Meniscus and Dislocations in Free-Standing Films of Smectic-A Liquid Crystals

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A flat, freely suspended film of smectic-*A* liquid crystal supports a pressure difference, Δp, across its two free surfaces. The size of its meniscus is about 10 μm, 2 orders of magnitude smaller than the capillary length, and its profile is predicted to be circular, in accordance with our measurement. The measurement of its radius of curvature gives Δp. We nucleate *ex nihilo* an elementary edge dislocation loop, and from its critical radius and growth dynamics (governed by Δp), we find the line tension ($\sim 8 \times 10^{-7}$ dyn) and the mobility of an elementary edge dislocation ($\sim 4 \times 10^{-7}$ cm^2 s/g). [S0031-9007(97)02572-6]

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It is common knowledge that, in mechanical equilibrium, an isotropic liquid in contact with air must have the same pressure as the air providing its interface is flat [1]. This is not necessarily true in a smectic-*A* liquid crystal because its layers are elastic and can support a normal stress σ that will equilibrate any pressure difference providing it is not too large. The pressure difference contributes to the tension τ of the freely suspended smectic film,

$$\tau = 2\gamma_{SA} + \Delta p H \,, \tag{1}$$

where H is the thickness of the film, $\Delta p = p_{\text{air}} - p_{\text{smectic}}$, and γ_{SA} is the surface free energy of the smectic-air interface. This law has been found experimentally by Pieranski *et al.* [2,3], and will be discussed in this article.

Because freely suspended smectic films are stressed in accordance with Eq. (1), many of their physical properties [4–11] will be affected. In particular, the stress contribution due to Δp depends on the way the freely suspended film is prepared, on the amount of material near the edges, and on the applied external forces.

There has not been any systematic study of the meniscus, or any theoretical model which allows us to relate the meniscus profile to this pressure difference. We shall see that a smectic phase near edges or walls, where a meniscus forms, behaves differently from an ordinary liquid, and we shall explain why films are always thin in the presence of steps (or edge dislocations).

We shall also see how to control experimentally the nucleation *ex nihilo* of an edge dislocation loop and how to precisely measure its line tension and its mobility. This study is pertinent to the field of liquid crystals. Indeed, although the line tension of an edge dislocation has been calculated theoretically [12–14] (apart from its core contribution), there is no precise measurement of this quantity beyond a preliminary estimate of Pieranski *et al.* [3]. In addition, the mobility of a dislocation has never been measured directly, to our knowledge, but only indirectly via creep experiments of thick samples sandwiched between two glass plates [15,16].

To produce a film, we draw out one side of a rectangular frame whose sides are wet due to a droplet of smectic-*A* liquid crystal [3]. A mixture of 80 wt % of octyl-cyanobiphenyl (8CB) and of 20 wt % of 10CB was used (we did not use pure 8CB because its nematic-smectic-*A* phase transition temperature was too close to the room temperature during the summer; we also emphasize that the nematic-smectic-*A* phase transition is second order within a very good approximation in the mixture chosen [17]). The frame is placed in an oven whose temperature is controlled within 0.01 °C. We performed all our experiments at 34 °C, i.e., 4 °C below the nematic-smectic-*A* phase transition. The film is observed with a video camera via reflected light microscopy. Its thickness is obtained by measuring its reflectivity as a function of the light wavelength λ [18].

In order to observe the meniscus, a stainless steel needle of diameter 0.6 mm (initially coated with the liquid crystal and placed just below the film) is raised through the film (Fig. 1). The profile of the meniscus surrounding the needle is determined by observing in monochromatic light the fringes that form at mechanical equilibrium [Fig. 2(a)]: The thickness of the film increases by $\lambda/4n$ between bright and dark lines (n is the refractive index). The meniscus profile is shown in Fig. 2(b). We immediately note that its height h [5 μm in the thickest part of the meniscus experimentally observed, see Fig. 2(b)] is much smaller than in ordinary fluids. Indeed, with ordinary fluids, the meniscus height h_0, at a point

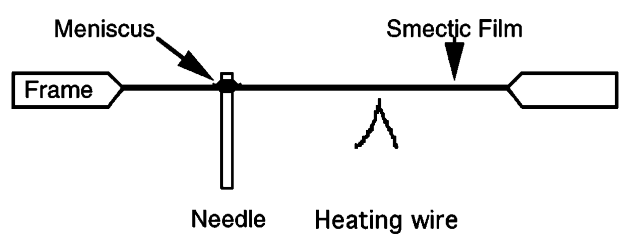

FIG. 1. Schematic representation of the experiment.

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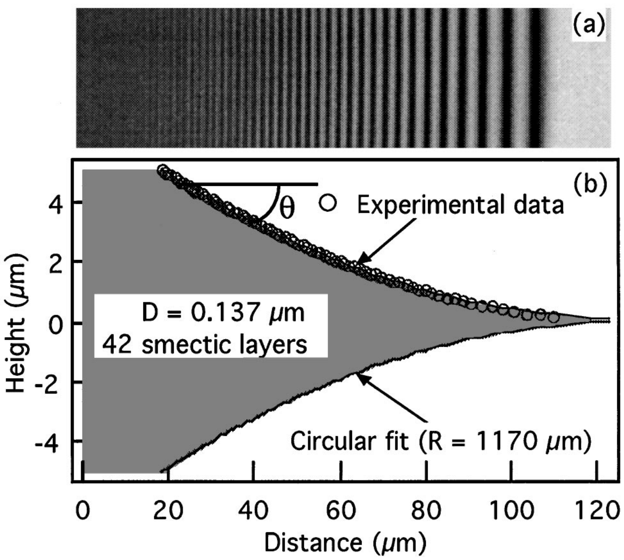

FIG. 2. Experimental determination of the meniscus profile. (a) Fringes observed around the needle. (b) Meniscus profile.

where the surface makes an angle θ with the horizontal plane, equals $\alpha\theta$ [see formula (6) below], where $\alpha = \sqrt{\gamma/\rho g}$ is the gravitational capillary length [1], γ the smectic-air surface tension, ρ the smectic density, and g the gravitation acceleration. Taking typical numbers and $\theta = 0.08rd$ [Fig. 2(b)], we find $\alpha = 0.2$ cm and $h_0 = 150\ \mu$m instead of the 5 μm found experimentally. This result shows that gravity is negligible and that the shape of a smectic meniscus is not fixed by the competition between gravity and surface tension.

In order to explain these observations, we assume that the meniscus is composed of a collection of steps [2,3]. These "steps" are no doubt bulk edge dislocations because these defects are repelled from the free surfaces [19]. We then calculate the elastic energy (per unit length) associated with the creation of the meniscus. It has the following form:

$$F[h(x)] = 2\gamma_{SA}\int_0^\infty dx\left[\sqrt{1 + (dh/dx)^2} - 1\right] + 2(\gamma_{WS} - \gamma_{WA})h(0) + 2\Delta p\int_0^\infty dx h(x) + \int_0^\infty dx E[h(x)]\,\frac{2}{b}\,\frac{dh}{dx}. \tag{2}$$

Here, $h(x)$ is the height of the meniscus above the flat surface of the film, and x is the distance from the needle (wall). The following surface tensions appear: γ_{SA}, γ_{WS}, and γ_{WA}, where W stands for wall, S for smectic, and A for air. Also, Δp is the difference between the air pressure and the pressure in the middle of the smectic film, b is the thickness of the smectic layer, and $\rho(x) = (dh/dx)(2/b)$ is the density of dislocations in the film. Finally, $E[h(x)]$ is the elastic energy, per unit length, of dislocation [14] located in the film of thickness $D + 2h(x)$:

$$E(h) = E_c + \frac{\sqrt{KB}\,b^2}{2r_c} + \frac{\sqrt{KB}\,b^2}{4\pi}\int_{-\infty}^{+\infty} dq \times \frac{(1 - a)}{(1 + a)\exp[\lambda_1 q^2(D + 2h)] + (1 - a)}, \tag{3}$$

where $\lambda_1 = \sqrt{K/B}$ and $a = \gamma/\sqrt{KB}$, K, B are smectic elastic constants, r_c is the core of the dislocation, and E_c is the core energy. In Eq. (2), we have neglected the gravitational forces and the interactions between dislocations. This is based on the following estimate of the orders of magnitude for various quantities: The surface tensions are of the order of 20–30 dyn/cm, the energy of dislocation per unit area of the meniscus is of the order of 1–5 dyn/cm, the pressure difference multiplied by the height of the meniscus near the needle is of the order of 1 dyn/cm, gravitational forces give 10^{-3} dyn/cm, and the same estimate holds for interactions between dislocations [14]. Therefore, neglecting the latter two forces is completely justified. Note that the height of the meniscus near the edge, $h(0)$, is fixed by the irreversible process of its creation [$h(0) = Nb/2$, where N is the number of layers in the film].

Minimizing Eq. (2) with respect to $h(x)$ [with $h(0)$ kept fixed] leads to the following form of the meniscus:

$$h(x) = \frac{\gamma_{SA}}{\Delta p}\left[1 - \sqrt{1 - (c - x\Delta p/\gamma_{SA})^2}\right], \tag{4}$$

where

$$c = \sqrt{1 - [1 - \Delta p h(0)/\gamma_{SA}]^2}\,. \tag{5}$$

This mathematical form for the shape of the meniscus (a circle of radius $\gamma/\Delta p$) should be compared with the shape of the meniscus for the isotropic liquid which, far from the wall where the gradients are small, has the following form:

$$h(x) = \sqrt{2(1 - \cos\theta)}\,\alpha\exp(-x/\alpha)\,, \tag{6}$$

where α is the capillary length and θ is the complement of the contact angle. We find experimentally that the profile of the meniscus is circular and that the pressure difference between the inside and outside of the film is usually about 100–1000 dyn/cm^2, the same as measured by a different method in Refs. [2,3]. Note that we can neglect the other radius of curvature due to the circular geometry of the meniscus because it is of the order of r/θ (where r is the distance from the center of the needle) and, thus, always much larger than the radius of curvature measured in the radial plane. Note also that, from the form of the meniscus, we in fact obtain only the ratio of $\gamma_{SA}/\Delta p$. However, there are many independent methods for measuring the smectic-air surface tension [3,6,8]. It is found to be close to 25 dyn/cm, and therefore by using this value we can estimate the pressure difference from the measured ratio.

It is possible (without removing the first needle) to place a heating wire (a 2-mm-long segment of a Constantan wire of 100 μm diameter, of resistance 0.14 Ω, and folded at its middle) very close to the film (typical distance ~ 50 μm), see Fig. 1. Sending a pulse of very short duration (~ 100 μs, ~ 2 V) through the wire can then nucleate an edge-dislocation loop. If the voltage is adjusted carefully (within a few mV) it is possible to systematically nucleate elementary loops of edge dislocation. Increasing slightly the pulse current leads to the nucleation of several concentric edge-dislocation loops. One can also notice that the nucleation of the loop is only due to the thermal effect, the film and the heating wire remaining at the same electric potential. Furthermore, the intensity of the pulse needed to create a loop decreases when the temperature is increased. We also observed that the film reflectivity locally changes a fraction of a second (one or two video frames) before the nucleation process. This contrast variation corresponds to a relative increase of the optical path nH of $\sim 10^{-3}$, which we attribute to the increase of the ordinary index n when the temperature locally increases.

Before explaining the nucleation process, let us first describe the loop evolution. Depending on its initial value, the radius R of the loop increases or decreases in time. Indeed, the edge dislocation is first affected by its line tension $E = E(h = 0)$ [Eq. (3)] (we are away from the meniscus) which tends to reduce its size. The resulting force per unit length is

$$F_T = -\frac{E}{R}. \tag{7}$$

Second, the pressure difference Δp tends to enlarge the radius of the loop: Indeed, the thickness of the film is smaller inside the loop, and the film pressure is less than that of the air. The resulting force can be written as

$$F_P = b\Delta p\,, \tag{8}$$

where $\Delta p > 0$. Finally, a dissipation force reduces the velocity of the dislocation line:

$$F_D = -\frac{b}{\mu}\frac{dR}{dt}\,, \tag{9}$$

where μ is the mobility of the edge dislocation. The competition between line tension and pressure difference allows us to define a critical radius $R_c = E/b\Delta p$.

Experimentally, we are able to produce an edge-dislocation loop with $R < R_c$ and then to observe the collapse of the loop. The film thickness remains unchanged. We, afterwards, increase the intensity of the pulse in order to produce a dislocation with an initial radius larger than R_c. The radius R increases and, when $R \gg R_c$, the velocity of the dislocation remains constant and equals $V = \mu\Delta p$. We deduce from this experiment the line tension E and the mobility μ of an elementary edge dislocation in a film of well known thickness at a given temperature, see Fig. 3. For instance, we found in the mixture 8CB/10CB at $T = 34$ °C and by taking $\gamma = 25$ dyn/cm, $E = 8 \times 10^{-7}$ dyn and $\mu = 4 \times 10^{-7}$ cm^2 s g^{-1}. This value of the mobility is comparable to that found previously in thick samples of 8CB via creep experiments [15,16].

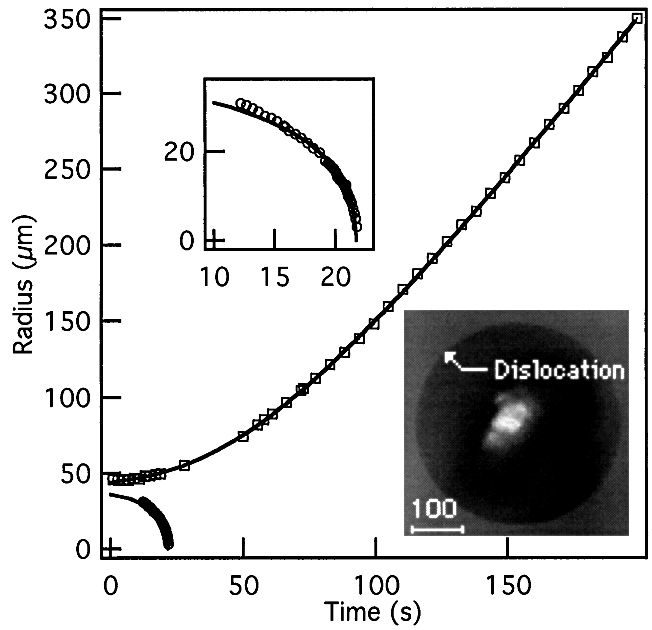

FIG. 3. Experimental determination of E and μ. Radius as a function of time. From this experiment we deduce $E \sim 8.10^{-7}$ dyn and $\mu \sim 4.10^{-7}$ cm^2 s/g. Inset: photograph of the dislocation loop. In the center, one can see the out-of-focus image of the heating wire.

Finally, we return to the problem of nucleation. We have shown that the film must be heated locally for observing nucleation. This process is thermally activated. Far from the nematic-smectic-A transition, the activation energy is very large. It is equal to the difference between the excess of line energy at the critical radius and the work of the stress (or the pressure difference),

$$E_{\text{act}} = 2\pi R_c E - \pi E_c^2 b\Delta p = \pi\frac{E^2}{b\Delta p}. \tag{10}$$

Typically, E_{act} is much larger than $10k_BT$, and homogeneous nucleation is impossible. This explains the remarkable stability of smectic films. By contrast, nucleation becomes possible if E_{act} is comparable to $10k_BT$, which we achieve by transiently heating the film to a temperature very close to the nematic-smectic transition temperature. Indeed, this transition is second order and B vanishes at the transition, whereas K remains constant. Knowing that E scales like $\sqrt{KB}\,b$ [14,20], E_{act} scales like $\frac{KBb}{\Delta P}$. Thus, E_{act} is comparable to $10k_BT$ providing B is of the order of 1000 erg/cm^3. Such a value is reached within $1/100$ °C of the phase transition, which explains why the voltage must be adjusted so precisely experimentally. Note that, at this temperature, the strain of the layers ϵ is close to 10% with $\Delta P = 100$ dyn/cm^2 (because $\sigma = -\Delta P = B\epsilon$). This is the usual value for getting homogeneous nucleation in metals on laboratory time scales [21]. We also emphasize that dislocations with Burgers vectors $2b$ (or more) do not nucleate in these conditions because their activation energy is 2 times larger than for elementary dislocations.

In summary, by careful measurements of the shape of the smectic meniscus, critical radius of dislocation loops, and mobility of dislocations, we have shown that smectics support a static pressure difference across flat surfaces. Additionally, we have presented a direct method for nucleating and measuring mobility and line tension of edge dislocations. Systematic measurements of these two quantities are now in progress in order to explore possible confinement and surface effects on dislocations. Most certainly the behavior of complex fluids near edges is far from being understood [22], and we hope that theoretical analysis combined here with experimental techniques will be a good guide for future experiments.

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