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Surface tension measurements in freely suspended bubbles of thermotropic smectic liquid crystals

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We present an experimental technique for the inflation of freely suspended films of thermotropic smectic liquid crystals to macroscopic bubbles. These bubbles have many properties in common with well known lyotropic soap bubbles, but on the other hand represent a completely different class of material with different physical properties and new phenomena. We describe the generation of such smectic bubbles and compare their physical properties with those of lyotropic soap bubbles. The measurement of inner pressure versus curvature is used for the determination of surface tensions of the smectic materials.

1. Introduction

Freely suspended films of smectic liquid crystals have long been known to represent ideal systems for the study of highly ordered liquid crystalline (LC) layers. They can easily be drawn in dimensions up to several square centimetres. Since their first description [1–3], their static and dynamic properties have been extensively studied experimentally as well as theoretically. These studies have been basically restricted to planar films, with a few exceptions. The idea to bend such smectic films by pressure to perform dynamic experiments was first reported by Oswald [4]. The deflection of planar films by acoustic fields was studied, e.g. by Pieranski *et al.* [5, 6], and Galerne *et al.* reported bent films on nematic droplet surfaces [7].

If a planar smectic free standing film is exposed to air pressure from one side, the film surface bends towards the low pressure side to establish an equilibrium between pressure difference and surface tension. In a similar way, it is possible to inflate the planar film into a bubble, like soap bubbles from lyotropic material. This analogy has been pointed out already by Pieranski [5]. In this paper we describe the set-up for the production of smectic bubbles, discuss some of their properties observed in the experiment, particularly differences and similarities to lyotropic bubbles, and we demonstrate the determination of the smectic surface tension from the measurement of inner pressure versus bubble diameter.

2. Experimental

Experiments have been performed with two materials. The standard smectic material 4-*n*-octyl-4′-cyano-biphenyl (8CB) was used for investigations of the SmA phase. The commercial mixture (ZLI 4237-100, E. Merck) of low molecular weight LC was used for the investigation of the ferroelectric SmC* phase.

For the generation of the bubbles, we used tapered glass capillaries with openings of a few millimetres. A freely suspended film is drawn on the opening at the tapered end. The opposite end of the glass capillary is connected to a syringe and a specially designed and very sensitive pressure gauge (figure 1). The pressure gauge consists of a pair of oblique glass pipes, parallel to each other and connected at their lower ends, filled with liquid. It is suitable for pressure difference measurements with an accuracy of 1 Pa. In order to protect the films from the influence of convective air flow, the system is encapsulated in a transparent box of approximately $8 \times 8 \times 8\,\mathrm{cm}^3$.

A controlled volume of air is slowly injected into the closed system by means of the syringe. After relaxation of the system, the pressure in the bubble is measured and the film deformation is recorded by means of a video camera with a HAMAMATSU controller for contrast enhancement. The images of the generated bubbles are processed digitally to determine their shapes and to extract their curvatures. The experiments are performed at ambient temperature.

3. Results

Figure 2 shows two characteristic images of smectic bubbles of (*a*) ZLI 4237-100 in the ferroelectric SmC* phase and (*b*) 8CB in the SmA phase. The experiments (and the figure) show that the deformed film surfaces are perfectly spherical within experimental error. This can

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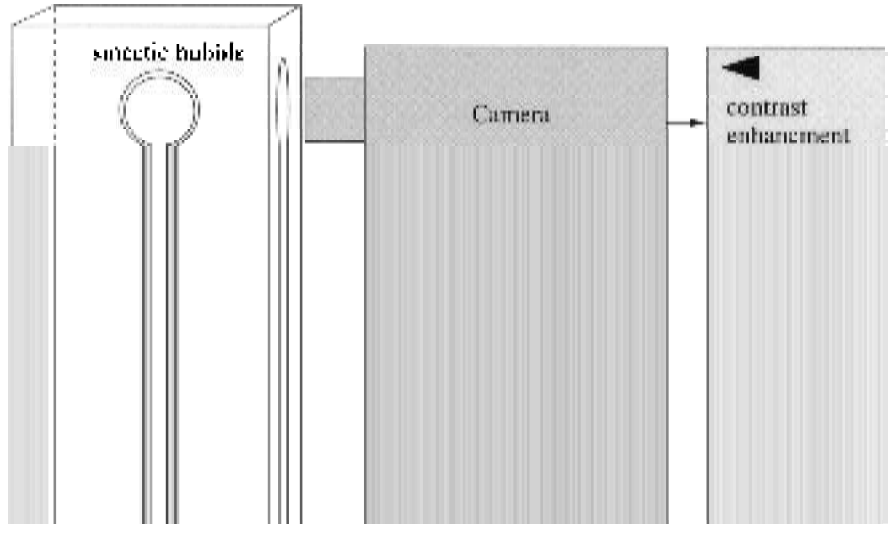


Figure 1. Experimental set-up for the generation and study of smectic bubbles. The pressure is measured with an oblique capillary gauge; the radius is obtained photometrically. The bubble is illuminated with diffuse white light and observed in transmission by means of a video enhanced CCD camera.

be expected when the simple standard relation

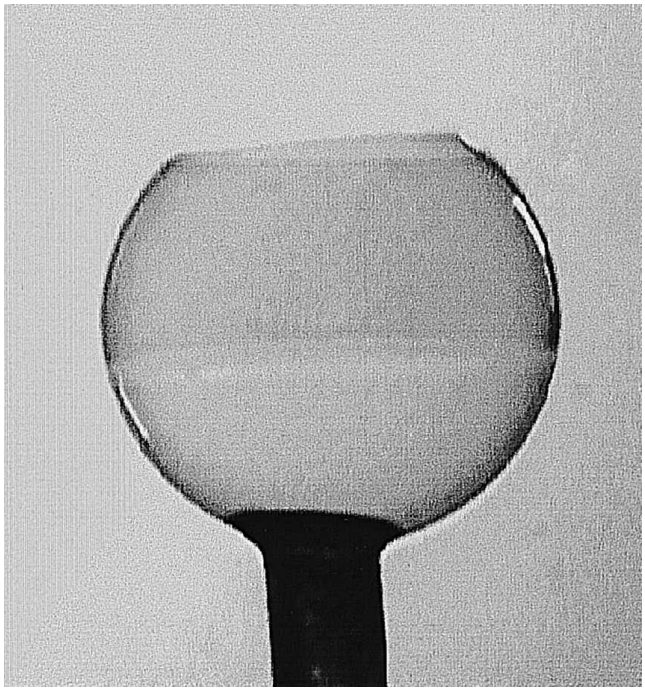
$$p = \frac{4\sigma}{R} \qquad (1)$$

holds between the surface tension σ, the pressure difference p and the local radius of curvature R of the membrane, which is equivalent to the radius of a spherical bubble (we note that the deformed film has two surfaces, the inner and the outer, both contributing to the surface energy).

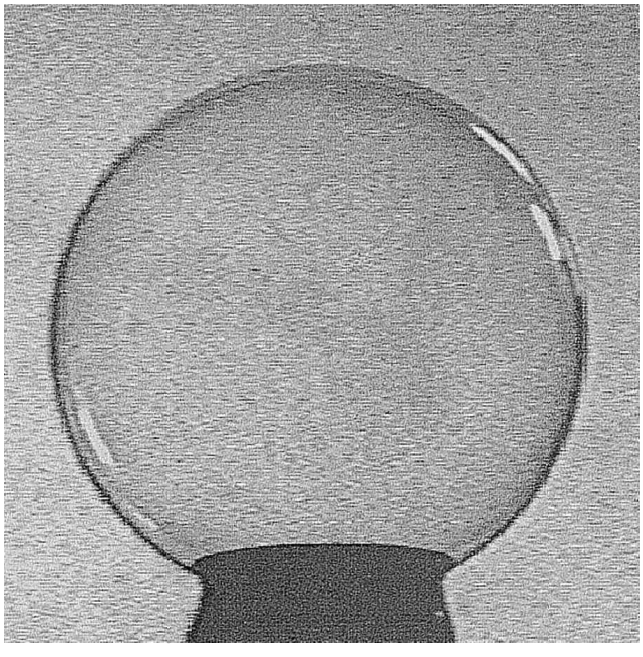
Starting with a planar film corresponding to $R = \infty$, the excess of pressure in the capillary is zero. On increasing the pressure, the film bends and the curvature increases as shown in the inset of figure 3. A minimum radius of curvature $R_{\min}$ and correspondingly a maximum pressure $p_{\max}$ are reached when the bubble diameter is equal to the capillary mouth diameter, the film then forming a half sphere. On further inflation, the inner pressure decreases again with decreasing curvature of the film as the bubble diameter increases. Figure 3 shows the normalized theoretical inner pressure characteristics as a function of the bubble height, measured from the capillary mouth.

During the inflation, the film surface constantly grows. When the bubbles are inflated slowly, the film thickness remains constant. Material is supplied by a constant flow from the excess of material in the smectic LC bulge at the capillary. We are able to produce stable bubbles in this way up to several centimetres in diameter. The film thickness is easily controlled by the speed of inflation. Thin bubbles consist of only a few molecular layers, while bubbles with membrane thickness of several micrometers can also be produced when the bubble is generated sufficiently slowly. Even in the case of nanometer film thickness, the bubbles are stabilized by the layered film structure in the same way as planar films. An interesting feature is seen in figure 2 (*a*): after fast inflation of the bubble, a 'hole' with a considerably lower film thickness has been created at the bubble surface. This hole consists of a spherical cap of stationary shape with definite boundaries and diameter. In some ways this is analogous to the holes and islands in planar films described earlier [5]. The hole can float freely on the bubble surface; due to gravitational forces, the holes move to the bubble top, while islands of excessive layers flow to the bottom of the bubble in a few seconds. Homogeneous thin membranes are produced as follows: after rapid inflation, a hole of sufficient size is generated; then, the bubble is deflated again until the thinned area covers the whole sphere uniformly.

An interesting feature of the spherical bubbles is the direct access to the surface tension by simple geometrical measurements, equation (1). The results of quantitative surface tension measurements are presented in figures 4 (*a*) and 4 (*b*). The figures show the difference between the inner and outer pressures of the bubbles versus their curvature for the smectic A sample of 8CB and for the smectic C* phase of ZLI 4237 at room temperature, respectively. A fit to equation (1) is shown by the solid lines. We note that curvature error increases somewhat for small radii in the vicinity of the capillary mouth because the bubble shape is reduced there to a half-sphere and the radius of curvature is not as exactly measurable as in complete spheres. For large radii $R > r_m$, influences of the capillary can be completely neglected and the determination of shape and radius are



(*a*)



(*b*)

Figure 2. Thermotropic smectic bubbles (contrast enhanced images) of the (*a*) SmC* phase of ZLI 4237 ($T = 27°C$, $p = 29{\cdot}2$ Pa, 7·3 mm bubble diameter) and (*b*) the SmA phase of 8CB ($T = 26°C$, $p = 25{\cdot}6$ Pa, 7·5 mm bubble diameter). Note the cap-shaped 'hole' in the bubble (*a*) which has moved, driven by buoyancy, to the top of the sphere.

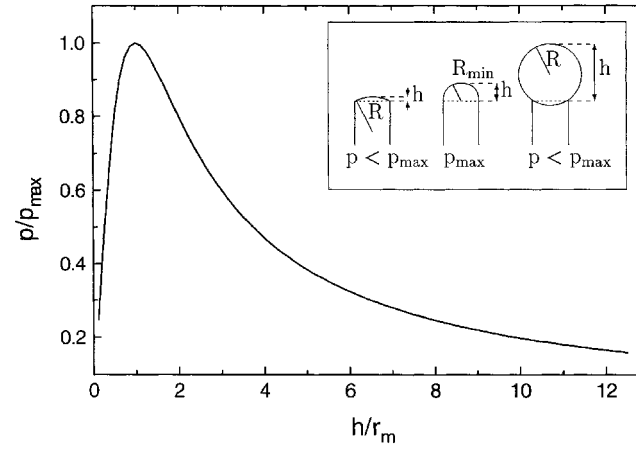


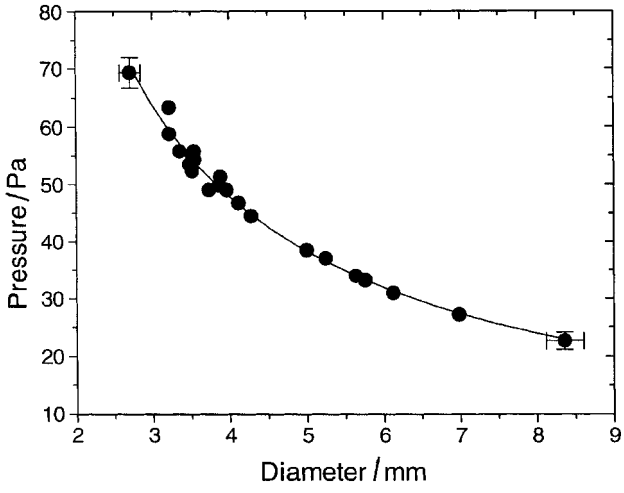
Figure 3. Pressure difference, p, between the inner and outer pressures of a bubble as a function of the bubble height measured from the capillary opening with radius r_m (theory). Scaled height $h' = h/r_m$ and pressure $p' = p/p_{max} = pr_m/(4\sigma)$ have been introduced. R is the bubble radius defined by equation (1) in text.

very reliable. The only fit parameter of the data in figures 4(*a*) and 4(*b*) is the surface tension σ; all data points are in good agreement with the expected pressure curve within experimental accuracy. The fit provides directly the surface tensions of the smectic material, and we have found $\sigma = (26{\cdot}8 \pm 0{\cdot}3) \times 10^{-3}$ N m^{-1} for ZLI 4237 at 26·8°C and $\sigma = (24{\cdot}0 \pm 0{\cdot}3) \times 10^{-3}$ N m^{-1} for 8CB at 26°C.

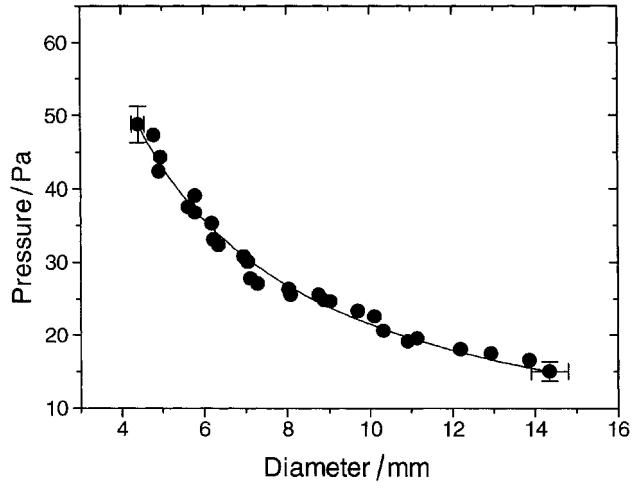
A possible dependence of σ upon the membrane thickness would lead to two effects. First, the curvature would be different for regions of different film thickness; the bubble geometry itself is a very sensitive measure of tiny changes in surface tension. In the experiments, we have not detected any differences in curvature within an experimental error of about 2% between holes and islands on the same bubble. The second effect would be through a constant growth of the domains of lower surface tension at the expense of energetically less favoured regions. Such growth processes however are very slow and only a qualitative estimate is possible. A slight decrease of the surface tension for thin regions might be indicated by the fact that holes grow slowly (a few percent on the timescale of hours).

4. Discussion and summary

A basic difference between smectic bubbles and lyotropic soap bubbles is their internal structure and stability. The stability of soap films with respect to membrane fluctuations basically determines their life time. A comprehensive treatment of the fluctuations in closed and open membranes has been given by Brochard [8] and David [9]. The systems considered here belong



a) 8CB



b) ZLI 4237

Figure 4. Inner excess pressure of (*a*) SmA 8CB bubbles at $T = 26°C$ and (*b*) ferroelectric SmC* bubbles of ZLI 4237 at $T = 26{\cdot}8°C$. The solid lines are fitted curves with surface tensions $\sigma = 24{\cdot}0 \times 10^{-3}$ N m^{-1} and $\sigma = 26{\cdot}8 \times 10^{-3}$ N m^{-1}, respectively.

to open systems, where excess of material at the capillary can flow into the film or vice versa.

The inner and outer surfaces of the bubble are exposed to fluctuations. To a first approximation, we can perform a harmonic analysis and distinguish between two types of fluctuations—symmetric (in phase) and antisymmetric undulations of the opposite membrane surfaces. While the first have a minor influence on the film stability, the latter lead to critical local thickness changes and finally to film rupture. The second type of fluctuations, accompanied by a continuous flow and transfer of water within the layer, makes the lyotropic soap bubbles unstable. Without special precautions, loss of water may change the composition of the lyotropic systems and thins the film. In thermotropic smectic bubbles, the film thickness is given by the number of smectic layers, and the second type of fluctuations which changes the film thickness will be negligible. Flow processes can be completely suppressed when the bubble is in equilibrium, and the smectic bubble represents a stable structure.

It should be mentioned that although elastic splay and flexoelectric terms enter the free energy of the curved smectic layers, influences of both contributions on the bubble curvature can be completely neglected in the observed films. They are orders of magnitude smaller than contributions of the surface tension and even that of gravitation. Gravitational forces can lead to the directed motion of holes and islands on the film. However, their influence on the bubble shape is negligible. The pressure acting on the bubble due to its weight is proportional to the film thickness. A 1 μm film adds approximately 1 μm of water column (0 01 Pa) to the pressure, and thus deformations of the bubble in the gravitational field are below experimental resolution.

We have to mention here that the surface tension of liquid crystals is actually not a scalar, but a tensor quantity [10]. In the experiment, we have not however detected any indications which require the introduction of more than a scalar surface tension.

In summary, we propose here a straightforward experiment to measure surface tensions of smectic phases using a classical technique. We consider our approach more direct than the various approaches described in the literature, for example in [5, 11, 12]. The reported surface tension can be compared with results by other authors obtained by different methods. For example, Eberhardt and Meyer designed a specially modified Wilhelmi balance to measure surface tensions [12]. Their 8CB value is slightly larger than ours. In making a comparison of both methods, one may conclude that surface tension data obtained in both approaches are of comparable accuracy. The approach of Eberhardt and Meyer certainly has the advantage of very accurate current measurements, but the geometry, in particular at the film edges, is relatively complex and an absolute systematic offset may influence the data. In contrast, the geometry of the bubbles is well defined, the influences of the glass capillary, in particular at high bubble diameters, can be completely neglected and we consider that absolute systematic errors are very small. On the other hand, the pressure measurements at present limit the accuracy of our experimental set-up.

Investigations of electric field effects and a description of the dynamics of smectic bubbles are in progress.

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