A Transient Instability in Thin Films of $n$CB Liquid Crystals

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A transient surface instability is reported in thin nematic films of 5CB and 8CB, occurring near the nematic–isotropic phase transition. Although this instability leads to patterns reminiscent of spinodal dewetting, we show that it is actually based on a nucleation mechanism. Its characteristic wavelength does not depend markedly on film thickness, but strongly on the heating rate.

Following several studies on the spreading behavior of liquid crystals (LC) from the $n$CB homologous series [1,2], undulative instabilities have been observed in thin films of the LC 5AB$_4$ [3], and 5CB [4] near the nematic–isotropic (N–I) phase transition. In the case of 5CB, these results have led to some discussion whether a spinodal dewetting mechanism driven by van der Waals forces is at work, as proposed by Vandenbrouck et al. [4], or whether the instability is driven by a pseudo-Casimir force based on the restricted spectrum of director fluctuations in thin nematic films [5]. In the present paper, we show that neither is true for $n$CB thin films. Instead, the instability is caused by textures in the nematic film which largely determine the characteristic wavelength of the emerging pattern. This is not the case, however, in 5AB$_4$.

5CB and 8CB were obtained from Merck KGaA (Darmstadt, Germany) and Frinton Laboratories Inc. (Vineland, NJ) respectively. They were used without further purification. Silicon wafers (100–oriented, p–(Boron–) doped) provided by Wacker Chemitronics (Burghausen, Germany) were used as solid substrates. The wafers were cut to samples approximately 1 cm$^2$ in size and cleaned with a Snowjet$^TM$, which uses a cold CO$_2$ gas stream mixed with small particles of dry ice to remove particulate and organic contamination, followed by ultrasonication in ethanol, acetone, and hexane, subsequently.

Immediately after this cleaning process, LC films were spin-cast onto the samples from hexane solutions. Variation of concentration and spinning rate allows to deposit films of variable thickness. The preparation procedure was performed in a class 100 clean room environment at room temperature. Therefore, the films were initially in the nematic (5CB) or smectic A (8CB) state, respectively. Film thicknesses were recorded with an ellipsometer (Optrel GbR, Berlin, Germany). The samples were placed on a Linkam THMSG 600 heat stage (temperature control better than 0.1 C) and observed in-situ with a Zeiss Axiophot microscope equipped with a digital camera. Unless otherwise noted, no polarizers were used in the microscope setup.

Observations at room temperature showed films of 5CB and 8CB to be stable for hours at thicknesses ranging from 50 nm to 200 nm. Close to the nematic–isotropic transition temperature a surface undulation with a characteristic wavelength can be observed in both types of samples (see figure 1).

FIG. 1. Surface instability of an 85.9(3) nm thick film of 8CB at 39.9(1) C. The scale bar has a length of 100 µm. The inset Fourier transform gives a wavelength of 40 µm.

The observed undulation does not lead to a complete dewetting of the LC film but rather disappears once the phase transition is complete. The film becomes homogeneous again in the isotropic phase. Upon cooling, a similar transient instability occurs. Complete dewetting of the samples will occur only by heating a few degrees above the N–I transition, resulting in an array of isotropic droplets. Heating/cooling of the sample between the nematic and isotropic phase can be repeated as indicated in fig. 2 every time resulting in nearly identical undulation patterns. The instability will develop only if the samples are heated or cooled. Keeping them at a fixed temperature close to the N–I phase transition will result in the nucleation of only a few holes in the film. These observations have been made for 5CB and for 8CB, at all film thicknesses investigated. The pattern was found to vanish faster for thicker films after completion of the phase transition.
Polarization microscopy confirmed the coincidence of the instability with the N–I phase transition.

Careful examination of the contrast profile of the images revealed the formation of nematic domains in 8CB films when heated above the smectic A–nematic transition temperature for the first time after preparation (cf. fig. 3). This domain pattern is preserved during the subsequent heating and cooling of the samples which was limited to a few degrees around the N–I transition temperature. On the left hand side of the figure, contrast is enhanced in order to clearly show the domain boundaries, while on the right hand side, the undulative instability occurring near the phase transition is superimposed on the domain boundary pattern. It is clearly seen from the overlay that the undulative pattern is strongly correlated with the domain boundary pattern.

Since films of 5CB are nematic at room temperature, the domain pattern observed immediately after preparation is less pronounced, but nevertheless present. As in the case of 8CB films, this pattern is not influenced during repeated temperature changes of the sample.

Since we have found that the undulations appear only when the sample temperature is swept through the phase transition, it is of interest to investigate the impact of the heating rate. We have thus varied the heating rate form 0.01 K/min to 10 K/min. As shown in fig. 4, the heating rate is indeed a major defining parameter for the wavelength of the undulation: The faster the samples are heated to the isotropic phase, the smaller is the undulation wavelength.

To explain the instability as such we propose the following scenario: After preparation (for 5CB) or after heating to the nematic phase for the first time (for 8CB), a pattern of nematic domains exists in the films that is preserved during the course of the experiment, since close to the substrate nematic or even smectic order exists even at temperatures substantially above the clearing point (see e.g. [6]). The domain boundaries act as nucleation sites for the isotropic phase upon further heating. Since the surface tension of the liquid crystalline compounds in question is several percent higher in the isotropic than in the nematic phase (see e.g. [7]), a Marangoni flow drives the instability. Once the phase transition is completed, the gradient in surface tension vanishes, resulting in a flat isotropic film. It is possible to explain the pronounced effect of the heating upon the wavelength of the undulation with a few assumptions on the nucleation sites. This is beyond the scope of this note, and will be published in a forthcoming paper. It should be noted that apparently similar observations in 5AB4 [3] do not belong to this class of nucleated undulation phenomena, since in that study the temperature was kept constant, and the undulation was not transient, but remained once it was formed.

It is interesting to note that there is no systematic dependence of the patterns observed with 8CB on the film thickness. Samples of different thickness (3 thicknesses each for 5CB and 8CB) show no pronounced dependence of the undulation wavelength on film thickness, as shown
In particular, no indication of a quadratic dependence of the wavelength on film thickness could be detected, which would be expected of a spinodal dewetting scenario, which might be assumed to be present on the basis of the appearance of the patterns.

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