Labyrinthine instability in polar free-standing liquid crystalline films

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We report the first study of fingering and labyrinthine instabilities in freely suspended polar liquid-crystalline films. This phenomenon is in a way the electric analogy to the labyrinthine instability in thin films of magnetic fluids. Because of the existence of a permanent polarization in the smectic films, an external electric field is not required for the spontaneous formation of the instability. It forms upon temperature controlled transitions between mesophases with different polarizations in the films. External electric fields of several kV/m applied in the film plane can reversibly influence the formation of the finger textures. In case of our materials, we assume, that the labyrinthine pattern is intrinsically related to regular splay deformations of the local polarization field, coupled to the local director.

I. Introduction

Intricately patterned labyrinthine and fingering instabilities appear to be a rather general phenomenon in complex fluids, they have been observed in various physical and chemical systems such as reaction-diffusion systems [1], amphiphilic monolayers [2], and ferrofluids [3]. We report the discovery of a labyrinthine instability in thin freely suspended ferroelectric smectic films. It is reminiscent to the labyrinthine instability in suspensions of ferromagnetic particles (ferrofluids). In case of ferrofluids, emergence of the spatiotemporal order is substantially influenced by interactions of magnetized particles, suspended in a liquid, with the external magnetic field. The feedback, produced by the coupling between the local magnetization with the magnetic field influenced by the volume and the geometry of the fluid domain, expresses non-locality of the interactions in the system [4] and leads to a number of ferrohydrodynamic instabilities. A thin layer of ferrofluid (Figure 1a), confined together with an immiscible diamagnetic liquid between two glass plates, becomes perturbed when a magnetic field is applied perpendicular to the interface boundary separating the two liquids. These perturbations develop into fingers in order to reduce the magnetic energy of the system.

It is noteworthy to mention that ferrofluid suspensions are superparamagnetics and, in contrast to ferromagnets, cannot be spontaneously polarized (magnetized). Is it possible to have a system what would combine the properties of flowing liquids and solid ferromagnets or ferroelectrics? It turns out that such an example is liquid crystals [6], which combine the viscous properties of fluids with elasticity of solids. In a liquid crystalline phase (mesophase), the average orientation direction of the molecules can be described by a director **n** (see Figure 1b). In case of nematics only the orientational symmetry is broken. In smectic phases, additionally, the molecules are packed into fluid layers. Spontaneous polarization in smectics can appear either as a result of the symmetry breaking introduced by the tilt of the molecules (in the layers) together with their chirality (smectic-C*) [6], or by sterical hindrance caused by the strong anisotropy of the molecular shape (bent-core mesogens in smectic-CP phase, refs. [7-9]) (see Figure 1b). The fingering patterns have been observed so far only in chiral nematics (cholesteric) which cannot be polar due to the head-to-tail invariance of the director. The origin of the cholesteric fingers lies in the topological constraints induced by the boundaries and the helical structure of the cholesteric phase (the details are given in refs. [10, 11]).

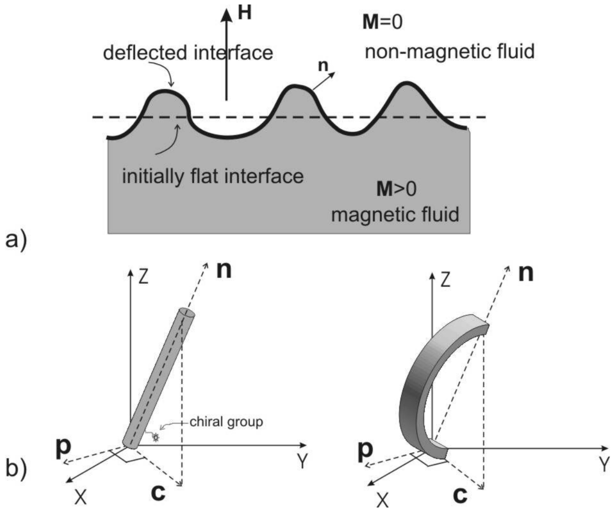

Figure 1. (a) Instability of the interface between a magnetic fluid confined together with an immiscible non-magnetic fluid, the external magnetic field H is perpendicular to the undisturbed interface; (b) definition of the directors in the smectic-C* (left) and in the smectic-CP phase (right); c-director is the direction of the molecular tilt, the p-director shows the direction of the local spontaneous polarization.

Recently, we have observed a new type of fingering and labyrinthine instability in smectic liquid crystals. This instability takes place in polar free-standing smectic films formed by bent-shaped molecules. The smectic layer structure restricts the geometry of the director: only rotation of the director **n** on a cone around the layer normal is allowed. Therefore, the instability mechanism in our case is entirely different from the one in cholesteric phases but is, in many respects, reminiscent of the patterns in magnetic fluids.

II. Experimental Results

We study the behavior of the fluorinated bent-core liquid crystalline compound already described in our previous publication [12]. This material exhibits polar tilted smectic phases in the sequence:

iso 161°C smectic-X 143°C smectic-CP 96°C cr

The structure of the smectic-X phase is not fully understood. Our previous studies showed that this phase is very similar to the smectic-CP phase. The difference between those phases probably lies in the character of the in-plane order and/or polarization [12, 13].

In our experiments, free-standing films with thickness in the range of 100-1000 nm have been mechanically pulled over a custom-made glass frame (Figure 2), which was mounted into a heating stage (Linkam TMS 600). The temperature was controlled with the accuracy ±0.2 K. Electrodes attached to the support allowed us to apply an electric field either parallel to the film surface or perpendicular to it. We observed the films with a polarizing microscope (Carl-Zeiss Axioscope 40 Pol) in reflection mode. Under crossed polarizers the films appear almost black (the optical axis is probably close to the film normal), particularly in the smectic-X phase. To overcome this obstacle, we used an image-enhancing technique. Additionally, slightly decrossing the polarizers we considerably improved the contrast of the picture. Besides, a two-fold extinction degeneracy, achieved with decrossed polarizers, enabled us to determine the director field unambiguously.

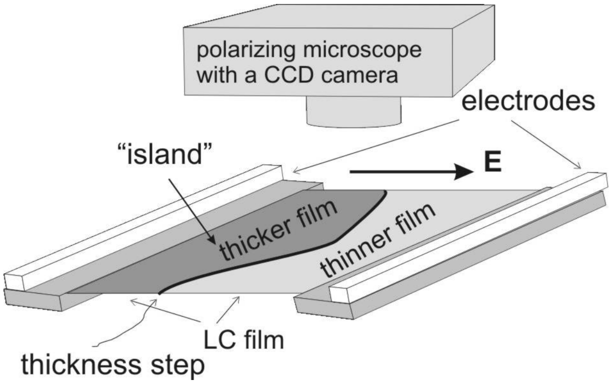

Figure 2. Experimental setup

Straightforward attempts to pull the films directly in the smectic-X phase have failed. The films got torn and instead, bundles of fibrils (filaments) appeared [13]. However, at sufficiently low temperatures in the smectic-CP phase, thin stable films can be drawn. In the reflection microscope, a free-standing smectic-CP film looks like a brightly colored mosaic. The intense interference colors appear when the film thickness is in the range of several hundred nanometers. Since the thickness is not homogeneous, different uniform domains of the film appear in different colors. The typical size of the domains is 100-300 μm. The thickness of the domains can be estimated by evaluating the apparent reflection color at incident white light [14] as well as by direct measurements of the reflected light spectrum. Close to the transition into the smectic-X phase, the domains of different film thickness ("islands") rearrange. Some islands become larger while the others shrink and disappear. Single steps coalesce to multi-layer steps, the number of thickness steps decreases.

When the temperature reaches the transition point, the straight boundaries of the islands, representing thickness steps, become perturbed (Figure 3). Further elevation of temperature initiates the growth of the distortions into fingers. It is remarkable that the equilibrium finger structures are static: suspending heating, the fingers stop growing. The structure formation is reversible: on cooling, the fingers retract and the pattern disappears. To elucidate the molecular ordering within the fingers, we have employed polarizing microscopy, which helps to visualize the direction of the molecular tilt, i.e. c-director (see also Figure 1b).

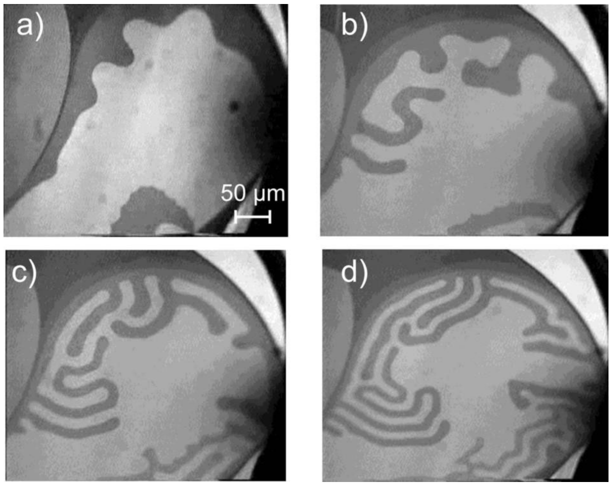

Figure 3. Onset of the instability and development of a labyrinthine pattern (a)-(d) in absence of external electric fields at a constant heating rate 1 K/min, the time between subsequent images is 40 s

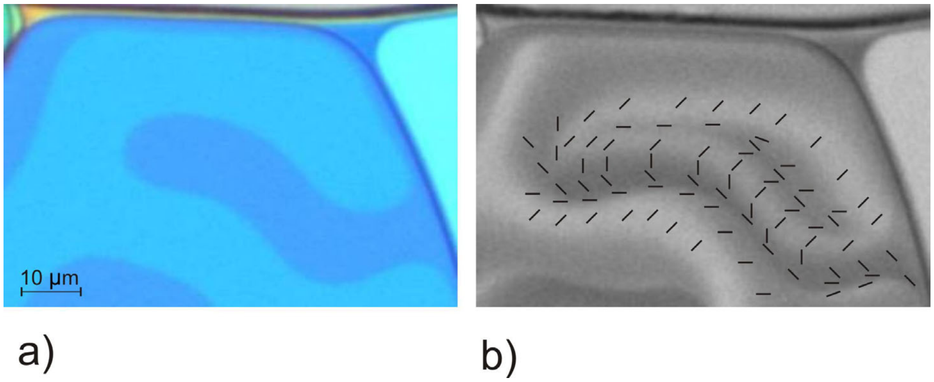

Figure 4. The c-director field within the finger between slightly decrossed polarizers (a), and the same image without the polarizers (b) (smectic-X phase, 147°C). The p-director is at right angle to the c-director (i.e. perpendicular to the boundary)

In the smectic-CP phase, one can observe typical schlieren textures characteristic for smectic-C-like phase. In the high-temperature phase the schlieren texture remains at least at lower temperature when the fingering starts. We assume that on the free boundary of the layer step the c-director is oriented parallel to the edge (Figure 3). During the instability onset, when the boundary becomes perturbed, the director field starts bending, following the interface curvature. The deformation of the director field continues when the fingers are already formed. As the fingers grow, they become narrower and, ultimately, they cover, separated by regular spacings, the whole area of the respective thinner film region, developing a space-filling labyrinth.

Not only do the labyrinths grow spontaneously, but they also can be manipulated by the external electric field applied across the film. The experiments with electric fields are particularly difficult since high DC voltages induce electroconvection in the film plane, that advects and distorts the islands. As it is shown in Figure 5, the finger growth can be driven by a moderate external DC electric field applied parallel to the film surface. Interestingly, a field oriented perpendicular to the interface boundary can either destabilize the boundary and promote fingering, or make the fingers shrink, depending on the polarity. We will call the electric field "destabilizing" if this field promotes fingering. The field of opposite polarity we will call "stabilizing". Under the "destabilizing" field, the fingers grow in the field direction, become narrower and bifurcate. A field of the reversed polarity, on the contrary, initiates shrinkage of the fingers, both under isothermal conditions. This shrinkage is accompanied with a broadening of the fingers and their merging (Figure 5b). When the fingers disappear, the boundary of the islands straightens, which means that the electric field of this polarity has a stabilizing effect.

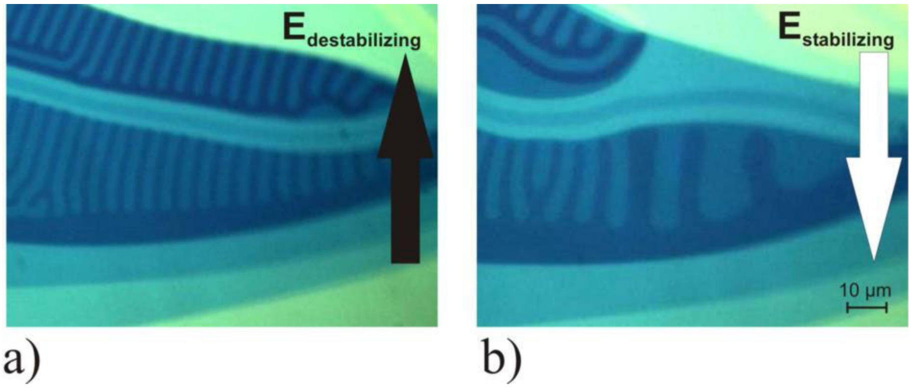

Figure 5. The electric field perpendicular to the boundary favors finger growth (a); the electric field of the opposite polarity makes the fingers shrink and disappear (b) (smectic-X phase, 146°C)

The stabilizing/destabilizing effect of the electric field is also reflected in its influence on the critical temperature of the instability onset. For a given boundary of the "islands" positioned perpendicular to the electric field direction, the critical temperature of the instability onset depends on the magnitude and polarity of the field. The onset temperature becomes smaller, when the polarity of the field corresponds to the destabilizing behavior and the onset temperature grows for the field of the opposite polarity (i.e. "stabilizing", see Figure 6a).

III. Discussion

Summarizing the results of experimental observations, we emphasize the following features of the smectic fingers: (a) the fingers are composed of surplus layers on the film, (b) they start growing spontaneously in the smectic-X phase, however, represent static structures, (c) within the finger the molecular order remains liquid-like, the director field is deformed, (d) during the onset, the boundary of the film islands and the growing fingers respond to the external electric field depending on its polarity, (e) the electric field does not reverse the c-director orientation in the fingers, (f) an out-of-plane component of the spontaneous polarization does not contribute into the instability mechanism.

As the experiments have shown, the labyrinthine growth in case of the smectic-X phase is very different from the fingering in cholesteric phases since the geometrical constrains induced by the presence of smectic layers allow the director **n** rotating only on the cone around the layer normal.

The behavior of the director field in the labyrinths is reminiscent to the case of the twist-bent instability. Such instability has already been observed by Pang et al [15] in achiral homogeneous free-standing smectic-C films which showed similar patterns in polarized light. This instability, interpreted as a chiral-symmetry-breaking transition, has been suggested to occur due to the polar ordered layers originating as a result of the strong difference of the opposing perfluoro and perhydro alkyl fragments of the molecules. However, in case of our compounds, the labyrinthine pattern is formed by the island boundaries of the non-homogeneous (in thickness) films and, therefore, can be observed without polarizers. Additionally, in contrast to the observation in ref [15], our compound is symmetric and the instability develops with increasing temperature. Therefore, in case of this material, we deal with a totally new type of instability in liquid crystal films.

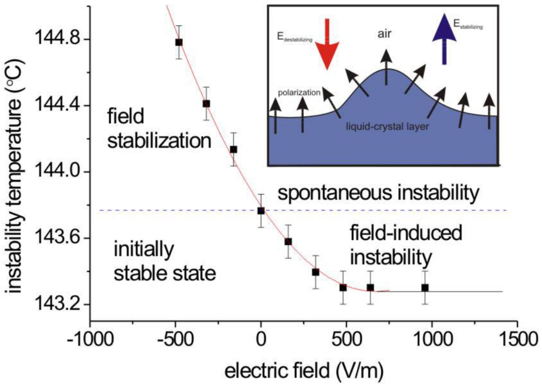

Figure 6. (a) Stabilizing and destabilizing effects of the external electric field on the onset temperature (points denote the onset of fingering, the curve guides the eye); (b) fingering in a homogeneously polarized film. The p-director (direction of the polarization) is perpendicular to the boundary. Application of external electric field antiparallel to the p-director favors its splay.

Since the external electric field significantly affects the instability onset, it seems, that an important role is played by the spontaneous polarization of the smectic layers. This type of materials represent ferroelectrics: each layer possesses spontaneous macroscopic polarization. Therefore, the dependence of the dielectric displacement **D** on the electric field **E** should include the term $\mathbf{D}_r$ - the residual displacement: $\mathbf{D} = \varepsilon_0 \varepsilon \mathbf{E} + \mathbf{D}_r$. The residual displacement is equal to the spontaneous polarization. Additionally, the direction of the spontaneous polarization is coupled with the direction of the molecular tilt, given by the c-director (see Figure 1). This connection couples the dielectric properties of the film with its elasticity determined by the director configuration. The third contribution to the free energy is given by the island boundary. This term favors the shortest boundary, additionally, due to the ancoring of the c-director on the boundary, this term creates a feedback of the surface profile on the director field and further on the electric field in the film. On one hand, the most preferable configuration for the elastic energy is a homogeneously oriented c-director (and, consequently, p-director) (see, for instance, [6]). On the other hand, this configuration costs electrostatic energy, since all dipoles of the molecules will be parallel. The interplay between the electrostatic, elastic and surface energy may result in destabilization of the homogeneous director field. The order of the magnitude of the electrostatic energy can be roughly estimated knowing the magnitude of the spontaneous polarization.

The electrostatic energy per molecule is in the order of $(1/4\pi\varepsilon_0)P^2 v \approx 10^{-24} - 10^{-18}$ J per molecule, where P is the spontaneous polarization in the range from 1 nC/cm² to 1 µC/cm², $v \approx 10^{-3}$ Å^3 is an effective volume occupied by the molecule. Since the energy is proportional to the square of the polarization P, a change from 1 nC/cm² to 1 µC/cm² corresponds to six orders of magnitude of energy. The elastic energy is of the order of $\sim 10^{-20}$ J per molecule [16], which can easily be overcome in case of the bent-core compounds, where the spontaneous polarization reaches µC/cm². Therefore, it seems plausible that, the instability can result from the interplay between the elastic and electrostatic interactions in a free-standing film if the formation of an antiferroelectric arrangement of the layers is, for some reason, prohibited. By this oversimplified approach, one can also explain the effect of the external electric field. Assuming that the p-director is perpendicular to the boundary (Figure 6), the external electric field along the direction of the spontaneous polarization will decrease the electrostatic energy and stabilize undisturbed boundary. On the other hand, the field of the opposite polarity would increase the electric energy, thus, destabilizing the director field.

Remarkably, labyrinthine instabilities have never been observed in a chiral smectic-C* phase. There can be several reasons for that. The spontaneous polarization in most of chiral smectics is much lower than in the polar "banana" phases. Additionally, the electrostatic interactions between adjacent layers tend to cancel the macroscopic polarization inducing a helical order. The attempts to synthesize the materials (smectic-C*) with even higher spontaneous polarization, eventually led to the discovery of antiferroelectric smectic-C$_a^*$ phases, where the pitch of the helix was reduced to the value of the layer spacing. Most of "banana" smectic-CP phases are switchable antiferroelectric. In contrast, the smectic-X phase does not show electro-optical switching, and at the same time, it is polar. It may indicate that the internal structure of the mesophase hinders the rotation of the c-director, prohibiting polar switching. The behavior of the fingers in the electric field, depicted in Figure 5, shows that the in-plane polarization has the largest contribution into the instability. A speculated out-of-plane component of the spontaneous polarization is not affected in this geometry. Ultimately, such structure may produce multilayer fragments ("islands") of the film with very high spontaneous polarization.

Despite its superficially similar appearance, the instability in liquid crystalline films seems to be a great deal more complex phenomenon than the fingering instability in ferromagnetic suspensions. A detailed stability analysis has to be done to examine the possibility for formation of labyrinthine patterns in the frame of the abovementioned model.

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IV. References

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