On the Capillarity of Smectic-A Free Surfaces in Drops and Free Standing Films

J.B. Fournier (*)

Laboratoire de Physique des Solides, Université Paris-Sud, Bât. 510, 91405 Orsay Cedex, France
Materials department, University of California at Santa Barbara, CA 93106, USA

(Received 20 October 1995, revised 20 December 1995, accepted 2 April 1996)

PACS.61.30.Cz – Theory and models of liquid crystal structure
PACS.68.10.Cr – Surface energy (surface tension, interface tension, angle of contact, etc.)
PACS.68.10.Et – Interface elasticity, viscosity, and viscoelasticity

Abstract. — Smectic-A free surfaces are discussed in the spirit of capillarity. It is shown that for most practical cases the bulk cannot be treated as a semi infinite medium: the natural length over which a perturbation relaxes along a free surface is just that creating bulk distortions that propagate over the smectic thickness. Hence, the bulk distortions do not simply renormalize the surface tension as in a semi-infinite medium. The relaxation of the layers' distortion within the bulk is fairly linear in most cases: this allows to develop a functional analysis involving only the free surfaces, instead of all the layers. In drops with thickness h, the surface is found to relax exponentially with two capillary lengths $\sim (\lambda h)^{1/2}$, where $\lambda^2 = K/B$ is the ratio of the curvature over the dilation elastic constant. This allows to match boundary conditions both on the height and the tangent of the surface extremities. Films have two independent modes: i) an "average" mode describing the film medium layer. It involves a pure *curvature*-capillary length $\mu = (Kh/\Gamma)^{1/2}$, where Γ is the smectic surface tension, and ii) a "differential" mode of behavior similar to the drop one. The effects of added surfactants and applied external fields are discussed together with the possibility of free surface instabilities.

1. Introduction

Smectic-A liquid crystals are semicrystalline materials [1]. They consist in the regular piling of flexible liquid monolayers, made of rodlike molecules oriented perpendicularly to the layers. At free surfaces, smectic layers always orient parallel to the smectic/air boundary. The free surface of a smectic-A can thus be viewed as a liquid surface with underlying crystalline properties. Smectics-A in the free drop geometry [2–6] and the free standing film geometry [7–10] have been widely studied, however never in the spirit of *capillarity*: there is no real understanding of elementary problems similar to that of simple liquids. For instance, over which characteristic length would heal a lateral surface perturbation caused by a floating object? Does the healing length depends on the thickness of the smectic? Do films and drops behave in the same way, etc?

It has long ago been shown that in a semi-infinite smectic-A sample, the elastic distortions induced by a free surface perturbation simply renormalize the surface tension [1]. More recently,

(*) e-mail: fournier@itp.ucsb.edu

it has been argued that the free surfaces of thick confocal smectic films, *i.e.*, thick films with perfectly equidistant layers, should display a *curvature*-capillarity [11]. The healing length results then from a competition between the surface tension and the bulk curvature elasticity. The purpose of the present work is to classify the different situations and to discuss from a general point of view the capillary properties of smectic drops and films.

2. Smectic-A Elasticity

Smectics layers always orient parallel to free surfaces. Thus, any perturbation of the free surface induces a distortion that propagates inside the bulk: in smectics, capillarity and elasticity are coupled. Let us first recall the basic formulation of smectic-A elasticity.

We consider the *linear* elastic theory and we restrict our attention to problems invariant by translation in one direction, say the y-axis. Elastic distortions in smectic-A's can be described by the displacement function $U(x,z)$ of the actual layers with respect to the planar equidistant layers of an undistorted reference state [1]. In the limit of distortions with a scale much larger than the layer thickness, the elastic free energy density writes as

$$f_{\rm el} = \frac{1}{2}K\left(\frac{\partial^2 U}{\partial x^2}\right)^2 + \frac{1}{2}B\left(\frac{\partial U}{\partial z}\right)^2 \tag{1}$$

The first term is the elastic energy due to the curvature of the layers and the second one is that due to their thickness variations. The elastic constants K and B define a characteristic length $\lambda = \sqrt{K/B}$. It compares with the layers thickness for well condensed smectics, but diverges near second-order smectic-A to nematic transitions. The Euler-Lagrange equation associated to equation (1) is

$$\lambda^2 \frac{\partial^4 U}{\partial x^4} = \frac{\partial^2 U}{\partial z^2}. \tag{2}$$

This equation describes the bulk equilibrium of the smectic layers; it is the fundamental equation of smectic-A elasticity. It should be noted that dealing with a pure mean field elastic theory, we disregard any energy term arising from fluctuations (such as Casimir-like forces).

3. Smectic-A Slab with Free Boundaries

In order to discuss simultaneously smectic drops and films, we consider a set of smectic layers of thickness $\sim h$ (Fig. 1). The first and last layers are supposed to coincide either with a free surface or a flat substrate. The slab layers are described by the function $U(x,z)$, as previously defined, with x indefinite and $z \in [-h, 0]$. The equations of the boundary layers are respectively

$$u(x) = U(x,0) = \sum_q u_q e^{iqx} \tag{3a}$$

$$v(x) = U(x,-h) = \sum_q v_q e^{iqx}, \tag{3b}$$

in which we have performed a Fourier decomposition.

Given the boundary layers, the shape of all layers within the slab can be determined in the following way. For each mode q, equation (2) has two solutions of the type $\exp(iqx \pm \lambda q^2 z)$. The complete solution of (2), subject to the boundary conditions (3) is therefore

$$U(x,z) = \sum_q \left\{ u_q \frac{\sinh \lambda q^2 (z+h)}{\sinh \lambda q^2 h} - v_q \frac{\sinh \lambda q^2 z}{\sinh \lambda q^2 h} \right\} e^{iqx}, \tag{4}$$

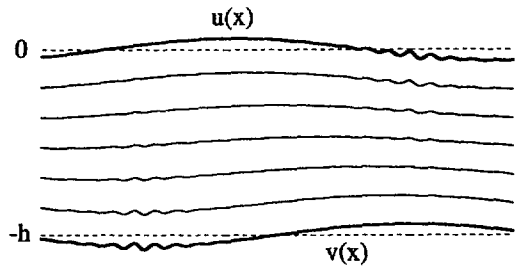

Fig. 1. — Smectic-A slab of macroscopic thickness h limited by two free surfaces with fixed shapes. The layers within the slab evolve according to the smectic-A elasticity (cf. Eq. (4)). The distortions with typical wavelength $d \gtrsim (\lambda h)^{1/2}$ transform linearly from one free surface to the other. Conversely, the short scale distortions with $d \ll (\lambda h)^{1/2}$ relax before reaching the opposite free surface.

which defines the whole slab texture. The total free energy of the slab is given by the integral

$$F = \int \mathrm{d}x \int_{-h}^{0} \mathrm{d}z \left\{ \frac{K}{2} \left(\frac{\partial^2 U}{\partial x^2} \right)^2 + \frac{B}{2} \left(\frac{\partial U}{\partial z} \right)^2 \right\} + \int \mathrm{d}x \, \frac{1}{2} \Gamma \left(u'^2(x) + v'^2(x) \right) . \tag{5}$$

The second term in (5) describes the energy excess of the two free surfaces, assumed identical for the sake of simplicity. Indeed, the excess length $\mathrm{d}s - \mathrm{d}x$ of the upper free surface is $\sim (1/2) u'^2(x) \, \mathrm{d}x$, the free surface tilt being $\sim u'(x)$. Using the decomposition in modes (4), the integrals defining F can be easily performed. One obtains the free energy of the slab (per unit length along the y direction) as a function of the amplitudes u_q and v_q of the free surface modes:

$$f = \sum_q \frac{1}{2} q^2 \Big\{ \left(\Gamma + \sqrt{KB} \coth \lambda q^2 h \right) \left(|u_q|^2 + |v_q|^2 \right) - \frac{\sqrt{KB}}{\sinh \lambda q^2 h} \left(u_q v_q^* + u_q^* v_q \right) \Big\} . \tag{6}$$

4. Infinite Thickness: Renormalization of the Surface Tension

In a semi-infinite smectic, the bulk distortion induced by a free surface with shape $u(x)$ is given by

$$U(x,z) = \sum_q u_q \mathrm{e}^{\lambda q^2 z} \mathrm{e}^{\imath q x} , \tag{7}$$

which can be obtained from (4) by setting $v = 0$ and taking the limit $h \to \infty$ (while keeping q fixed). In this limit, the energy per unit length resulting from (6) is simply

$$f = \sum_q \frac{1}{2} \left(\Gamma + \sqrt{KB} \right) q^2 |u_q|^2 = \left(\Gamma + \sqrt{KB} \right) \int \mathrm{d}x \, \frac{1}{2} u'^2(x) . \tag{8}$$

Hence, as discussed in reference [1], the elastic distortion induced by the free surface renormalizes the surface tension by an amount $\sqrt{KB}$.

This result must however be taken with care. In practice, a realistic system is a smectic drop with a large but *finite* thickness h, laying on a flat substrate at the contact of which the layers are bound to be parallel. As can be seen from (6), the bulk distortion energy yields a contribution $\propto q^2$ only if $\coth \lambda q^2 h \sim 1$, *i.e.*, for distortions having completely relaxed before

reaching the substrate (cf. Eq. (7)). The surface tension renormalization is thus valid only for wavevectors in the range

$$q \gtrsim (\lambda h)^{-1/2} \tag{9}$$

For such wavevectors the system can be considered as having only *surface tension* and the natural relaxation wavevelength of the free surface is defined by the distance L between the surface boundaries. The validity of condition (9) requires then that the drop be thicker than L^2/λ. Since L is a macroscopic length and λ a microscopic length, this condition is very restrictive. Taking for instance $L \sim 10\,\mu$m (which is already a small value for experiments), with $\lambda \sim 100\,$Å, the minimum thickness of the drop is found to be 0.1 m. This value is very large because layer ondulation propagate very far in smectics [12]. In the absence of lateral boundaries the situation is even worse. If the smectic drop has only "surface tension", the free surface perturbations will relax over the gravitational capillary length $\ell_c = (\Gamma + \sqrt{KB})^{1/2}/(\rho g)^{1/2} \sim 1\,$mm as for ordinary liquids, since usually $\sqrt{KB} \sim 10\,\mathrm{erg/cm^2}$. With $L = \ell_c$, we find that the thickness of the drop must be of order *one kilometer* to satisfy (9). Hence, in practice, elastic distortions do not simply renormalize the surface tension: one must take into account the finite thickness of the drop. We shall see that this amounts to introducing new capillary lengths arising from the smectic elasticity. As these lengths will be much smaller than ℓ_c, we shall neglect gravitation in the following.

5. Smectic Drop

Let us consider a smectic drop, indefinite in the x direction. We assume that it lies on a flat substrate at the contact of which the layers are bound to be parallel. Were the boundary condition perpendicular, focal-conic defects would appear in the drop [2], making the discussion much more complicated. The drop under consideration can be obtained from the slab described in Section 3 by setting $v = 0$. For an arbitrary surface shape $u(x)$, the bulk distortion (4) becomes

$$U(x,z) = \sum_q u_q \frac{\sinh \lambda q^2 (z+h)}{\sinh \lambda q^2 h} \, \mathrm{e}^{\mathrm{i}qx}\,, \tag{10}$$

and the drop energy (6) is transformed to

$$f = \sum_q \frac{1}{2} \left(\Gamma + \sqrt{KB} \coth \lambda q^2 h\right) q^2 |u_q|^2. \tag{11}$$

From the above discussion, we know that if there exists a free surface characteristic length arising from the smectic elasticity, it must be as large as to yield bulk distortions that propagate up to the substrate (otherwise the bulk distortion just renormalizes the surface tension). The corresponding surface wavevectors must then satisfy

$$\lambda q^2 h \lesssim 1 \tag{12}$$

Let us now assume that the characteristic surface distortions have wavevectors in the range (12), which will be checked afterwards. The shape of the bulk relaxation in (10) can then be approximated by

$$\frac{\sinh \lambda q^2 (z+h)}{\sinh \lambda q^2 h} \sim 1 + \frac{z}{h}. \tag{13}$$

This approximation is excellent for wavevectors such that $\lambda q^2 h \ll 1$ and implies an error of order 7%, maximum at mid-height of the drop, when $\lambda q^2 h \sim 1$. With the above simplification,

(11) becomes

$$U(x,z) \sim \left(1+\frac{z}{h}\right) u(x), \tag{14}$$

i.e., the distortion relaxes *linearly* in the bulk. The total free energy F of the drop, given by (5), takes then the form

$$F = \int \mathrm{d}x \left\{ \frac{1}{6} K h u''^2 + \frac{1}{2} \Gamma u'^2 + \frac{1}{2} \frac{B}{h} u^2 \right\}. \tag{15}$$

This approximation corresponds to the expansion of (11) for small q's up to fourth order, since $q^2 \coth \lambda h q^2 = (\lambda h)^{-1} + (1/3)\lambda h q^4 + \mathcal{O}(q^8)$.

The Euler-Lagrange equation associated with (15), which describes the drop free surface equilibrium, is

$$\mu^2 m^2 u^{\mathrm{IV}} - 2m^2 u'' + u = 0, \tag{16}$$

where u^{IV} denotes the fourth derivative of u, and

$$\mu = \sqrt{\frac{2}{3}} \left(\frac{K}{\Gamma} h\right)^{1/2} \tag{17a}$$

$$m = \sqrt{\frac{1}{2}} \left(\frac{\Gamma}{B} h\right)^{1/2} \tag{17b}$$

are two bare capillary lengths. The first one is a *curvature*-capillary length as introduced in reference [11], and the second one is a *dilation*-capillary length. The general solution of (16) can be written as

$$u(x) = \mathcal{R}\mathrm{e} \sum_{\ell=1,2} \left[A_\ell^{(+)} \mathrm{e}^{k_\ell x} + A_\ell^{(-)} \mathrm{e}^{-k_\ell x} \right], \tag{18}$$

in which $\pm k_\ell$ ($\ell = 1, 2$) are the four roots of

$$k_\ell^2 = \left[1 + (-1)^\ell \sqrt{1 - \frac{\mu^2}{m^2}} \right] \mu^{-2} \tag{19}$$

Contrary to the case of a liquid, four boundary conditions are thus required to determine the shape of a smectic free surface: since smectics can sustain torques, one can fix the tangents to the free surface in addition to the heights of the end-points. Note that if $\mu > m$, the roots of (19) are complex and the solutions are sine-exponential functions. This means that free surface perturbations will relax with damped oscillations.

For usual smectic-A's, K/Γ defines a *microscopic* length ~ 30 Å comparable to the layer thickness. Hence μ can be either a *meso*scopic length or a *macro*scopic length, according to the height of the drop. For a small drop, $h \sim 30\,\mu$m yields $\mu \sim 3000$ Å, whereas for a thick drop, $h \sim 1$ cm yields $\mu \sim 5\,\mu$m. Thick drops generally exhibit steps and defects localized on their borders, and in the center a large "facet"; capillary experiments could be performed in this region. From (17), we have $\mu/m \sim \sqrt{KB}/\Gamma$. With for smectic-A's $\sqrt{KB} \sim 10\,\mathrm{erg/cm^2}$, and assuming a somewhat larger value for Γ (of the order of the surface tension of molecular liquids), we expect

$$\frac{\mu}{m} \lesssim 1. \tag{20}$$

The two capillary wavevectors defined by (19) are then real: the smectic free surface will relax exponentially on the sides of a perturbation. The corresponding capillary wavevectors, k_1 and k_2, are of the order of μ or m; equivalently, since $\mu m = \lambda h/\sqrt{3}$, we obtain

$$k_1 \lesssim k_2 \sim (\lambda h)^{-1/2} \tag{21}$$

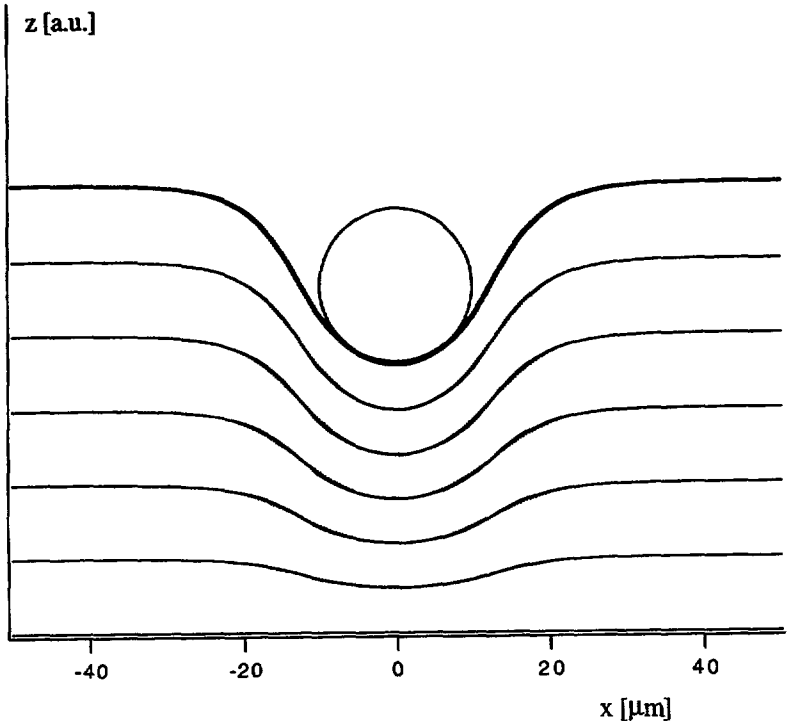

Fig. 2. — A cylinder with radius $R = 10\,\mu$m pushed against the free surface of a smectic drop with height $h = 2$ cm (the drop height is much reduced for the sake of clarity). The layers leave the cylinder's surface at $x_0 = 10\,\mu$m. For a well condensed smectic with $\lambda = 12$ Å, the bare capillary lengths are $\mu = 3.6\,\mu$m and $m = 3.8\,\mu$m, and the capillary wavelengths are $1/k_1 = 3.2\,\mu$m and $1/k_2 = 4.3\,\mu$m. The solid lines represent the free surface and bulk layers, according to our approximated model. The dotted lines represent the exact bulk elastic relaxation (cf. Eq. (4)), resulting from the free surface under consideration. The perfect agreement justifies our approximations.

5.1. Validity of the Theory. — According to (12), our linear theory lies just at the boundary of its validity domain $\lambda q^2 h \lesssim 1$. For wavevectors $q \sim (\lambda h)^{-1/2}$ however, the linear relaxation approximation (13) is still good, as it implies less than 7% of relative error. Nevertheless, one must verify that the exponential functions in (18) do not interfere to build wavevectors q much smaller than k_1 and k_2. This is indeed possible under certain boundary conditions. For instance, our theory does not apply to smectics within capillary tubes of width less than $(\lambda h)^{1/2}$ It applies however well to our starting problem of the relaxation of a free surface perturbation, as illustrated in Figures 2 and 3. Figure 2 shows the distortion produced by a cylinder that is pushed against the free surface of a smectic material. The cylinder is assumed to provide tangential boundary conditions for the layers. This might be realized by coating the cylinder's surface with silane or any surfactant providing homeotropic alignment of the nematic director [1]. The free surface relaxation involves on each side of the cylinder two exponential functions that allow to match the height and the tangent of the contact point. The solid lines represent the shape of the free surface and bulk layers within our approximation. The dotted lines represent the exact bulk elastic relaxation given by (4), that would result from the free surface under consideration. The almost perfect concordance between the solid

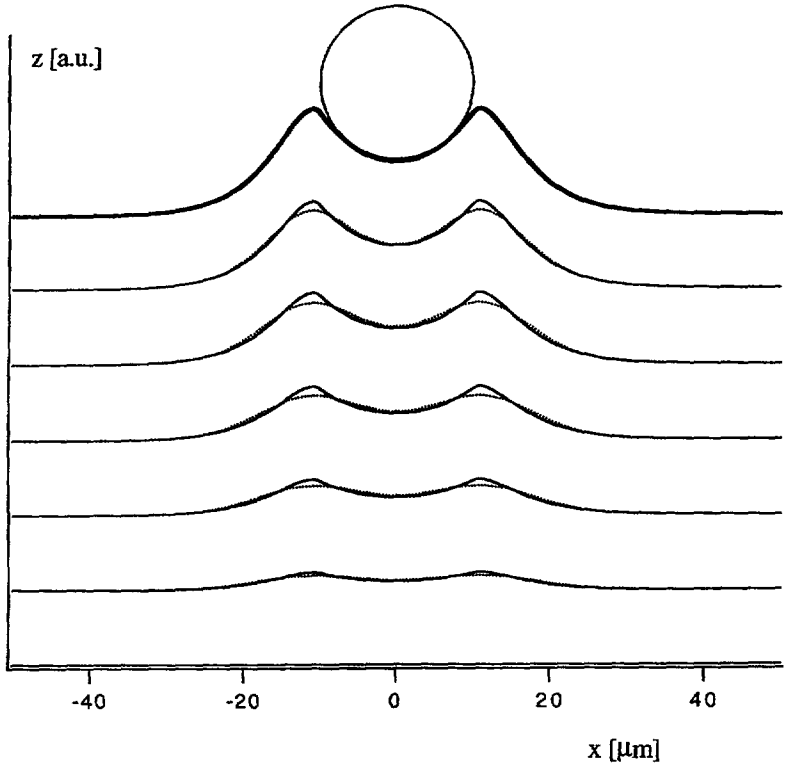

Fig. 3. — The cylinder is now dragging the free surface to which it adheres (same data as in the previous figure). The agreement between the solid and the dotted lines is less good as higher frequency distortions have appeared.

and the dotted lines shows that our approximation is excellent in this case. Figure 3 shows the same cylinder now dragging the free surface to which it is assumed to adhere. This might be realized by applying an upward vertical force on the cylinder, *e.g.*, by means of a magnetic field acting on a magnetic cylinder to get a tunable force. The interference between the exponential functions implies now distortions with higher wavevectors. Comparison between the solid and dotted lines shows that the approximation is less good; however, the qualitative behavior of the surface is probably still correct.

5.2. Effect of a Surfactant or a Magnetic Field. — Let us consider a smectic-A drop with a low surface tension $\Gamma < \sqrt{KB}$. It might be realized for instance by introducing a surfactant inside the smectic or by using a drop surrounded by a surfactant isotropic liquid. Another possibility is to apply on the drop a destabilizing magnetic field H. Indeed, we shall show that this is somehow equivalent to lowering the surface tension. The magnetic energy density in the limit of weak bulk distortions is

$$f_{\mathrm{m}} = -\frac{1}{2}\chi_{\mathrm{a}} H^2 \left(\frac{\partial U}{\partial x}\right)^2 \tag{22}$$

For a destabilizing field, χ_a is positive. The magnetic energy yields the contribution $\chi_a H^2 B^{-1} \times \partial^2 U/\partial x^2$ in the left-hand side of equation (2). As a consequence, the inverse penetration depth of a mode with wavevector q is multiplied by $\sqrt{1-\chi_a H^2/(Kq^2)}$: in the presence of the field, the layer distortions tend to propagate deeper in the bulk. Hence, we can safely use the linear approximation (14) as previously. This gives the contribution

$$F_m = -\int dx \frac{1}{6}\chi_a H^2 h\, u'^2 \tag{23}$$

to (15), *i.e.*, the following renormalization:

$$\Gamma \to \Gamma - \frac{1}{3}\chi_a H^2 h. \tag{24}$$

Let us consider the limit of very small Γ's, for which

$$\frac{\mu}{m} \gg 1, \tag{25}$$

From (19), we deduce that the capillary wavevectors become

$$k_\ell \sim \frac{1}{\sqrt{2}} \frac{1+(-1)^\ell i}{\sqrt{\mu m}}, \tag{26}$$

where $i^2 = -1$. Thus, whereas μ/m varies much as Γ is reduced, the actual capillary lengths remain of order $(\lambda h)^{1/2}$ This is due to the fact that curvature and dilation are strongly coupled, because bulk distortions must relax on the substrate. The capillary lengths however have become *complex*, which means that a surface perturbation should relax with damped oscillations. This prediction would be interesting to check experimentally. For strong fields, the renormalized Γ can become negative and the capillary wavevectors purely imaginary: a free surface instability will develop. According to (24), this will occur when $\chi_a H^2 h$ is of order Γ, *i.e.*, for magnetic fields with coherence length [1]

$$\xi_H \sim \mu. \tag{27}$$

With μ in the micron range, this value is accessible experimentally.

5.3. Vicinity of a Second-Order Nematic Transition. — Close to a second order phase transition, the dilation elastic modulus B tends to zero. Hence the characteristic length m diverges, yielding now

$$\frac{\mu}{m} \ll 1. \tag{28}$$

In this case, we have simply

$$k_1 \sim \frac{1}{\sqrt{2}} m^{-1} \quad \text{and} \quad k_2 \sim \sqrt{2}\mu^{-1} \quad (k_1 \ll k_2), \tag{29}$$

The actual capillary lengths coincide with the bare ones. The relaxation of a free surface perturbation will therefore involve first a *short*, then a *long* capillary length. If the heights of the boundaries are not constrained, we expect that the short scale relaxation will transform the boundary contact angle into the "Young angle" [13] matching the remaining long scale exponential relaxation.

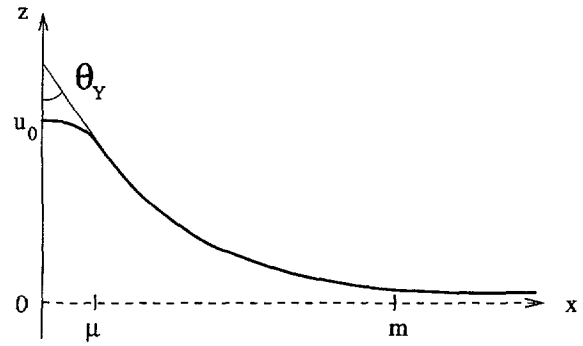

Fig. 4. — The free surface of a smectic-A wetting a wall that forces a perpendicular anchoring of the smectic layers. Usually, the free surface relaxes exponentially with two comparable decay lengths. In the vicinity of a second-order nematic transition, however, the decay length are well separated. As a result, the actual zero contact angle is transformed to the Young angle after a "foot" of width μ.

Let us work this out in a precise case. Consider for example a smectic-A free surface contacting a boundary wall treated in such a way that the smectic layers are constrained to orient normally to the wall's surface (Fig. 4). This might be realized by a surface treatment, such as mechanical rubbing, providing a planar alignment of the nematic director [1]. Let us assume that the smectic tends to wet the wall, *i.e.*, that the difference in surface free energy between the dry and the wet wall is $\Delta\gamma > 0$. According to (18), the profile of the free surface is given by

$$u(x) = u_0 \left[\frac{k_2}{k_2 - k_1} \mathrm{e}^{-k_1 x} - \frac{k_1}{k_2 - k_1} \mathrm{e}^{-k_2 x} \right], \tag{30}$$

where u_0 is the meniscus height. In the limit $k_1 \ll k_2$, the total energy of the smectic given by (15) is

$$F(u_0) \sim \frac{1}{2} \left(\frac{1}{6} K h k_1^2 k_2 + \frac{1}{2} \Gamma k_1 + \frac{1}{2} \frac{B}{h} \frac{1}{k_1} \right) u_0^2, \tag{31}$$

If the meniscus height is free to adjust, the equilibrium u_0 is obtained by minimizing $F(u_0) - \Delta\gamma\, u_0$. This yields

$$u_0 = \frac{1}{k_1} \frac{\Delta\gamma}{(1/6) K h k_1 k_2 + (1/2)\Gamma + (1/2) B h^{-1} k_1^{-2}}. \tag{32}$$

From the values of k_1 and k_2 given by (29), the first term of the denominator is of order K/λ, much smaller that Γ since λ diverges close to a second-order phase transition. As the third term of the denominator is exactly equal to $\Gamma/2$, the whole denominator is equal to Γ. It follows that the angle extrapolated from the long scale exponential, $\theta = k_1 u_0$, is the Young angle

$$\theta_Y \sim \frac{\Delta\gamma}{\Gamma}, \tag{33}$$

For a simple van der Waals liquid, a similar phenomenon exists: the macroscopic Young contact angle is only established after a microscopic foot, the shape of which is dictated by short range interactions [13]. In the smectic case, what exactly happens is that the curvature energy is negligible in the long scale exponential and the dilation energy $\propto u^2$ plays the same role as gravity for a simple liquid.

From the beginning, we have neglected the possibility or the molecules to tilt with respect to the layers' normal. This approximation is correct as long as the distortion scales are large compared to $\lambda_\perp = \sqrt{K/B_\perp}$ where $B_\perp$ is the tilt elastic constant. Usually, as $B_\perp \sim 10^6$ cgs, $\lambda_\perp$ is a microscopic length and the approximation is justified. However, $\lambda_\perp$ diverges as $B_\perp \to 0$ in the vicinity of a second-order transition. Our model will be valid as long as $\mu \gg \lambda_\perp$, *i.e.*, as long as $B_\perp \gg \Gamma/h$. This is not a drastic condition. With $\Gamma/h \sim 10 - 100$ cgs for a 1 cm high drop, we have $\Gamma/h \ll 10^6$ cgs, hence our model is correct except *very* close to a second-order nematic transition.

6. Smectic Film

Let us now consider a smectic film with a macroscopic thickness $\sim h$. Usually, free standing films are very thin [7–10], but there is no difficulty in principle to realize thick films, *e.g.*, with $h \sim 100\,\mu$m. In the case of thin films, a *microscopic* length similar to μ was already introduced to discuss X-rays roughness measurements of monolayers [14] and to discuss the exact shape of adherent membranes [15]. It is necessary however that h be macroscopic in order that the lengths (17) play the role of capillary lengths.

The film is identical to the slab described in Section 3. To discuss its capillary properties, let us make the same linear approximation as in the case of the drop. We thus replace (4) by

$$U(x,z) \sim u(x)\left(1+\frac{z}{h}\right) - v(x)\frac{z}{h}. \tag{34}$$

For distortions in the range (12), the above approximation implies a maximum error better than 2% when u and v are locally opposite, or better than 11% when u and v are locally equal. Within this approximation, the total free energy F of the film, given by (5), can be expressed in the real space as

$$F = \int \mathrm{d}x \left\{ \frac{1}{6}Kh(u''^2 + v''^2 + u''v'') + \frac{1}{2}\frac{B}{h}(u-v)^2 + \frac{1}{2}\Gamma(u'^2+v'^2) \right\} \tag{35}$$

6.1. Capillary Modes. — The Euler-Lagrange equilibrium equations associated with (35) define a system of two *coupled* linear differential equations of fourth order. It can be diagonalized by setting

$$\overline{u}(x) = \frac{1}{2}\left[u(x)+v(x)\right] \tag{36a}$$

$$\epsilon(x) = \frac{1}{h}\left[u(x)-v(x)\right]. \tag{36b}$$

$\overline{u}(x)$ describe the *medium layer* of the film, and $\epsilon = \partial U/\partial z$ describes the *film dilation*, which is constant throughout the film in the approximation (34). In terms of these new variables, the energy of the film writes as

$$F = \int \mathrm{d}x \left\{ \frac{1}{6}Kh\left(3\overline{u}''^2 + \frac{h^2}{4}\epsilon''^2\right) + \frac{1}{2}Bh\epsilon^2 + \Gamma\left(\overline{u}'^2 + \frac{h^2}{4}\epsilon'^2\right) \right\} \tag{37}$$

which yields the now *decoupled* equilibrium equations

$$\frac{3}{4}\mu^2\overline{u}^{(\mathrm{IV})} - \overline{u}'' = 0 \tag{38a}$$

$$\frac{1}{4}\mu^2 m^2 \epsilon^{(\mathrm{IV})} - m^2\epsilon'' + \epsilon = 0 \tag{38b}$$

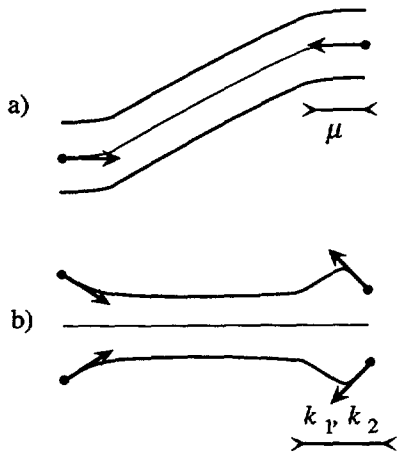

Fig. 5. — Capillary modes of a thick smectic-A film. a) The "average" mode describing the medium layer $\overline{u}$. Only the *curvature*-capillary length μ is involved. The film average layer makes a straight segment after screening the tangent boundary conditions. b) the "differential mode" describing the dilation ϵ of the film. Its behavior is similar to that of the surface distortion in a smectic drop.

The film has thus two independent modes: an *average* mode corresponding to $\overline{u}$ (Fig. 5a) and a *differential* mode corresponding to ϵ (Fig. 5b). These modes are analogous to the curvature and peristaltic modes of thin films. The shape of the medium layer, solution of (38a), is given by

$$\overline{u}(x) = A + Bx + Ce^{\frac{2}{\sqrt{3}}\frac{x}{\mu}} + De^{-\frac{2}{\sqrt{3}}\frac{x}{\mu}} \tag{39}$$

The dilation of the film, solution of (38b), is given by four exponential functions or sine-exponential functions, as in (18), with

$$k_\ell^2 = \left[1 + (-1)^\ell \sqrt{1 - \frac{\mu^2}{m^2}}\right] 2\mu^{-2} \tag{40}$$

A thick smectic film has therefore three independent capillary lengths: $\mu\sqrt{3}/2$, the curvature-capillary length relative to the medium layer, and k_1 and k_2, the mixed curvature and dilation-capillary lengths relative to the layer's dilation. The latter are $\sqrt{2}$ times larger than in the case of the drop. In the differential equations (38), one can define *eight* boundary conditions: the positions and tangents of the four edges of a piece of film. Making use of (36), these conditions can be transformed into conditions on the boundary values of $\overline{u}$ and ϵ and their derivatives. Note that if the lower free surface is free to adjust, by minimizing with respect to its boundary conditions, some dilation of the film will in general appear, even if only the upper free surface is constrained.

6.2. Effect of a Surfactant or a Magnetic Field. — As in the case of the drop, Γ can be reduced by using a surfactant or by applying a magnetic field. In the latter case, using (22), (34) and (36), one obtains the film magnetic energy

$$F_m = -\int dx \, \frac{1}{6}\chi_a H^2 h \left(3\overline{u}'^2 + \frac{h^2}{4}\epsilon'^2\right) \tag{41}$$

yielding a renormalization of Γ of the order $-\chi_a H^2 h$. Reducing Γ does not affect much the "differential" mode. Indeed, due to the similitude between (19) and (40), the moduli of the capillary wavelengths remain $\sim (\lambda h)^{1/2}$, *i.e.*, mesoscopic. However, reducing Γ has a strong effect on the "average" mode, since the capillary length μ diverges as $\Gamma \to 0$. Hence, the capillary length relative to the relaxation of the medium layer becomes *macroscopic* and should be easily observable by means of optical microscopy.

6.3. VICINITY OF A SECOND-ORDER NEMATIC TRANSITION. — As m increases while $B \to 0$, one of the capillary length of the "differential" mode, k_1^{-1}, becomes macroscopic, whereas the other one, k_2^{-1}, remains mesoscopic. The capillary length of the "average" mode remains also mesoscopic.

6.4. CONFOCAL FILMS. — Smectic textures sometimes consist of perfectly equidistant layers, as for instance in focal conic defects [2, 16, 17]. Textures made of equidistant layers have no dilation and are called "confocal", since all layers share a common curvature center locus, also called *focal* surface [18]. Let us investigate under which condition a thick smectic film will be confocal.

A confocal film has equidistant layers. In the frame of weak distortion elasticity, this means that $\partial U/\partial z = 0$: all the layers have the same identical shape. The problem we are interested in can thus be addressed in the following terms: if we impose some boundary conditions on the upper free surface of a film — while the lower one is free to adjust — under which conditions will the lower free surface follow exactly the upper one? This problem is reminiscent of the "cicatrisation length" introduced by de Gennes for a thin Van der Waals film deposited on a rough substrate [13]. To answer the above problem, let us consider a variation δv_q at fixed u_q. It yields a variation of the film energy per unit length (6)

$$\delta f = \sum_q q^2 \, \delta v_q^* \left\{ \left(\Gamma + \sqrt{KB} \coth \lambda h q^2 \right) v_q - \frac{\sqrt{KB}}{\sinh \lambda h q^2} u_q \right\} \tag{42}$$

By minimizing, we find that the equilibrium v_q for a fixed u_q is given by

$$v_q = \frac{u_q}{\cosh \lambda h q^2 + \dfrac{\Gamma}{\sqrt{KB}} \sinh \lambda h q^2} \tag{43}$$

In the range $\lambda h q^2 \lesssim 1$, each mode is thus reduced by a factor $f(q) = 1 - (\Gamma/\sqrt{KB})\lambda h q^2 + \mathcal{O}(\lambda^2 h^2 q^4)$. This shows that the shape of the lower surface relaxes in order to reduce its surface energy principally, then the film curvature energy in second approximation. In general, films will *not* be confocal since their capillary wavevectors are in the range $q \sim (\lambda h)^{1/2}$. However, if $\Gamma \ll \sqrt{KB}$, the second order term in $f(q)$ becomes negligible, and the film will be fairly confocal in the whole capillary range $q \lesssim (\lambda h)^{1/2}$. The same result holds if the film is subject to a destabilizing magnetic field, which reduces the effective Γ, as previously shown. In such conditions, a film with one unconstrained free surface will be confocal. The dilation ϵ is then zero, and the upper free surface $u(x)$ is identical to the medium layer $\overline{u}(x)$. Hence it displays a pure-curvature capillarity as predicted in reference [11], described by equation (38a) in which μ is now macroscopic.

7. Conclusion

How does the free surface of a smectic-A relax on the sides of a perturbation? In usual smectic drops, the layers are parallel to the free surface on the upper side, and to a flat substrate on the

lower side. Hence, any surface perturbation induces a bulk distortion that must relax at the substrate level. If the distortion wavelength, d, satisfies $d \ll (\lambda h)^{1/2}$, with h the drop thickness and λ a characteristic microscopic length [1], the surface perturbation relaxes exponentially over the depth $\sim d^2/\lambda$, *before* reaching the substrate. In this case the bulk distortion energy simply renormalizes the free surface energy [1]. For larger perturbations with $d \gtrsim (\lambda h)^{1/2}$, the distortion propagates up to the substrate as an hyperbolic sine function, whose characteristic length is then larger than the drop thickness. This allows for a dramatic simplification: the bulk relaxation can be fairly approximated by a *linear* function. We showed that the surface relaxation on the sides of a perturbation always belongs to the second class. Indeed, a system possessing only "surface tension" would spread up to the surface boundaries the distortion on the sides a perturbation (or relax over the gravitational length $\sim$ 1mm): this yields bulk distortions reaching the substrate for every reasonable drop.

In the approximation that the bulk distortions relax *linearly* up to the substrate, the elastic free energy of the drop can be expressed as a simple functional of the free surface shape. In a self-consistent analysis, we deduce that the natural surface relaxation length around a perturbation in a smectic drop is of order $(\lambda h)^{1/2}$ The free surface shape is governed by a fourth-order linear differential equation in which two bare capillary lengths appear: $\mu = [(K/\Gamma)h]^{1/2}$ a *curvature*-capillary length, and $m = [(\Gamma/B)h]^{1/2}$ a *dilation*-capillary length. For drops thickness in the range 0.01–1 cm, these length are comparable and in the range 0.1–5 μm. The actual capillary lengths (resulting from the differential equation) are combinations of the bare ones of the same order. A surface perturbation relaxes with two exponential functions on each side of the perturbation, allowing to match four boundary conditions: the height and the tangent of the free surface at each boundary. The validity of our hypothesis of linear bulk relaxation has been checked in various situations. It is correct in general but can possibly be wrong when the exponential relaxations interfere to build short wavelength distortions. We have discussed the case of low surface tensions or, equivalently, the application of a destabilizing magnetic field. We found that the surface relaxation should involve damped oscillations still with characteristic length $\sim (\lambda h)^{1/2}$. This would be interesting to check experimentally. In addition, magnetic fields with coherence length smaller than μ should produce free surface instabilities. In the vicinity of a second-order smectic-A to nematic transition, the two capillary lengths coincide with the bare ones and the *dilation*-capillary length becomes macroscopic.

The linear bulk relaxation approximation can also be applied to thick smectic films with two free surfaces. It yields a system of coupled fourth-order differential equations that can be diagonalized in terms of two independent variables: the medium layer shape $\overline{u}$ and the film dilation ϵ. The "average" mode $\overline{u}$ is governed by a fourth-order capillary equation that involves *only* the *curvature*-capillary length μ. Hence, to join two points at different heights with arbitrary tangent boundary conditions, a smectic film will first screen the tangent boundary conditions exponentially over the length μ, then build a straight segment in between. The "differential" mode ϵ is governed by an equation almost identical to that of the drop: the film dilation relaxes with two exponential waves with characteristic length $\sim (\lambda h)^{1/2}$ on each side of the perturbation. A perturbation exerted on one free surface, the upper one for instance, will in general excite both the "average" and the "differential" mode. For low surface tensions, or equivalently if a magnetic field is applied on the film, the boundary screening becomes macroscopic as μ diverges. In addition, the film dilation is not excited if only one free surface is concerned by the perturbation. In this case, the film builds a "confocal" texture as all layers follow identically to the medium one $\overline{u}$ [11]. For the "differential" mode the conclusions are the same as in the case of the drop. Finally, analysing the free surface relaxation around floating objects could provide interesting measurements of solid–smectic adhesion energies.

Acknowledgments

The author acknowledges fruitful discussions with I. Dozov, G. Durand, C. Marques, D. Morse, P. Pincus and M. Turner. This work was partially supported by the CNRS, the NSF under grant DMR-93-01199 and MRL Program under grant DMR-9123048, and a by a NATO fellowship.

References

[1] de Gennes P.G. and Prost J., The Physics of Liquid Crystals (Clarendon Press, Oxford, 1993).
[2] Friedel G. and Grandjean F., *Bull. Soc. Fr. Miner. Crist.* **33** (1910) 192.
[3] Williams C., PhD thesis (Université Paris-Sud, France, 1976).
[4] Fournier J.B., Dozov I. and Durand G., *Phys. Rev. A* **41** (1990) 2252.
[5] Bechhoefer J., Lejcek L. and Oswald P., *J. Phys. II France* **2** (1992) 27.
[6] Galerne Y. and Liebert L., *Phys. Rev. Lett.* **64** (1990) 906.
[7] Young C.Y., Pindak R., Clark N.A. and Meyer R.B., *Phys. Rev. Lett.* **40** (1978) 773.
[8] Pindak R., Young C.Y., Meyer R.B. and Clark N.A., *Phys. Rev. Lett.* **45** (1980) 1193.
[9] Pieranski P. *et al. Physica A* **194** (1993) 364.
[10] Kraus I., PhD thesis (Université Paris-Sud, France, 1995).
[11] Fournier J.B., Virga E.G. and Durand G., *Europhys. Lett.* **28** (1994) 109.
[12] Durand G., *C. R. Hebd. Seances Acad. Sci. Ser. B* **275** (1972) 629.
[13] de Gennes P.G., *Rev. Mod. Phys.* **57** (1985) 827.
[14] Daillan J., Bosio L., Harzallah B. and Benattar J.J., *J. Phys. II France* **1** (1991) 149.
[15] Kozlov M.M. and Markin V.S., *J. Phys. II France* **1** (1991) 805.
[16] Bouligand Y., *J. Phys. France* **33** (1972) 525.
[17] Kléman M., *J. Phys. France* **38** (1977) 1511.
[18] Salmon G., Analytic Geometry of Three dimension (Chelsea, New York, 1952).