Thin Nematic Films: Metastability And Spinodal Dewetting

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We present new results about the stability of 5CB nematic films spun cast onto silicon wafers. We observe experimentally the dewetting of thin films while thick ones remain stable. We interpret this behavior as a competition between elasticity and van der Waals forces. At later stages, the experimentally observed dewetting instability leads to the formation of structures (islands) which grow and finally merge to form a film of uniform thickness. We show that the islands' characteristic size $L(t)$ scales as $t^{1/3}$ as expected from late stage growth theories. [S0031-9007(99)08781-5]

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Dewetting may occur in thin liquid films because of the high deformability of the liquid-air interface. This has been extensively studied for mainly two reasons. Dewetting may hinder technological applications such as coatings or lubrication. From a more fundamental perspective, a better knowledge of specific interactions involved during (de-)wetting processes is necessary. Two main mechanisms have been identified as inducing dewetting [1–3]: dry patches nucleation due to material heterogeneity (dust, defects), or amplification of thermal fluctuations at the free surface of the liquid film. The latter dewetting mechanism is called *spinodal dewetting.* While the stability of thin polymeric liquid films has been largely studied [4,5], little is actually known about the dewetting of liquid crystals [6]. Spinodal dewetting has been only recently observed in "soft solid" liquid crystal films [7]. As far as liquid crystals are concerned, a significant effort has been carried out, for the last two decades, to achieve a precise understanding of the solid/liquid crystal interface: anchoring mechanisms [8], surface-induced orientational order [9], and orientational wetting [10] have been and still are the objects of intensive research.

In previous Letters, we have reported on a detailed investigation of the spreading of 5CB nematic droplets on silicon wafers [11,12]. The anchoring conditions are antagonist (strong homeotropic anchoring at the free nematic-air interface and weak planar anchoring close to the solid surface) and thus induce an elastic distortion in the film. Ellipsometric profiles of the drops reveal two characteristic thicknesses. The first, belonging to the molecular scale, corresponds to a trilayer structure (tilted monolayer bearing a smecticlike bilayer). The second belongs to the mesoscopic scale (tens of nanometers) and corresponds to the equilibrium thickness of the drop. That previous study allowed us to identify the basic interactions which account for the structure of wetting nematic droplets on silicon wafers. Now, we focus our attention on the dewetting of thin 5CB nematic films spun cast onto the same surfaces. The inner structure of the film, induced by the boundary conditions and resulting from the strong coupling of both interfaces, significantly affects the dewetting behavior of such films. We report in this Letter on spinodal dewetting occurring in 5CB nematic films and propose a first quantitative theoretical interpretation of such a behavior that is specific to liquid crystals. In the second part, we discuss the relaxation towards equilibrium of initially unstable films: the dewetting instability yields to a formation of islands which spread and finally coalesce to form a film of uniform thickness. This coalescence process is very similar to an Ostwald ripening.

Samples of 5CB were purchased from BDH Ltd. and used without further purification (purity better than 99%). 5CB exhibits solid, nematic, and isotropic phases. In the bulk, 5CB molecules associate in dimers. The apparent thickness of this bilayer is estimated to 25 Å [13] while the individual molecule length is 18.7 Å. As solid substrates, we use silicon wafers (type n, dopant P, orientation (100) purchased from Siltronix) bearing a natural oxide layer of 2 nm. These substrates are cleaned by an UV-ozone exposure [14]. Nematic films are spun cast from toluene solutions at a typical spin rate of 240 rad $\cdot$ s^{-1}. The thickness of the films (typically tens of nanometers) is controlled by concentration and spin rate, and measured using ellipsometry. We have used polarized optical microscopy to follow the dewetting of the nematic films. The microscope is coupled to a video camera which allows one to capture images of the dewetting process.

Preliminary observations have been performed at ambient temperature ($T = 20 \pm 1$ °C). A 17 nm thick nematic film dewets a few minutes after deposition while a 42.8 nm thick film remains stable over days. There is thus a strong influence of the initial thickness of the film: it seems that thin films are unstable while thicker ones remain stable. To explain this behavior, we propose an extension of existing models of dewetting [1–3] by taking into account the specificity of nematic liquid crystals. The central hypothesis of spinodal dewetting models is that long-range van der Waals forces induce the amplification of capillary waves. Our previous study of nematic droplets on silicon wafers showed that the elastic distortion, which results from antagonist anchoring conditions, may stabilize the droplet in a metastable state. We argue here that elasticity may act as a restoring force able to balance van der Waals forces. Let us call h_0 the initial thickness of an infinite nematic film on a solid surface. One considers a one-dimensional sine deformation of the free surface in the x direction parallel to the substrate. The film thickness at a given point of the free surface is written as: $h(x,t) = h_0 + \xi_0(t)\sin(qx)$, where q is the wave vector of the considered fluctuation. We assume that $\xi_0 \ll h_0$ in order to perform a linear stability analysis. The free energy per unit surface of the nematic film may be written as

$$F(h) = \gamma_{sl} + \gamma_{lv} + \frac{1}{2}\frac{K\theta^2}{h} - \frac{A}{12\pi h^2}, \qquad (1)$$

where γ_{sl} and γ_{lv}, respectively, represent the surface tension between the solid and the liquid, and between the liquid and the air. The third term in Eq. (1) corresponds to the elastic energy [11]: K is an elastic constant (in a one approximation constant), and θ is the anchoring angle defined as the angle between the normal to the surface and the director orientation at the solid surface. The anchoring energy may be included in γ_{sl}. We neglect in this study any coupling between h and θ [11]. The last term is the van der Waals energy: A is the Hamaker constant. The potential energy per unit volume of the film is written as

$$e_p(h) = \frac{\partial F}{\partial h} = -\frac{K\theta^2}{2h^2} + \frac{A}{6\pi h^3}. \qquad (2)$$

The deformation of the free surface induces an incompressible viscous flow in the film. We suppose that this flow is bidimensional so that the flow velocity is written as $\mathbf{v} = u(x,z)\mathbf{u_x} + v(x,z)\mathbf{u_z}$. The dynamic viscosity η of the nematic liquid crystal is supposed to be isotropic. The pressure field is given by the Laplace law: $p(x,t) = p_0 - \gamma_{lv}(\frac{\partial^2 h}{\partial x^2}) = p_0 + \gamma_{lv}\xi_0 q^2\sin(qx)$. Then we solve the Navier-Stokes equations in the lubrication approximation ($qh_0 \ll 1$). Taking into account the following boundary conditions, no slip at the solid surface ($\mathbf{v} = \mathbf{0}$) and no tangential stress at the free surface [$\eta(\frac{\partial u}{\partial z})_{z=h_0} = 0$], we can calculate the flow in the film:

$$u(x,z) = \frac{\xi_0 h_0}{2\eta}\,\alpha(q)\left(\frac{z}{h_0} - 2\right)(qz)\cos(qx), \qquad (3)$$

$$v(x,z) = \frac{\xi_0 h_0}{6\eta}\,\alpha(q)\left(\frac{z}{h_0} - 3\right)(qz)^2\sin(qx), \qquad (4)$$

with $\alpha(q) = [\gamma_{lv}q^2 + (\frac{K\theta^2}{h_0^3} - \frac{A}{2\pi h_0^4})]$. Writing the boundary condition at the free interface [$\frac{\partial h}{\partial t} = v(x, z = h_0)$] gives the following equation: $\frac{d\xi_0}{dt} + s(q)\xi_0 = 0$ with $s(q) = \frac{h_0^3}{3\eta}q^2[\gamma_{lv}q^2 + (\frac{K\theta^2}{h_0^3} - \frac{A}{2\pi h_0^4})]$. Thermal fluctuations grow exponentially if $s(q) < 0$ while they decay if $s(q) > 0$. Thus the spinodal dewetting of a nematic film may be initiated for long wavelength fluctuations ($q \rightarrow 0$) and if the Hamaker constant A is positive [15] so that the term $(\frac{K\theta^2}{h_0^3} - \frac{A}{2\pi h_0^4})$ is negative. This latter condition also writes $h_0 < h^*$, where the thickness h^* is defined as

$$h^* = \frac{A}{2\pi K\theta^2}. \qquad (5)$$

We conclude that elasticity renormalizes the Hamaker constant. We can define an effective Hamaker constant: $A_{\text{eff}} = A(1 - \frac{h_0}{h^*})$. Instability develops if $A_{\text{eff}} > 0$. The critical wave vector, below which fluctuations grow and lead to the rupture of the film, can be expressed as a function of the effective Hamaker constant: $q_c = \sqrt{\frac{A_{\text{eff}}}{2\pi\gamma_{lv}h_0^4}}$. The fastest growing mode corresponds to $\lambda_m = \frac{2\pi}{q_m} = \sqrt{\frac{16\pi^3\gamma_{lv}h_0^4}{A_{\text{eff}}}}$. The associated time constant is $\tau = \frac{48\pi^2 h_0^5\gamma_{lv}\eta}{A_{\text{eff}}^2}$. Taking typical values ($h_0 = 30$ nm, $\gamma_{lv} = 30\ \text{mN}\cdot m^{-1}$, $\eta = 0.01$ P and $A_{\text{eff}} = 10^{-20}$ J), one obtains $\lambda_m \approx 30\ \mu$m. The order of magnitude of τ is the minute. We note that this model properly corresponds to this preliminary experimental fact: thin nematic films dewet while thicker ones remain metastable. In order to check further these predictions, we have performed complementary experiments.

At ambient temperature, a 20 nm thick film remains stable while dewetting has been observed for a 17 nm thick film. This gives an evaluation of h^*:

$$17 < h^* < 20\ \text{nm} \qquad (T = 20 \pm 1\ ^\circ\text{C}).$$

The values ($h^* = 20$ nm, $K \sim 10^{-11}$ N and $A \sim 10^{-20}$ J) yield to $\theta \sim 10^{-1}$ rad. We note that this value of θ is compatible with the assumption of a weak anchoring at the solid surface. So, a weak elasticity distortion is sufficient to cancel the destabilizing effect of van der Waals forces. It is well known that the nematic elastic constant vanishes close to the nematic-to-isotropic (N/I) transition [16]. The Hamaker constant should not vary significantly at the N/I transition. Thus we expect h^* to increase close to the N/I transition and h^* should be infinite for isotropic films. In order to check this assumption, we have heated the 42.8 nm thick film from the ambient temperature where it remains stable, to a temperature of 33.5 ± 0.5 °C close to the N/I transition (for our samples $T_{\text{NI}} = 34.8 \pm 0.3$ °C [12]). At this temperature, the thickness of the film ($h_0 = 42.8$ nm) is supposed to be smaller than h^*. As expected, we observe a spinodal dewetting. Figure 1 provides a snapshot of the early stages of this process. The characteristic length scale on this picture has been estimated to 30 μm. The order of magnitude of this estimate is in very good agreement with the theoretical prediction. Note that the observed dewetting pattern is reminiscent of Wilson's pictures dedicated to the study of the critical point in second order phase transitions [17]. If h^* is infinite for isotropic films, they should never be stable whatever their initial thickness. Experiment also confirms this

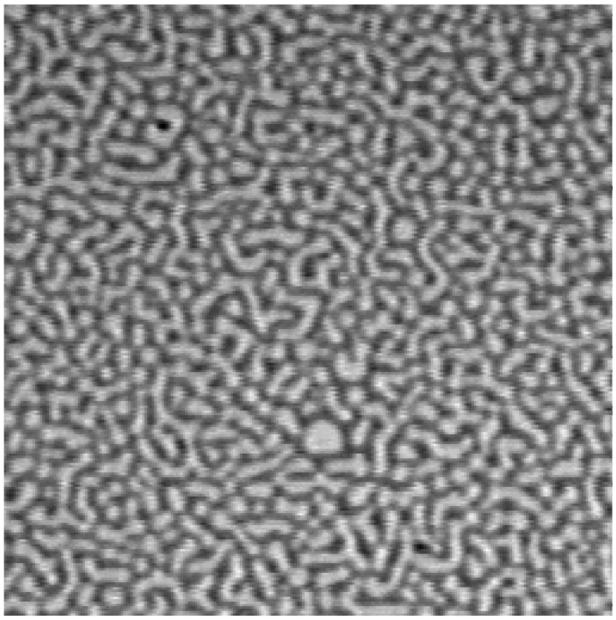

FIG. 1. View of spinodal dewetting of a 42.8-nm-thick film ($T = 33.5 \pm 0.5\,^{\circ}\mathrm{C}$). This pattern is reminiscent of those observed in spinodal decomposition studies. The image size is 460 μm × 460 μm.

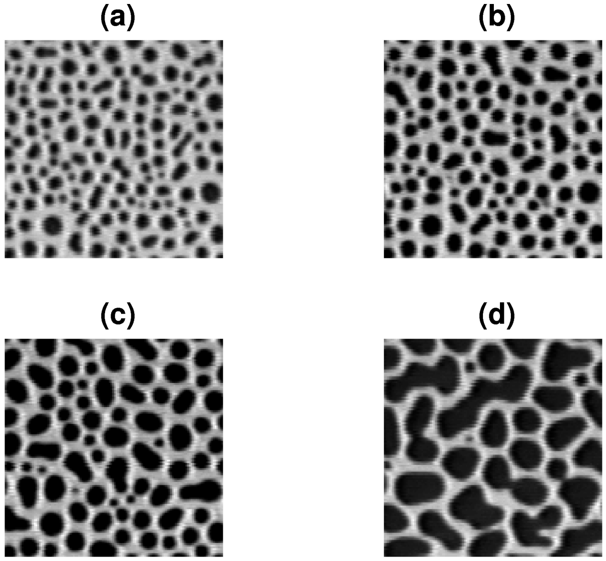

FIG. 2. Snapshot of the islands' coalescence process: (a) $t = 0$ s; (b) $t = 34$ s; (c) $t = 126$ s; (d) $t = 416$ s. The initial film thickness is 25 nm and $T = 25 \pm 0.5\,^{\circ}\mathrm{C}$. Note that the time origin is arbitrary. One can clearly see in views (c) and (d) that small islands of high curvature retract. The size of an image is 230 μm × 230 μm.

prediction. As a first conclusion, we emphasize the very good agreement between theoretical predictions and experimental observations.

Dewetting usually yields to a polygonal pattern of droplets on the substrate [4]. That is what we observe for isotropic films. However, the final state can be different for a nematic film. We have observed that spinodal dewetting leads to the formation of structures (islands) on top of a very thin nematic film. Its thickness cannot be precisely measured with our ellipsometer which has a limited spatial resolution (25 × 200 $\mu\mathrm{m}^2$). This film might well be the trilayer which is usually observed in this kind of system [11], but we are not able at present to check this assumption. The thickness of the islands increases until they begin to spread and finally merge. A metastable nematic film, whose thickness is uniform, results from this coalescence process. We have studied the dynamics of coalescence of the islands. Figure 2 provides a view of this process. Assuming that the islands' distribution is isotropic across the film, we have applied a 2D Fourier transform to our images. Figure 3(a) displays a typical radial averaged power spectra, $S(k,t)$. The main feature in $S(k,t)$ is the existence of a peak. Thus we can represent the islands' distribution by a single time-dependent characteristic length scale $L(t)$. To determine this characteristic length scale, we fit our data using the Binder-Stauffer structure function [18]:

$$S(k,t) = \frac{A_1}{L(t)^{-2} + k^2}\{1 - \exp[-A_2 D(t) k^2 t]\}. \quad (6)$$

The first Lorentzian factor corresponds to the Ornstein-Zernike structure function [19,20], while the second factor is introduced to account for a relaxation towards equilibrium via a diffusive process. The diffusion coefficient $D(t)$ may vary in time. Assuming that $L(t)$ follows a scaling law, we write $A_2 D(t) t = A_3 L(t)^2$. Then the Binder-Stauffer structure function is written as [19]

$$S(k,t) = L(t)^2 F_{\mathrm{BS}}(x), \quad (7)$$

where $x = kL$ and $F_{\mathrm{BS}}(x) = \frac{A_1}{1+x^2}[1 - \exp(-A_3 x^2)]$. We have plotted $L(t)^{-2} S(k,t)$ as a function of kL [see Fig. 3(b)]. We observe the collapse of the experimental curves on the master curve $F_{\mathrm{BS}}(kL)$. This validates the scaling hypothesis. The plot in Fig. 4(a) displays $L(t)^3$ as a function of time. We obtain a straight line. It suggests that $L(t) \propto t^{1/3}$. This asymptotic growth law is known

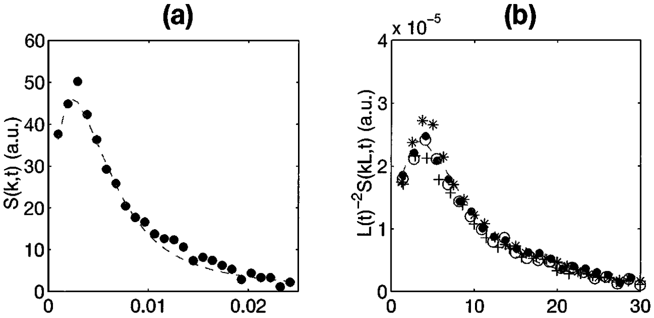

FIG. 3. (a) Radial averaged power spectra $S(k,t)$ as a function of k and its fit by the Binder-Stauffer structure function (dashed line). (b) Test of the scaling hypothesis: experimental curves $L(t)^{-2} S(kL,t)$ (with $t = 126$ s; $t = 206$ s; $t = 266$ s; $t = 326$ s) collapse on the master curve $F_{\mathrm{BS}}(kL)$ (dashed line).

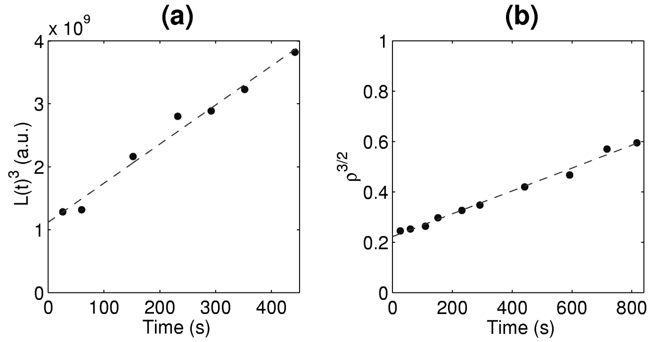

FIG. 4. (a) Characteristic length scale to the power of 3 (in arbitrary units) as a function of time. Note that the time origin is arbitrary. This plot suggests that $L(t) \propto t^{1/3}$. The dashed line is only a guide to the eyes. (b) Islands' coverage rate to the power of $3/2$ as a function of time: ρ scales as $t^{2/3}$. This scaling law is also valid when the islands have begun to connect ($t \geq 400$ s). The dashed line is a guide to the eyes.

as the Lifshitz-Slyozov-Wagner law. One can notice on Fig. 2 that small islands of high curvature disappear during the coalescence process. Thus the islands' coalescence process is very similar to an Ostwald ripening. We also note that the Lifshitz-Slyozov-Wagner law may be derived heuristically by considering the diffusive motion of the islands' walls [21]. Once islands have begun to connect, they form anisotropic structures and the procedure that we have used to analyze the images is no longer relevant. Therefore we have measured the islands' coverage rate ρ as a function of time. If the characteristic size of an island scales as $t^{1/3}$, then the area occupied by this island must behave like $t^{2/3}$. It can be seen indeed in Fig. 4(b) that ρ scales as $t^{2/3}$. So we conclude that the islands' coalescence process may be characterized by the scaling law $L(t) \propto t^{1/3}$, which is indeed very common in late stage growth experiments and theories [19,22].

In this Letter, we have clearly shown, for the first time, that thin elastic nematic films are unstable while the thicker ones are stable. We analyze this behavior as a balance between nematic elasticity and long-range van der Waals forces which tend to thin the film. Our theoretical interpretation of preliminary experiments exhibits a critical thickness $h^* = \frac{A}{2\pi K\theta^2}$ below which nematic films are unstable and produce patterns very similar to those observed in spinodal decomposition. This model also accounts for the immediate dewetting of isotropic films on silicon substrates, whatever their initial thickness. Unstable nematic films also present this unusual feature: they can relax to a metastable film of uniform thickness while isotropic films finally give an array of droplets. During this relaxation process, one observes the coalescence of islands which have been formed by the dewetting instability. The characteristic size of the islands scales like $t^{1/3}$ showing that the coalescence regime is very similar to an Ostwald ripening. A more systematic study of the first stages of the spinodal dewetting process is under way.

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[1] A. Vrij, Discuss. Faraday Soc. **42**, 23 (1966); A. Vrij and J. Th. G. Overbeek, J. Am. Chem. Soc. **90**, 3074 (1968).
[2] E. Ruckenstein and R. K. Jain, Faraday Trans. II **70**, 132 (1974).
[3] F. Brochard-Wyart and J. Daillant, Can. J. Phys. **68**, 1084 (1990).
[4] G. Reiter, Phys. Rev. Lett. **68**, 75 (1992); G. Reiter, Langmuir **9**, 1344 (1993).
[5] M. Maaloum, D. Ausserre, D. Chatenay, and Y. Gallot, Phys. Rev. Lett. **70**, 2577 (1993).
[6] A. Vix, Ph.D. Thesis, Université Paris VI, 1998.
[7] S. Herminghaus *et al.*, Science **282**, 916 (1998).
[8] B. Jérôme, Rep. Prog. Phys. **54**, 391 (1991).
[9] G. P. Crawford, R. Stannarius, and J. W. Doane, Phys. Rev. A **44**, 2558 (1991).
[10] G. P. Crawford *et al.*, Phys. Rev. Lett. **70**, 1838 (1993); G. P. Crawford *et al.*, Phys. Rev. E **53**, 3647 (1996).
[11] M. P. Valignat *et al.*, Phys. Rev. Lett. **77**, 1994 (1996).
[12] F. Vandenbrouck, S. Bardon, M. P. Valignat, and A. M. Cazabat, Phys. Rev. Lett. **81**, 610 (1998).
[13] A. J. Leadbetter, R. M. Richardson, and C. N. Colling, J. Phys. (Paris) Colloq. **36**, C1-37 (1975).
[14] J. R. Vig, J. Vac. Sci. Technol. A **3**, 1027 (1985).
[15] A positive Hamaker constant tends to thin the film.
[16] S. Chandrasekhar, *Liquid Crystals* (Cambridge University Press, Cambridge, England, 1992), 2nd ed.
[17] K. Wilson and J. Kogut, Phys. Rep. **12C**, 75 (1974).
[18] K. Binder and D. Stauffer, Phys. Rev. Lett. **33**, 1006 (1974).
[19] J. D. Gunton *et al.*, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1983), Vol. 8.
[20] M. Le Bellac, *Des Phénomènes Critiques aux Champs de Jauge* (InterÉditions/Éditions du CNRS, Paris, 1988).
[21] A. J. Bray, Adv. Phys. **43**, 357 (1994).
[22] A. Steyer, P. Guenoun, D. Beysens, and C. M. Knobler, Phys. Rev. A **44**, 8271 (1991).