A 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 nCB homologous series (4'-n-alkyl-4-cyanobiphenyl) [1–6], undulatory instabilities have been observed in thin films of the LC 5AB₄ [7], and 5CB [8] 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. [8], or whether the instability is driven by a pseudo–Casimir force based on the director fluctuations in thin nematic films [9–13]. In the present paper, we show that neither is true for nCB thin films. Instead, the instability is caused by textures in the nematic film which largely determine the characteristic wavelength of the emerging pattern.

5CB and 8CB were obtained from Merck KGaA (Darmstadt, Germany) and Frinton Laboratories Inc. (Vineland, NJ) respectively, and used without further purification. Silicon wafers (100–oriented, p–(Boron–) doped) with a native oxide layer of 2 nm provided by Wacker Chemitronics (Burghausen, Germany) were used as solid substrates. The wafers were cut to samples approximately 1 cm² in size and cleaned with a Snowjet™ (Tectra, Frankfurt/M, Germany), a cold CO₂ stream effectively removing particulate and organic contamination [14], followed by ultrasonication in ethanol, acetone, and hexane, subsequently.

Immediately after this cleaning process, LC films were spincoated 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 heat stage (Linkam THMSG 600, 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. Upon heating, a surface undulation with a characteristic wavelength can be observed in both types of samples (see Figure 1) close to, but consistently below the N–I transition temperature (Tₙᵢ).
FIG. 2. Heating/cooling sequence showing the transient instability in a patch of 8CB (scale bar = 25 μm).

Careful examination 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 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 obtained before on the same spot. It is clearly seen from the overlay that the undulative pattern is strongly correlated with the domain boundary pattern.

FIG. 3. Left: 86 nm thick film of 8CB in the nematic state. Borders between nematic domains appear as dark lines. Right: Picture of the surface undulation superimposed on the network of domain borders, emphasizing the coincidence of surface undulations during the instability (bright areas, thick film) with domain borders in the nematic phase. (scale bar = 100 μm)

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 from 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 into 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. [15]). The domain boundaries act as nucleation sites for the isotropic phase upon further heating. It should be noted that apparently similar observations in 5AB4 [7] 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 nCB 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 Fig. 4. In particular, no indication of a quadratic dependence of the wavelength on film thickness could be detected, which would be expected of a spindoal dewetting scenario.

It is possible to explain the pronounced effect of the heating rate upon the wavelength of the undulation with a few assumptions on the nucleation sites. First we note that the undulations appear only in a certain temperature window, $T_l < T < T_h$, which is more extended and shifted to lower temperatures in thin films than in thicker ones. For thick films $T_h$ will approach the bulk N–I phase transition temperature in accordance to earlier studies [16]. Each nucleation site present in the film (e.g. the domain borders seen clearly in the 8CB samples) is expected to nucleate an isotropic domain, and concomitantly a modulation of the local film thickness, when a certain temperature $T_s$ within the interval $\Delta T = T_h - T_l$ is reached. This modulation, or domain then grows with a certain velocity $v$, and thus further nucleation within the domain is precluded, effectively reducing the number of nucleation sites to become active at a higher temperature. The total number density of isotropic domains $D$ that will develop in a film, and hence the dominant lateral scale of the undulation $\lambda \approx 1/\sqrt{D}$, thus depend on the heating rate. If $n(T_s)$ is the number density of nucleation
sites which nucleate a domain when the temperature $T_s$ is reached, $D$, will be given by

$$\frac{dD}{dt} = \alpha n(T(t)) e^{-A(t)}$$  \hspace{1cm} (1)$$

where $\alpha$ is the heating rate, and $A(t)$ is the total area fraction of the domains if they are assumed circular. The exponential takes care of the mutual overlap of these (circular) model domains. For simplicity, assume that $n(T) = n_0 = \text{const.}$ for $T_l \leq T \leq T_h$, and 0 otherwise. If we furthermore assume the growth rate $dr/dt$ of the domains to be constant, we have

$$\frac{d^2A}{dt^2} = 2\pi v^2 D$$  \hspace{1cm} (2)$$

and thus, after some rearrangements,

$$2\pi v^2 D'(D' + D''(D' - (D'')^2 = 0$$  \hspace{1cm} (3)$$

For investigating the effect of a temperature ramp, $T = T_l + \alpha t$, this must be solved with the initial conditions $D(0) = 0$ and $D'(0) = \alpha n_0$. The number density of domains formed in this way cannot be expressed analytically, but is well approximated by

$$D_{\text{max}} = \frac{N}{1 + 3(3/\alpha \alpha_0)^{2/3}}$$  \hspace{1cm} (4)$$

which gives the correct scaling for $\alpha \to 0$ as well as $\alpha \to \infty$. $N = n_0 \Delta T$ is the total number of nucleation sites and $\alpha_0 = \sqrt{2 N \pi v^2 \Delta T^2}$.

As shown in Fig. 4, the fit function in Eq. (4) does reproduce the heat rate dependence of the undulation wavelength rather well. The scatter in the calculated values for $N$ and $v$ is too large to confirm any systematic variation with film thickness, as it is expected for a nucleation process triggered by inhomogeneities. A systematic dependence on film thickness, as expected for spinodal dewetting, is not found. The different evolution of the nematic domains in 5CB (created upon spincasting the films) and 8CB (domains grow at first heating cycle), however, could lead to specific differences in the two types of samples. Further measurements are necessary to elucidate this point.

It is finally of interest to investigate the temperature range $\Delta T$, in which the modulation pattern persists. Values for $\Delta T$ (based on observation of the temperatures at which the undulation started to appear respectively ceased to be visible) were found to be independent of the heating rate as shown in Fig. 5 (a) but decrease with increasing film thickness, Fig. 5 (b).
are nucleated at defects (domain borders) in the nematic film and the growth and coalescence of these areas lead to the observed undulation patterns. Changing the heating rate during the experiments strongly influences the undulation patterns since less isotropic areas can be nucleated at high heating rates before the phase transition is complete. First experiments on substrates with artificially induced nucleation sites confirm the proposed nucleation mechanism. These findings will be covered in a forthcoming paper.

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