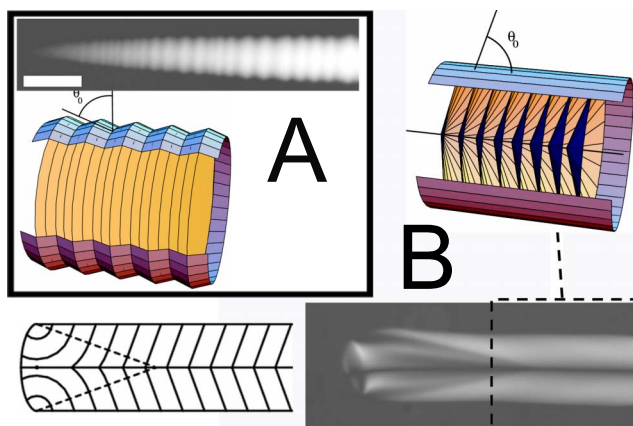


Fig. 6. (A) Micrograph of the tip obtained during a rapid growth sequence and its schematic structure. (B) Example of tip after a single rearrangement of the layers and the corresponding textures.

two-phase region, the lamellar phase therefore nucleates with a membrane chemical composition different from the one of the surrounding sponge phase (see Fig. 4). Gradients of hexanol and CPCl necessarily appear due to the flux through the growing front. We therefore checked if the rapid growth mechanism could be explained in the frame of the diffusion-limited solidification. By incorporating only the anisotropy of surface tension experimentally determined in Ref. 14), phase field simulations (collaboration with T. Börzsönyi, to be published) of the growth of a rigid lamellar phase in an isotropic phase reproduce the growth patterns of Fig. 6(A). Now the evolution of the temporal behavior can be rather simply explained. In solidification, the velocity of the dendrite depends strongly on the undercooling. When increasing the temperature quench, the velocity of the tip increases strongly. As in the recent experiments described in Ref. 22), above a certain size, the flat layers tend to deform to decrease the overall surface energy. This deformation is however plastic and its propagation does not depend on the ΔT -step but rather on the viscoelastic properties of the L_α phase and on the L_3 viscosity. The free growth sequences therefore increases with increasing ΔT steps, yielding a more and more crystalline shape to the L_α droplets.

Such an analysis is partly specific to the CPCl/brine/hexanol, but similar mechanisms yield a close scenario when the tangential contact is a local maximum for the surface tension. Diffusion-limited dendrites extend rapidly in this direction, which favors the appearing of plastic relaxation mechanisms, which in turn changes the dynamics. The coupling yields intermittent dynamics and the formation and inclusion of macroscopic defects in the bulk.

§4. Role of the dynamics in the formation of filaments

Patterns related to classic solidification instabilities are not observed (even transiently) when the preferred contact angle is $\theta = 0^\circ$. The formation of filaments and

the dynamics of their shapes have been described elsewhere.¹⁵⁾ Here I will not discuss the growth dynamics and the interesting related problems (like the buckling¹⁷⁾ phenomena) but rather the driving force and the origin of the morphological differences with batonnets.

First it should be noted that from the “crystalline” point of view an interface with a preferred contact angle $\theta = 0^\circ$ is likely to correspond to a facet for a lamellar material. The interface of an onion is therefore not rough and the Mullins-Sekerka instability²⁾ (responsible for the dendritic instability) is certainly much less relevant here than the kinetic attachment. Below the roughening transition, crystalline facets indeed grow very slowly because they require the nucleation of terraces or islands and their dynamics are usually very different from the one of rough interfaces. This behavior has already been clearly evidenced in lamellar materials in directional-solidification²⁵⁾ or free growth experiments.²⁶⁾ This general property of facets could explain the dynamical origin of filaments. An onion is an unusual crystal which exhibits a single curved facet. When a large undercooling is applied, the lamellar phase growth is hindered in the direction normal to the facets (layers) that is all over the onion surface. The presence of only a few defects like screw dislocations could allow the supply of matter from the isotropic phase (due to a large favorable free enthalpy difference). The external layers will therefore tend to increase their area under this lateral “pressure”. The increase of area of only the external layers combined with the plasticity of the bulk could be the main driving force responsible of the formation of filaments. This scenario has to be checked carefully in further works but experiments made in liquid crystals emulsions and described below suggest that the above ingredients are sufficient to yield the formation of filaments.

We have recently shown²⁸⁾ that the forced adsorption of amphitropic surfactants at a water-nematic interface yields the formation of nematic filaments, never been observed before. The liquid crystal was 4'-pentyl-4-cyanobiphenyl (5CB) which does not show a Sm-A phase. We have performed similar experiments with 4'-octyl-4-

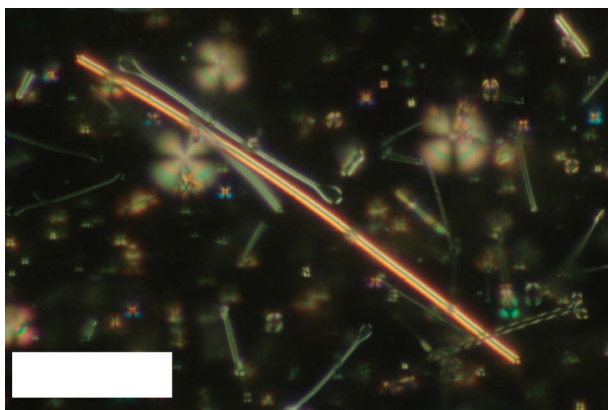


Fig. 7. Polarization optical micrograph of a 8CB/water emulsion after contact with a metastable CTAB solution. Smectic filaments form when CTAB molecules adsorb rapidly at the 8CB/water interface. Bar = 50 μm .

cyanobiphenyl (8CB) which is smectic at room temperature. We prepared smectic emulsions in water by mixing 1% wt. of 8CB in deionized water with 0.001% wt. of hexadecyl-trimethyl ammonium bromide (CTAB) at 22 °C. The latter component is a cationic surfactant soluble in water as micelles at low concentration and above the Krafft point (25 °C). Below this temperature, a concentrated solution of CTAB re-crystallizes. After mixing, 8CB droplets are stabilized in water as spherical onions because surfactants usually provide an strong homeotropic anchoring. A solution of 1%wt. of CTAB in water is then prepared at 40 °C. When mixed with the emulsion at 22 °C (either by contact experiments under microscope or in a test tube with a gentle mixing action) some spherical droplets rapidly extend and form smectic filaments as shown in Fig. 7. We have checked that this transformation is made at constant inner volume (experimental procedure is given in Ref. 28)). Since the smectic phase does not change (no exchange of matter in water and fixed temperature), this shows that surface effects — the spreading of surfactants — are sufficient to yield the formation of smectic filaments in emulsions. During the isotropic-to-smectic phase transition, the liquid crystal molecules which incorporate the external layer might play the same role as CTAB molecules do in emulsions.

§5. Conclusion

This short paper was intended to show that if the growth of crystals is a rapidly maturing subject and if many problems are now quantitatively approached in solidification, the growth patterns observed in soft materials (especially in mesophases) still raise difficult questions about the mechanisms in play. Softness, plasticity, elasticity, defects and topological questions all seem to combine to give complex shapes and textures as shown by the works dedicated to one of the most simplest case, the growth of a lamellar phase in an isotropic phase. Fundamental properties of solidification and crystalline growth, such as the non-linear dendritic growth of crystals or the properties of facets, are however valuable tools to understand the different stages occurring during the formation of a mesophase.

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