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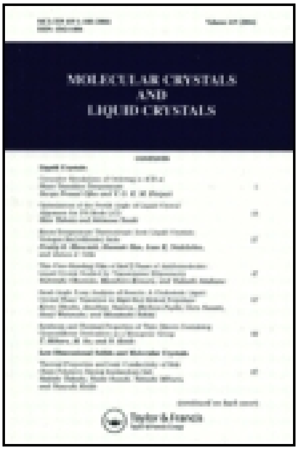

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Equilibrium Size and Textures of Islands in Free-Standing Smectic C* Films

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In free standing films of one smectic C^* material, Chisso 1015, we observe circular islands, of greater thickness than the background film. These islands, nucleated by smoke particles, grow to an equilibrium diameter that is a function of their thickness. We present data on island size, and a theory attributing the finite equilibrium size to a negative island edge energy arising from a spontaneous bend term in the elastic free energy for the islands. We also observe textural transformations within the islands, attributed to a difference between splay and bend elastic constants, combined with weak anchoring of the director at a point disclination at the center of an island.

Keywords: smectic C*; free standing films; islands; textures; equilibrium

INTRODUCTION

Free standing films of smectic liquid crystals tend to equilibrate to a uniform thickness. However, it is possible to create circular islands of a greater thickness, floating in the uniform background film. In films of the chiral ferroelectric smectic C* phase of a particular commercial mixture, Chisso 1015, we have observed some unusual aspects of the formation of these islands, and of the textures exhibited by the molecular tilt direction within the islands. First, once nucleated, the islands tend to grow to an equilibrium diameter, which is a function of their thickness. Second, within the islands, we see several different textures, depending on the size and previous history of the islands.

In the particular material studied, the free standing films appear to be smectic C* for all film thicknesses, at room temperature. We prepare thin films, of at most a few tens of nanometers in thickness, by drawing material over a 6mm hole in a thin metal foil. These films equilibrate to uniform thickness [1]. Islands are formed typically by blowing smoke over the film [2]; most of the smoke particles are sub-visible, but occasionally, one can see a particle in an island, and the thickness of the island appears to be proportional to the apparent particle size. Over the course of tens of minutes, the circular islands grow and reach an equilibrium diameter that then remains unchanged for hours to days. For most of the types of smoke we tried, the islands formed are normally within a small range of thicknesses, which is much less than a wavelength of visible light, as seen by a lack of birefringence or interference colors.

Using transmission polarized light microscopy, with crossed polarizers, we can study the texture of the molecular tilt direction within the islands. In general, we see a texture with a single point disclination near the center of the island, around which the molecular tilt direction rotates by 2π radians, consistent with the observation of a fixed boundary condition for the tilt direction at the outer boundary of the island. By adding a birefringent compensator to the microscope optics, we can determine that the boundary condition for the molecular tilt direction at the outer boundary of the islands is tangential. Moreover, by tilting the sample plane, relative to the microscope stage, we can observe an increase in brightness of the islands on one side, with a corresponding decrease in brightness on the opposite side of each island. This shows us that in all the islands, the molecular tilt direction is not only tangential at the outer boundary, but also uniformly counterclockwise, as seen from the top of the film.

ISLAND SIZE

The growth of islands to an equilibrium size is an unexpected phenomenon, in light of general arguments on the energetics of thin films. Normally, one thinks of some finite thickness surface layer

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of a phase as consisting of material of a higher free energy density than the material in the interior of the phase. General arguments concerning Van der Waals interactions support this argument, which is consistent with the usual concept of a positive surface tension, leading to compact phase shape. As applied to a thin film of a fixed area, that is in equilibrium with a reservoir of bulk material, as is the case for our films in contact with a meniscus of bulk material on the metal foil, this means that thinning the film by removal of smectic layers from its interior, transferring that material to the bulk phase, lowers the overall free energy of the system [1]. This argument applies when the film is thin enough so that even its innermost layers are somewhat higher in free energy density than the bulk phase. Since the growth of an island of greater thickness than the background film must raise the free energy by an amount proportional to the area of the island, such growth is initially unexpected [3].

To counter this effect, one must look for effects that lower the free energy of the island. The curvature elastic free energy for the molecular tilt direction is a possible source of such an effect. Denoting the molecular tilt direction by a unit vector in the plane of the film, the c-director $\hat{c}$, we can write the curvature elastic free energy density per unit area of the film as

$$f_{el} = K_s(\nabla \cdot \hat{c})^2 + K_b(\nabla \times \hat{c} - b_0)^2. \tag{1}$$

in which K_s and K_b are the splay and bend curvature elastic constants, and b_0 is a spontaneous bend, required by the chiral symmetry of the smectic C* phase [4]. For 2D vectors, the × operation produces a scalar. We now apply this expression to calculate the curvature elastic free energy of an island of a simple texture consistent with our observations. The c-director is everywhere tangential, between the outer boundary at radius R and a point disclination at the center of the island, of radius ϵ. The result is

$$F_{el,island} = 2\pi K_b[\ln(R/\epsilon) - 2b_0(R-\epsilon) + (R^2-\epsilon^2)b_0^2/2]. \tag{2}$$

The elastic free energy of the same volume of uncurved material in the bulk phase is $\pi R^2 K_b b_0^2$. To calculate the total free energy difference ΔF_{island} for forming the island, relative to both the bulk material and the area of background film that it replaces, one must add to the island free energy some edge energy for its outer boundary,

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$2\pi R\lambda$ where λ is a positive line tension arising from intermolecular forces, much like a positive surface tension. One must also add some core energy E_{core} for the point disclination, and a term proportional to the area of the island times a Van der Waals energy density difference ΔE, as argued above. Including in the core energy E_{core} those terms in ϵ, one arrives at

$$\Delta F_{island} = E_{core} + 2\pi K_b \ln(R) - 2\pi R(2K_b b_0 - \lambda) + \pi R^2 \Delta E. \quad (3)$$

If $(2K_b b_0 - \lambda)$ is positive and large enough, this expression is negative for a finite range of R with a minimum at the equilibrium radius $R = R_{eq}$. Moreover, for small R the free energy difference is positive, representing a nucleation barrier for the formation of islands.

This argument is consistent with our general observations. The smoke particles are necessary for heterogeneous nucleation of islands, which then grow to an equilibrium size. Each island contains a mean bend which is of the correct sign to lower the free energy relative to unbent bulk material, as evidenced by the tangential texture, with the c-director rotating counterclockwise in all islands. Of course, the model is simplified to make the main point, and there may be dependencies of parameters on film thickness, for instance. It also ignores electrostatic interactions which can surely play a role in island energetics of these ferroelectric materials.

The fundamental argument presented here for finite island size is a dangerous one, since it can lead to instability of the islands. The negative term in the free energy linear in $K_b b_0 \nabla \times \hat{c}$ is converted to a negative line energy at the outer boundary of the island by Stokes theorem. This is independent of the shape of the island, and of its internal texture, as long as the anchoring of the c-director at the outer boundary is strong, which it appears to be in our experiments. Evidently, this negative line energy is dominant over the positive one proportional to λ, making the net line tension for the edge of the island negative. Although this negative free energy, linear in island perimeter, is always overcome by the ΔE term proportional to area for circular islands, it could lead to development of noncircular islands if it were strong enough. The only term opposing this is the quadratic curvature free energy term, which is a weak one for slow curvatures. The lowest energy instability for a circular island, to increase its perimeter at constant area, is deformation into an elliptical shape. While keeping the core structure constant, this

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involves added splay and bend energy, which stabilize the circular shape for small enough R, but at large R the islands will become unstable to elliptical deformation. Depending on the relative values of parameters in this problem, there is a finite window of radii for stable circular islands. Our observations appear to lie within this window. We have not observed large elliptical islands.

Clearly, the most central prediction of this theory is the possibility of equilibrium island size in a chiral material, and no such phenomenon in the racemic version of the same compound. Unfortunately, we have observed this behavior in only one material, the Chisso 1015 mixture, for which a racemic version is not available.

The material parameters entering this model for equilibrium island size all depend on film thickness within the island, and to some extent on the thickness of the background film as well. K_s and K_b are in the simplest case proportional to a bulk curvature elastic constants, times the film thickness. The same argument may apply to the spontaneous curvature coefficient $K_b b_0$. However, the line tension λ is more likely proportional to the island thickness minus the background film thickness, since this represents the step height at the island boundary. The free energy difference ΔE is harder to model, but clearly depends on island thickness and on background film thickness as well. There are other terms in the free energy for island formation that depend on the texture of the c-director induced in the background film by the presence of the island, which might be thought of as a very large core $+2\pi$ disclination; it induces the formation of a companion -2π disclination in its vicinity. The energy of that accompanying texture is proportional to background film thickness. One can also replace the simple c-director model presented here with a nematic-like model of the smectic C* elasticity, with the nematic n-director tilted at some angle θ with respect to the layer normal. In that nematic-like model, one has both spontaneous twist and spontaneous bend, which produce terms like the b_0 term used here as well as the helix in the bulk smectic C* structure. Then, all the parameters of the model depend on the tilt angle θ, which depends on thickness of the island and of the background film.

Therefore, we have no definitive model of island size as a function of thickness. However, we can measure the dependence of equilibrium island diameter on island thickness, in a sample of constant background film thickness, measuring thickness by brightness of the

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island seen with crossed polarizers. A plot of brightness vs. island diameter is seen in Figure 1. We have not made a quantitative conversion of brightness to thickness, but the trend is clear, that thicker (brighter) islands are smaller in diameter.

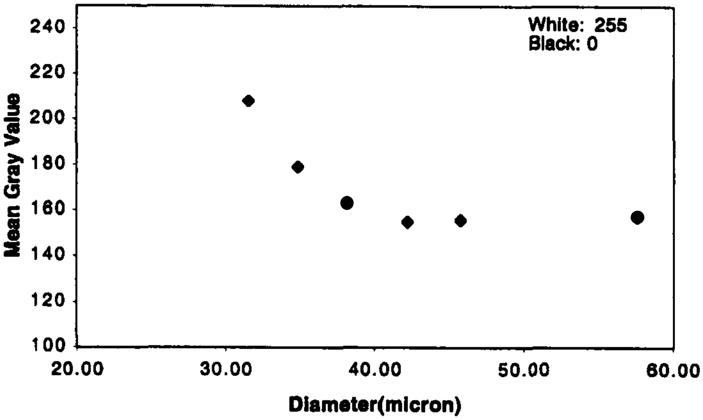

FIGURE 1. Brightness of islands *vs.* their diameter.

ISLAND TEXTURES

One of our motivations for studying these islands was to understand the c-director textures they display. Small islands tend to have the simple pure tangential texture. In most samples studied, above a certain critical island diameter, the texture switches to a reversing spiral, in which the tangential boundary conditions still apply at the outer boundary and the core, but in the intermediate area of the island, the director orientation switches to radial, replacing bend with splay deformation. This is driven by the splay elastic constant being less than the bend constant. Discussions of this textural transformation are presented elsewhere [5,6]. The critical island diameter depends on film and island thickness, and core size, but it is often in the range of tens of microns. However in some samples even very small islands have reversing spiral textures.

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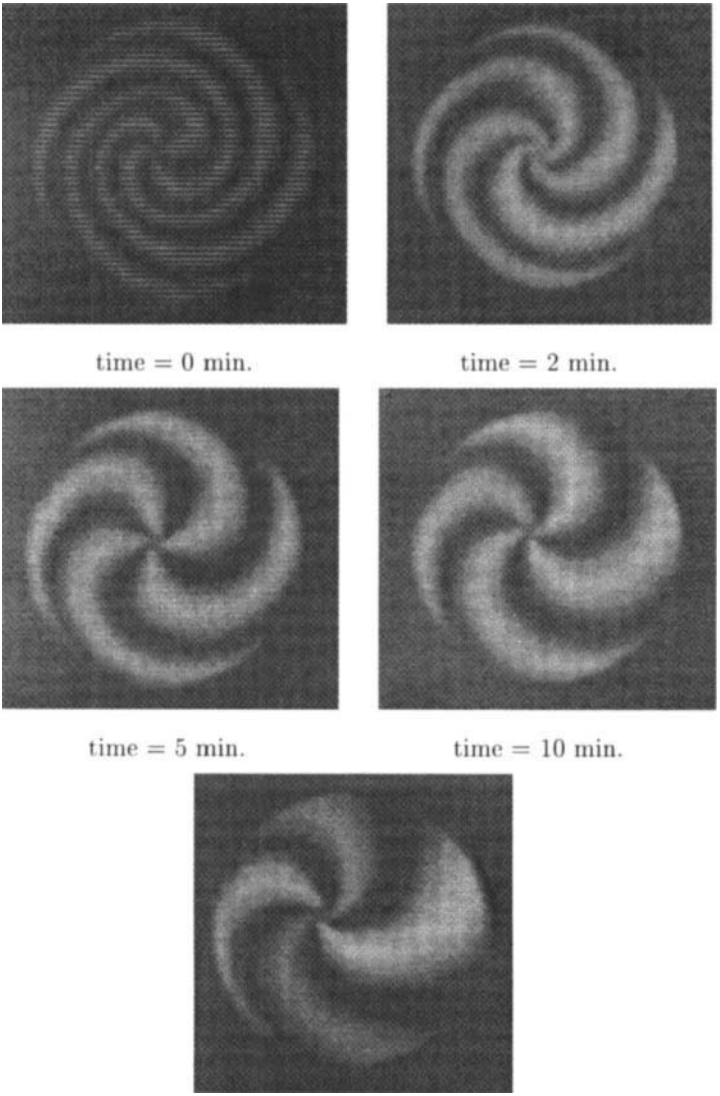

time = 0 min.

time = 2 min.

time = 5 min.

time = 10 min.

time = 20 min

FIGURE 2. Time evolution of a spiral after blowing.

We have tried to intervene actively to modify the island texture, to explore its stability. We have tried using magnetic grains as island nucleation particles, rather than smoke, with little success. We are trying electric fields and laser tweezers as well. However, so far the most interesting experiment has been blowing on the sample, most usefully by a small jet of gas, blown tangentially at the sample edge. The resulting rapid swirling often induces spiral formation within individual islands, as well as macroscopic spiraling of the texture in the background film. Figure 2 shows the results of one such experiment. Right after blowing, the spiral texture equilibrates to that shown as time = 0 with the c-director radial at the core, tangential at the outer boundary, and rotating by $3\pi/2$ from core to outer boundary. Then over the course of minutes, this texture relaxes by rotation of the director at the core, to a final state that has a radial director at the core, with a $\pi/2$ rotation to tangential at the outer boundary. We have seen even greater initial rotations between the core and the boundary, which always relax to the same final state.

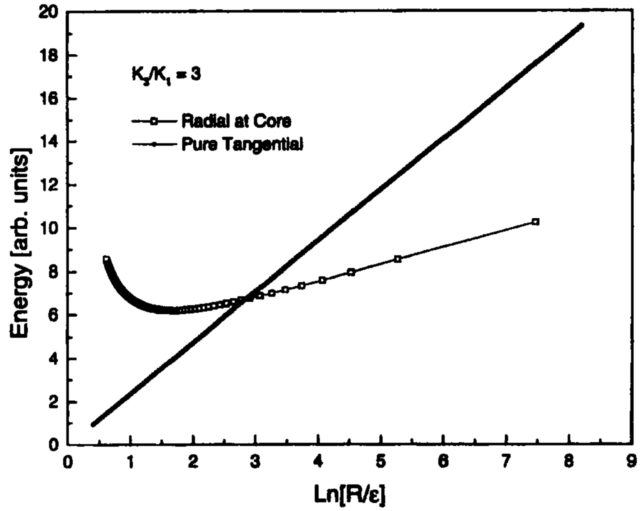

FIGURE 3. Elastic energies of the pure tangential and simple spiral textures, as a function of island radius.

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Before blowing, the islands were all in purely tangential textures, which they maintained while they grew to their equilibrium diameter. Thus, the change to a spiral texture by blowing demonstrates the existence of more than one stable or metastable texture for an island. The possibility of this situation was first pointed out by K. K. Loh, and observation of metastable reversing spirals has also been reported [6]. Switching from tangential to radial anchoring at the core replaces some bend texture with splay, lowering the elastic energy; however, the radial gradient of the c-director raises elastic energy. Therefore only in large islands does the switch to the spiral texture lower the total elastic energy. In Fig. 3, which compares the elastic energy of the simple spiral texture to that of the pure tangential texture, we can see that if K_s is less than K_b, there is a first order transition in the elastic energy at a critical radius, from pure tangential to a simple spiral with hybrid boundary conditions, as seen in Figure 2. To fully understand the relative textural stabilities, we need to include the unknown anchoring energy function at the core; clearly the anchoring is weak, and it may involve local minima for both tangential and radial orientations.

Acknowledgments
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[2] The origin of this method has been attributed to P. Pieranski, using cigarette smoke.
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