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# Nematic Bubbles in Freely Suspended Liquid Crystal Films

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# NEMATIC BUBBLES IN FREELY SUSPENDED LIQUID CRYSTAL FILMS

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Abstract Nematic bubbles form in smectic freely suspended liquid crystal films when they are heated well above the bulk smectic to nematic transition temperature. In thin films, nematic droplets form and cause rapid film rupture. In some films, individual layers are seen to sweep off the surface, depending on the temperature, the thickness and the substrate. In thick films, these droplets occasionally remain stable for long periods. The shape of the droplets (in plane and perpendicular to the plane) allows determination of the local surface tension. A variety of dynamics are seen as a precursor to film rupture. Occasionally, isotropic regions are seen to form on these thick films before they rupture.

## INTRODUCTION

We have studied the melting behavior of freely suspended films of 8CB in attempt to understand the interrelationship of the surface and bulk ordering as the temperature is varied. In thick films nematic bubbles are observed to form and remain for extended periods in the smectic film, well above the bulk smectic A to nematic transition. On occasion, isotropic regions are seen to form on these thick films as they rupture. In thin films, the formation of nematic drops results in rapid film thinning and rupture. As the temperature is increased to near the film transition temperature individual layers are observed to sweep off the film, allowing it to thin.

When a thin smectic film is drawn across an aperture in a chamber isolated from thermal and shear fluctuations, it may remain stable for several days, weeks or even months[1]. Other types of fluid films spontaneously thin in order to decrease the surface to volume ratio of the attached bulk fluid. If the film can thin continuously, at a critical thickness thermally excited pores of diameter comparable to the film thickness will form and cause film rupture. The stability of smectic films is associated with the quantized

nature of the thinning process: the thinning occurs only by removing layers of definite thickness.

Sirota et. al.[2] discussed the thickness dependence of the phase diagram of freely suspended films of 4-n-heptyloxybenzylidene-4-n-heptylaniline (7O.7). They showed that for some phases the surface enhanced the order of the lower temperature phase, thus increasing the transition temperature, while for others the effects of reduced dimensionality (more disorder) decrease the transition temperature. The reduced dimensionality should decrease order in the plane, and surface ordering should be enhanced perpendicular to the film plane. They did not discuss the smectic A to nematic transition in films of 7O.7. Since the smectic A to nematic transition involves melting of a density wave perpendicular to the smectic planes, the transition temperature should be higher in a freely suspended film than it is in bulk.

The smectic A layer displacement fluctuation profile was calculated by Hoylst et. al.[3] for a freely suspended film and shows that the surface tension quenches those fluctuations. In particular the typical layer fluctuation amplitude $\sigma$ is found to be ~ 8 Å in bulk and ~2-3 Å at a free surface. Hoylst et. al. also showed that the fluctuation amplitude of the surface layer varies with surface tension.

In general one expects that upon formation of a nematic bubble on the film, that location should rapidly thin and cause film rupture. We found that the thickness, uniformity, initial temperature, rate of temperature increase, and film support structure all seem to have an effect on the transition. In some cases it was possible to increase the temperature more than 10°C above the transition, where the bulk surrounding the film had even gone through the nematic to isotropic transition. In several cases, nematic drops appeared and the film temperature could still be increased before rupture. In thin films, smectic layers were observed to peel off the film as the temperature was increased.

## EXPERIMENTAL

We report observations of the smectic A to nematic transition in freely suspended films of 4-cyano-4'-8-alkylbiphenyl (8CB)[4]. The bulk phase diagram, as reported by the manufacturer, is crystal = 21.5°C = smectic A = 33.5°C = nematic = 40.5°C = isotropic.

## 3 NEMATIC BUBBLES IN FSLCF'S

Films were studied both on a microscope stage oven[5] and in a thermostatted chamber which has been described elsewhere.[6]

On the microscope stage oven, a series of thin uniform films were drawn in the smectic phase at temperatures close to the bulk nematic transition. The films were monitored as the temperature was raised stepwise. A plot of time versus temperature is shown in figure 1 for six films. Three of these films ruptured when the system reached the bulk smectic A - nematic transition temperature. Prior to rupture a nematic drop formed on one film, and the other two thinned by layers sweeping off the film from a nucleation point on the boundary. Another film was stable for two minutes at 33.7°C (0.2°C above the transition temperature). That film thinned by two layers sweeping off the film at 32.5°C and again at 33.5°C. The other two films remained stable at temperatures significantly above the bulk transition temperature.

Though no absolute measurements of film thickness were made on these films, the two films which remained stable above the bulk transition temperature were both very thin. Both these films thinned by a single layer three times before popping. The film that popped at 34.5°C was originally medium grey, suggesting fewer than ten layers. The film which popped at 38.1°C was originally dark grey, suggesting it was 5 or 6 layers originally. The asterisks on figure 1 indicate where in the temperature-time evolution of the films, films thinned by layer removal.

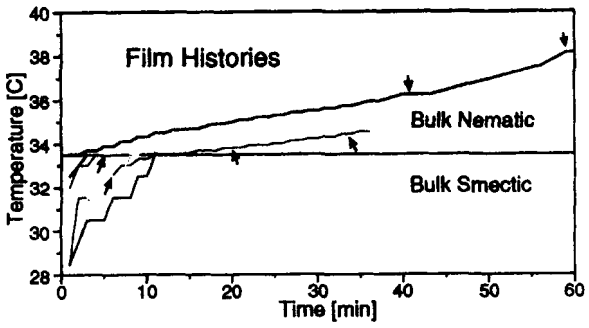


**Figure 1** Temperature versus time history of various films. The ↗ indicate a film thinned by a single layer.

The microscope stage oven had limitations which suggested use of another film chamber would be appropriate. The film was open to the room via the microscope viewing ports. This resulted in the film temperature being approximately 2.5°C cooler than the control thermistor temperature. It also allowed occasional drafts or sound wave

shocks to be felt by the films. Thus further experiments were done in a multi-stage thermostatted chamber sealed via windows from room air[6]. The films were imaged in reflected white light via an external microscope system.

In this thermostatted chamber, it was found much easier to raise the temperature of films well above the smectic A - nematic transition temperature. Very occasionally, a film remained stable above 40.5°C, the bulk nematic to isotropic transition temperature. In one case, a very thick film was observed stable at 95°C, and it only popped in response to violent shear. A variety of morphologies were observed in films in the temperature range 33.5 - 40.5°C.

In some cases at 33.5°C nematic droplets would form within a uniform smectic region. The photos shown in figure 2 demonstrate the presence of stable nematic droplets in otherwise smectic films. The nematic drops are distinguished from the smectic film by the white light interference contours which reflect the drop profile.

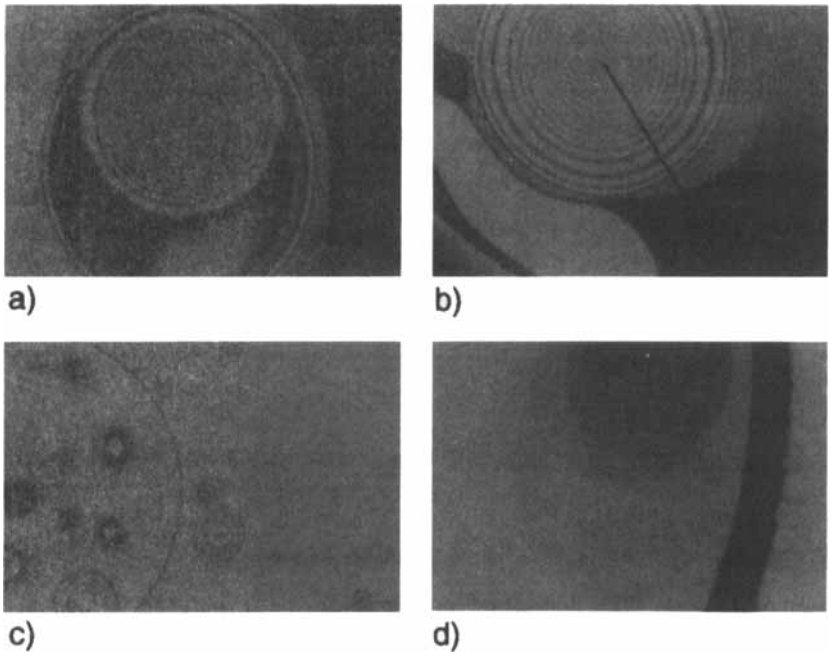


**Figure 2** a), b) and c) show nematic drops on a smectic film. d) shows a thin multilayer film and the edge of the film holder. (See Color Plate XXI).

## 5 NEMATIC BUBBLES IN FSLCF'S

These drops nucleate at points and grow on a timescale of tens of seconds before becoming stable at a particular size.

Several of these nematic drops are up to ten times thicker than the surrounding smectic films. A drop profile is shown in figure 3. The vertical scale is slightly expanded compared with the horizontal scale. The thickness of the drop as a function of position was determined using the expected reflected intensity as a function of thickness (see below).

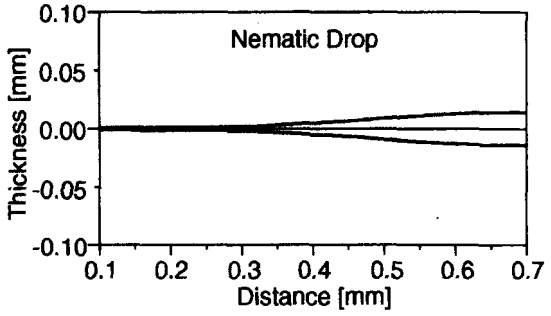


**Figure 3** A thickness profile of the nematic drop shown in figure 2b. (See Color Plate XXII).

When multi-thickness smectic films were heated, thicker regions melted into the nematic phase at lower temperature than thinner regions. Often at this point the nematic regions become extremely dynamic, with interference colors swirling around the film. Several times the thinner smectic region was observed to push the thicker nematic off the film. Figure 4 shows an image of the 6.3 mm diameter hole with a thin black smectic film pushing a thicker nematic region off the film. The temperature in this case was 34.5°C, though similar observations were made at other temperatures.

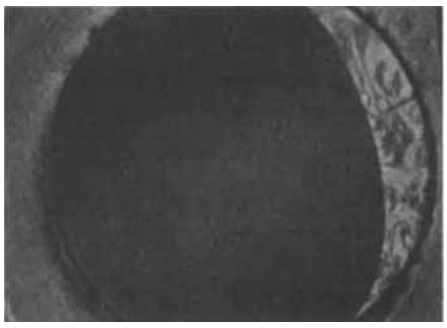

**Figure 4** A thin film of 8CB at 34.5°C, pushing a nematic region off the film. (See Color Plate XXIII).

Several two to five layer films were observed at temperatures as high as 39.5°C. These films remained for long periods at temperatures well above 33.5°C. No sweeping of layers off of these films was observed, nor did films pop upon reaching some critical temperature. These films could pop at any

elevated temperature between 33.5 and 39.5°C, seemingly dependent upon the gentleness with which they were handled.

## THICKNESS DETERMINATION

Film thickness was determined using the methodology outlined by Sirota et. al.[2] whereby the quartz lamp used was modeled as a blackbody radiator at 3100 K. Then the tristimulus values[7] x,y, and z for each wavelength were used to obtain X, Y, and Z intensities for each thickness. The values X, Y, and Z are obtained by integrating the reflected intensity function as $X = \int I(\lambda,N)\, x_\lambda\, d\lambda$, where $I(\lambda,N)$ is the light intensity of wavelength $\lambda$ reflected from a film of N layers of smectic liquid crystal of ordinary index of refraction $n_o$=1.46 and layer thickness 2.5 nm.

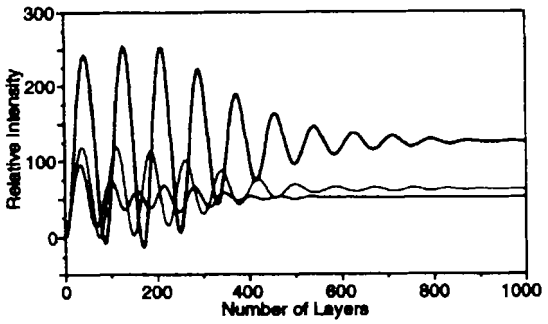


**Figure 5** A plot of the relative intensities of red green and blue components of white light reflected from films as a function of film thickness. (See Color Plate XXIV).

## ACKNOWLEDGEMENTS

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