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SMECTIC MENISCUS AND DISLOCATIONS*

J.-C. Géminard[a], R. Hołyst[a,b] and P. Oswald[a]

[a] Laboratoire de Physique de l'Ecole Normale Supérieure de Lyon
69364 Lyon cedex 07, France

[b]Institute of Physical Chemistry PAS and College of Science
Dept.III, Kasprzaka 44/52, 01224 Warsaw, Poland

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In ordinary liquids the size of a meniscus and its shape is set by a competition between surface tension and gravity. The thermodynamical process of its creation can be reversible. On the contrary, in smectic liquid crystals the formation of the meniscus is always an irreversible thermodynamic process since it involves the creation of dislocations (therefore it involves friction). Also the meniscus is usually small in experiments with smectics in comparison to the capillary length and, therefore, the gravity does not play any role in determining the meniscus shape. Here we discuss the relation between dislocations and meniscus in smectics. The theoretical predictions are supported by a recent experiment performed on freely suspended films of smectic liquid crystals. In this experiment the measurement of the meniscus radius of curvature gives the pressure difference, Δp, according to the Laplace law. From the measurements of the growth dynamics of a dislocation loop (governed by Δp) we find the line tension ($\sim 8\times10^{-8}$ dyn) and the mobility of an elementary edge dislocation ($\sim 4\times10^{-7}\mathrm{cm}^2$ s/g).

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1. Introduction

Molecules in smectic-A liquid crystalline phase are arranged in liquid like layers parallel to each other. The distance between the layers $b \approx 30$Å is set by the length, l, of the liquid crystalline molecules ($l \leq b \leq 2l$). Dislocations, known from the theory of solid structure [1], also appear in smectic liquid crystalline phases [2a]. If we try to change the thickness of a smectic sample we have to create elementary edge dislocations (Fig. 1). As we see on the figure, an elementary dislocation changes the thickness of the sample by one

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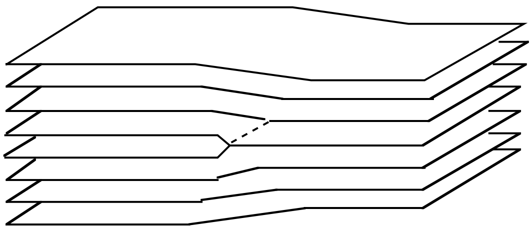


Fig. 1. The schematic representation of an elementary edge dislocation.

layer; in principle one can have edge dislocations that change the thickness of the sample by more than one layer. If we take a closed contour around the dislocation shown in Fig. 1 and trace the vector normal to the layers $\boldsymbol{n}$ we find irrespective of the shape of the contour that:

$$\oint \frac{\hat{\boldsymbol{n}}}{b} d\boldsymbol{l} = 1 \,, \tag{1.1}$$

The dislocation deforms the sample around it. The deformations affect the sample at large distances as is evident from Eq. (1.1) and Fig. 1. In the bulk sample one finds [2b] the deformation $u(x,z)$ as a function of the distance z perpendicular to layers and x parallel to the layers and perpendicular to the dislocation line located at $x=0$ and $z=0$:

$$\begin{aligned} u(x,z) &= \mathrm{sgn}(z)\left(\frac{b}{4\pi}\int dq \exp\left(-\lambda q^2|z|\right)\frac{\exp\left(iqx\right)}{i(q-i0^+)}\right) \\ &= \frac{d}{4}\mathrm{sgn(z)}\left(1+\mathrm{erf}\left(\frac{x}{2\sqrt{\lambda|z|}}\right)\right) \,, \end{aligned} \tag{1.2}$$

The deformation is the vertical displacement of the layers from their flat equilibrium position. Here $\lambda = \sqrt{K/B}$ is the characteristic length scale in smectics given by the ratio of two elastic constants characterizing smectic elasticity: K is the elastic constant for undulations and B is the elastic constant for compression of the layers. Typically (but not always) we have $K = 10^{-6}$ dyn and $B = 5 \cdot 10^7$ dyn/cm^2 and λ of the same order of magnitude as the smectic period b. In the bulk sample the energy of the deformation does not depend on the location of dislocation. The situation is more complicated when in the system we have a free surface. In this case, the deformation and its energy depends on the location of the dislocation with respect to the surface [3]. In order to predict the equilibrium location of dislocation we compare the typical energies for the surface and bulk deformations. The typical energy scale per unit area is given in the bulk smectic by $\sqrt{KB} \sim 7$ dyn/cm, which is smaller than the typical energy scale for surface deformations given by smectic (S)-air (A) surface tension $\gamma_{\rm SA} \approx 25$ dyn/cm^2. It means that dislocations are repelled from a free surface in smectics [3], contrary to the case of ordinary solids.

In order to observe edge dislocations it is necessary to obtain a well oriented sample of smectic liquid crystals. It is achieved most spectacularly in freely suspended smectic liquid crystal films. The films are obtained by smearing a smectic phase with a wiper across a fixed aperture made in a solid substrate. In this way we obtain a film attached to the aperture with two free surfaces and layers parallel to them. This technique used by most researchers and invented by Friedel 70 years ago [4] has been considerably improved by Pierański [5]. He used a rectangular frame of *variable* area, allowing precise control (up to one molecular layer *i.e.* 30 Å) of the film thickness. Although it is difficult to choose the thickness of the smectic film in advance, nevertheless one can change the thickness after the creation of the film by *e.g.* rapidly stretching the film to reduce the number of layers by 1–2 layers. Fig. 2 shows a schematic structure of the film near the edge of the aperture. It is clear that the formation of the meniscus must involve creation of dislocations. It is only in this way that we can change the thickness of the film. The dislocations are shown schematically in the middle of the meniscus, where they locate because of the repulsion by the free surfaces.

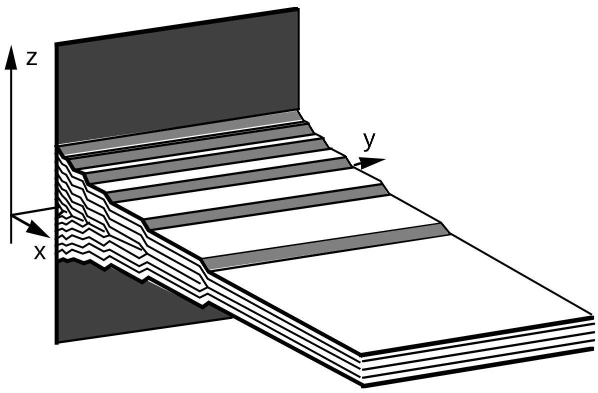


Fig. 2. The schematic and idealized picture of the smectic meniscus close to the wall (after Ref. [5]). The dislocations are stabilized in the mid-plane due to the repulsion form the two free surface shown in the picture.

2. Formation of the meniscus

Let us consider a smectic system with a flat wall located at $x = 0$. First of all in the process of the formation of the meniscus we create a certain number of dislocations, N. We assume that the height of the meniscus at the bounding wall $h(x=0)=Nb/2$ is fixed by this number. By contrast the height is set in ordinary liquids by the capillary forces and gravity *i.e.*

$$h(x=0)=\sqrt{2\frac{\gamma_{\rm LA}(1-\sin\theta)}{\rho g}}\,. \tag{2.1}$$

Here $\gamma_{\rm LA}$ is the liquid air surface tension, ρ is the density, g is the gravitational acceleration and θ is a contact angle given by

$$\cos\theta=\frac{\gamma_{\rm WA}-\gamma_{\rm WL}}{\gamma_{\rm LA}}\,. \tag{2.2}$$

The following surface tensions appear: $\gamma_{\rm LA}$, $\gamma_{\rm WL}$ and $\gamma_{\rm WA}$, where W stands for wall, L for liquid and A for air. This is a first clear difference between these two systems. Needless to say the creation of the meniscus in an ordinary liquid can be obtained in a reversible process. In smectic this is not true and any process leading to the creation of the meniscus must be irreversible. This is due to the creation of dislocations (which must involve friction in the system).

Finally we note that in an ordinary liquid the final state of the meniscus will be always the same irrespective of the particular process leading to its creation. This is not true in smectics, where different processes may lead to the differences in the final state. In one process we may create N dislocations and in the other $N+1$ and although we may reach the same thermodynamic state the meniscus will be different in these two cases.

Another difference between ordinary liquids and smectics is more subtle, yet it determines the shape of the smectic meniscus. It is a common knowledge that due to mechanical equilibrium, an isotropic liquid in contact with air must have the same pressure as the air providing its interface is flat [6]. It has not however to be so in a smectic A liquid crystal because its layers are elastic and can support a normal stress σ which will equilibrate any pressure difference providing it is not too large. This remark is crucial for understanding the *metastability* of smectic free-standing films of arbitrary thicknesses: indeed, the number m of layers in a film can be controlled one by one from m very large up to $m=2$ [5,7]. The pressure difference contributes to the tension τ of the film

$$\tau=2\gamma_{\rm SA}+\Delta pH\,, \tag{2.3}$$

where $H=h(x=\infty)=mb$ is the thickness of the film far from the meniscus, $\Delta p=p_{\rm air}-p_{\rm smectic}$ and $\gamma_{\rm SA}$ is the surface free energy of the smectic-air interface. This law has been found experimentally by Pierański *et al.* [5,8].

If the system is not coupled to a reservoir of particles at the same pressure as $p_{\rm air}$, the stress will be permanent and its value will be directly related to the total volume of the meniscus. The stress in the film is related to the shape of the meniscus. If we recall the Laplace law, we find that the meniscus is circular with a radius R given by

$$R = \frac{\gamma_{\rm SA}}{\Delta p} \,. \tag{2.4}$$

It is assumed here that the stress $\sigma = B\partial u/\partial z$ caused by *external forces* in the meniscus vanishes because of the dislocations. This is true providing that we can neglect the interactions between the dislocations. Since the dislocations are located in the same plane their interactions can be neglected [2b]. By contrast the pressure difference Δp in the film free of dislocations is equilibrated by the stress normal to the layers. Now it follows from Eq. (2.4) that the height of the meniscus $h(x)$ should satisfy the equation

$$(h(x) - R)^2 + (x - x_f)^2 = R^2 \,, \tag{2.5}$$

for $x < x_f$, where $x_f = \sqrt{R^2 - (h(0) - R)^2}$ (it assumed that the contact angle between the meniscus and the film is zero). Now if the volume, V, of the meniscus as well as the number $N = 2h(0)/b$ of dislocations are fixed, the relation between the pressure difference and the size of meniscus can be found from the following equation:

$$2 \int dy \int_0^{x_f} dx h(x) = V \,, \tag{2.6}$$

where it is assumed that the wall is parallel to the y direction. The factor 2 comes from the fact that we have two free surfaces in a freely suspended film (top and bottom) as shown in Fig. 2. This mathematical form for the shape of the meniscus 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 mathematical form:

$$h(x) = \sqrt{2(1 - \sin\theta)}\alpha \exp(-x/\alpha) \,, \tag{2.7}$$

where α is the capillary length given by $\sqrt{\gamma_{\rm LA}/(\rho g)}$ and θ is defined by Eq. (2.1). In this case the pressure difference across the curved meniscus is compensated by the gravity. Taking typical numbers we find $\alpha = 0.2$ cm and this is a reason why we can see the meniscus in capillaries. In smectics the height of the meniscus is usually of the order of micrometers and therefore gravity can be neglected. In the next section we present the experimental evidence of the aforementioned theoretical speculations.

The problem presented here, although concerned with smectics, is rather general and can be applied to other complex liquids such as columnar mesophases. It is the elastic behavior of complex liquids that leads to unusual forms of the meniscus. It does not mean of course that meniscus in each case will be circular. Indeed we can imagine situations when it is not circular even in the smectic phase. Nonetheless we will show an experimental evidence that the scenario presented above can be realized experimentally [9].

3. Freely suspended smectic liquid crystal film: experiment

To produce a film, a droplet of smectic A liquid crystal is expanded on a deformable frame Fig. 3(a) [5]. A mixture of 80wt% of 8CB and of 20wt% of 10CB is used. This frame is placed in an oven whose temperature is controlled within 0.01°C. The film is observed with a video camera via reflected light microscopy (Fig. 3(b)). Its thickness is obtained by measuring its reflectivity as a function of the light wavelength λ [10].The reflectivity depends on the thickness of the film H, on its refractive index n and of λ, and reads:

$$R(\lambda) = \frac{I(\lambda)}{I_0(\lambda)} = \frac{\sin^2 \frac{\delta}{2}}{\frac{(1-A)^2}{4A} + \sin^2 \frac{\delta}{2}}\,, \tag{3.1}$$

where

$$\delta = \frac{4\pi n H}{\lambda} \quad \text{and} \quad A = \left(\frac{n-1}{n+1}\right)^2 . \tag{3.2}$$

$I(\lambda)$ and $I_0(\lambda)$ are the intensities of, respectively, the reflected and the incident light. The microscope is also equipped with a monochromator and an optical chopper. The intensity of the reflected light is measured by a photodiode connected to a lock-in amplifier. Thus, the accurate measurement of $R(\lambda)$ allows us to determine the film thickness $H = mb$ where m is the number of layers and b the thickness of a molecular layer.

In order to observe the meniscus, a stainless steel needle of diameter 0.5mm (initially coated with the liquid crystal and approached from under) is passed through the film. The profile of the meniscus surrounding the needle is determined by observing in monochromatic light the fringes that form at mechanical equilibrium Fig. 5(a) : Eqs (3.1)–(3.2) shows that the thickness of the film is increased by $\lambda/4n$ between bright and dark lines. The meniscus profile is shown in Fig. 5(b). As predicted in Sec. 2 it is circular. We immediately note that its size (10 μm typically) is two orders of magnitude smaller than in ordinary fluids (Sec. 2). As we have observed it is possible to discern between the exponential profile given by Eq. (2.7) and the circular

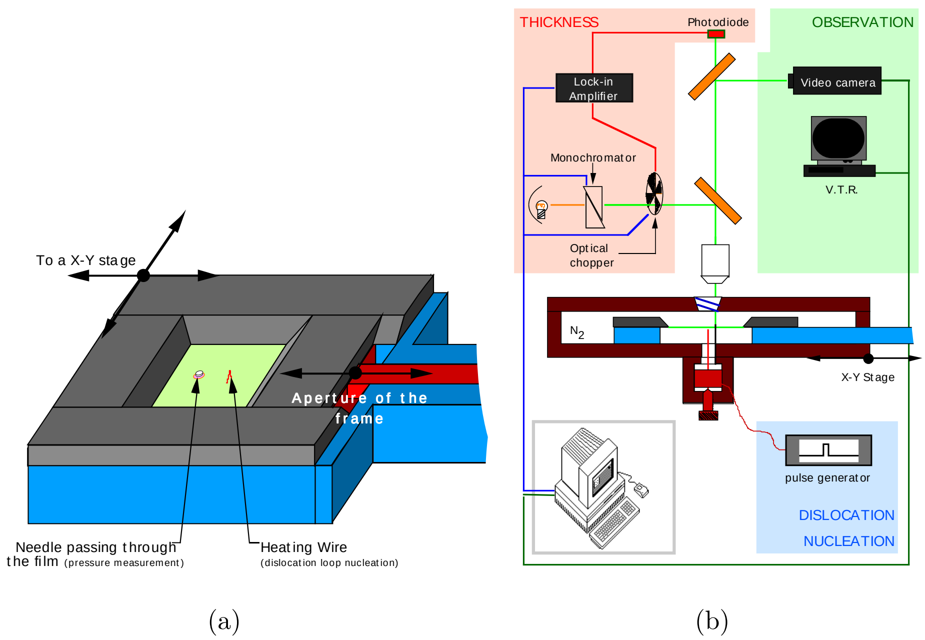
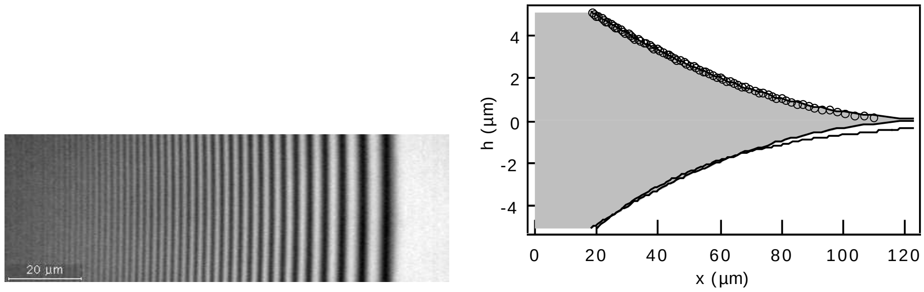


Fig. 3. (a): The schematic representation of the frame. One of its sides can be moved in order to change the aperture of the frame. The heating wire lies about $50\mu m$ below the film. The needle is used to create a meniscus in the film in place where it can be easily observed. The meniscus forms around the needle. (b): The schematic representation of experimental setup. The frame is placed in a temperature controlled oven. The film is observed through the reflecting microscope. The reflectivity as a function of the incident wavelength is determined with the help of a computer controlled monochromator. An optical chopper and a lock-in allow to exclude parasitic light.

profile defined by Eq. (2.5). We find that the profile of the meniscus is circular and the pressure difference between the inner and the outer of the film is usually about 100–1000 dyn/cm^2, same as obtained by measuring the film tension given by Eq. (2.3) [5]. Note that from the form of the meniscus we in fact obtain only the ratio of $\gamma_{\rm SA}/\Delta p$. However there are many independent methods for measuring smectic–air surface tension [5,11,12]. It is found to be between 20 dyn/cm and 30 dyn/cm and therefore using these experiments we can estimate the pressure difference from the measured ratio of the surface tension and pressure difference. The simple explanation for this phenomenon is related to the fact that smectics are elastic media. The pressure difference across the flat surfaces of the film can be well understood by imaginating the film as the system of two walls connected by a spring.

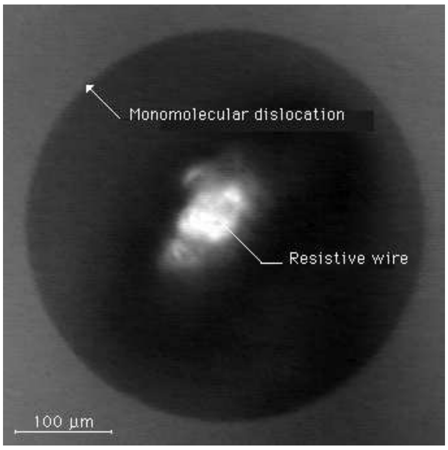


(a) (b)

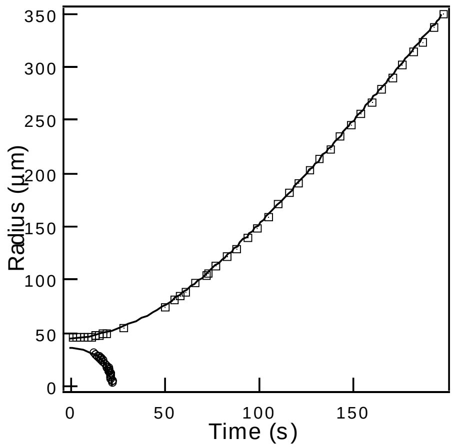
Fig. 4. (a): The fringes observed around the needle in the microscope. The homogeneous film corresponds to the right part of the photograph while the needle (not visible) is on the left. The fringes are due to the change of the thickness of the meniscus. (b): Experimental meniscus profile, obtained form the observed fringes (a). The circles correspond to the experimental data. The solid line is the theoretical profile given by Eq. (2.5). For comparison, the best exponential interpolation given by Eq. (2.7) is shown as the dotted line for the lower surface.

The pressure difference as we cross the wall is equilibrated by the force exerted by the squeezed spring. That is why flat smectic films can support a pressure difference. Of course in thermal equilibrium with its vapor the smectic is not subjected to any strain and, therefore, the pressure difference is zero. One experiment is however not sufficient to claim that indeed there is a pressure difference between the interior of the film and the air above the flat surface. After all, the shape of the meniscus can be fortuitously fitted to the form given by Eq. (2.5), although the physical origin of this shape can be different from the stated above. The second experiment performed simultaneously concerns the creation of dislocations loops in the smectic film as described below.

It is possible (without removing the first needle) to approach a heating wire (a 2mm-long segment of a Cu-Constantan wire of 100μm in diameter, of resistance 0.14Ω, and folded in its middle) very close to the film (typical distance $\sim 50\mu$m) (Fig. 3). The nucleation of an edge dislocation loop is obtained by sending a pulse of very short duration ($\sim 100\mu$s, $\sim$ 2V) through the wire. If the voltage is well adjusted (within a few mV) it is possible to systematically nucleate elementary loops of edge dislocation. Increasing the intensity of the pulse 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



(a)



(b)

Fig. 5. (a): Photograph of a monomolecular dislocation loop created with the heating wire (see Fig. 3(a)). (b): The radius of the dislocation shown in (a) as a function of time. Starting from a homogeneous film, a pulse is sent through the heating wire and a first dislocation loop is nucleated. When its initial radius is smaller than the critical radius it collapses (lower curve). The system returns to its initial state. A second pulse is sent through the heating wire. The power is chosen so that the initial radius is now larger than the critical radius and the loop grows (upper curve). From the fit to the theoretical profile given by Eq. (3.4) (solid line), we deduce $E(0) \sim 8.10^{-7}$ dynes and $\mu \sim 4.10^{-7}\mathrm{cm}^2.\mathrm{s/g}$.

to create a loop decreases when the temperature is increased and increases when the thickness of the film is decreased. We also observed that the film reflectivity locally changes during a fraction of a second (one or two video frames) just before the nucleation process. This contrast variation corresponds to a relative increase of the optical path nH of a few 10^{-3} which we simply attribute to the increase of the ordinary index n when the temperature locally increases.

The nucleation process of the dislocation loop is thermally activated. The heating wire locally induces smectic-A-nematic phase transition. Near the phase transition the barrier for the nucleation of the dislocation loop is sufficiently small [9].

Let us now 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 submitted to its line tension E (energy of dislocation associated to the deformations) [13] which tends to reduce its size. Assuming that indeed we have the pressure difference in the film Δp the dynamics of the dislocation is described by the following equation:

$$\frac{b}{\mu}\,\frac{dr}{dt} = -\frac{E}{r} + b\Delta p\,. \tag{3.3}$$

Here μ is the mobility of dislocation loop. The pressure difference Δp tends to enlarge the radius of the loop, while E tends to decrease the size of the loop. Indeed, the thickness of the film is smaller inside the loop and the pressure is less in the film than in the air. The large loops will grow while the small loops will collapse. The critical radius is given by $r_c = E/b\Delta p$. This equation is a 2D analog of the equation for the gas bubble in the liquid phase. Large bubble would grow due to the pressure difference while small bubbles would collapse due to the action of the surface tension. Setting the time constant $t_c = \mu r_c/\Delta p$ we find the following solution of the equation:

$$\frac{r(t)-r(0)}{r_c} + \ln\left(\frac{r(t)-r_c}{r(0)-r_c}\right) = \frac{t}{t_c}\,. \tag{3.4}$$

If the initial radius $r(0) > r_c$ the loop grows and in the limit of large t moves with a constant speed given by $V = r_c/t_c = \mu\Delta p$. Here r_c is measured independently and t_c can be deduced from the asymptotic limit. There are no adjustable parameters in this solution. The comparison of Eq. (3.4) with experiment is shown in Fig. 5(b). The same equation is applied to the case when $r(0) > r_c$ (growth) and when $r(0) < r_c$ (collapse of the loop). We deduce from this experiment, the line tension E and the mobility μ of an elementary edge dislocation in a film of a well known thickness at a given temperature. For instance, we found in the mixture 8CB/10CB at $T = 34°$ C (*i.e.* 4° C below the nematic–smectic A transition temperature), $E = 8\times 10^{-8} dyn$ and $\mu = 4\times 10^{-7}$ $\mathrm{cm^2sg^{-1}}$. This value of the mobility is comparable to that found previously in thick samples of 8CB via creep experiments [14,15].

4. Summary

We have carefully measured the shape of smectic meniscus, the critical radius of dislocation loop and the mobility of dislocations. We have shown that smectics can support a static pressure difference across flat surfaces and that the shape of the meniscus is circular due to this constant pressure difference. The values of the mobility and the line tension are in accordance with the theoretical predictions and experimental values of mobility found in the creep experiments [13–15]. We remark at the end that if the meniscus is coupled to a particle reservoir after some time (of the order of days) the slow flow accompanied by permeation would tend to reduce Δp leading to

$R \to \infty$. In a finite system the dislocations would close and eventually the meniscus would disappear.

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