

Surface tension of free-standing liquid-crystal films

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A unique system has been developed and used to determine the surface tension of free-standing films of three different liquid-crystal compounds in the smectic phases. The results obtained have been found to be in good agreement with the existing experimental data. For one of these compounds, the surface tension has also been found to be independent of film thickness from over 100 down to only 2 molecular layers.

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Free-standing liquid-crystal films constitute an easily realizable experimental system that has proven to be extremely rich and, in recent years, such films have been the focus of intensive experimental and theoretical studies. The films exist as layered structures in which the film normal is parallel to the layer normal and the interlayer spacing is roughly the length of the highly anisotropic liquid-crystal molecules (≈ 25 Å long and ≈ 5 Å in diameter). Under the appropriate conditions, uniformly thick films from many hundreds of layers down to only two molecular layers can be readily prepared and remain stable for days. Furthermore, their substrate-free nature allows the complicating effects due to any sample-substrate interaction to be avoided. The study of these films is therefore important to our understanding of the impact of reduced dimensionality and the importance of surface effects. In an effort to more fully understand the films and their free surfaces, we have developed a simple method of determining the surface tension of such free-standing films. In this paper, the experimental system will be presented and the results obtained will be shown to be in good agreement with the presently available data. It should be noted that the apparatus may be easily extended to determine the surface tension of virtually any sample that can be spread to form a free-standing film (lyotropes, polymers, soap solutions, etc.). Studies as a function of film thickness have also been included. Surprisingly, the surface tension has been found to be independent of film thickness from over 100 down to only 2 molecular layers.

The experimental system consists of an oven to regulate the sample temperature, a specialized film plate to support the free-standing film, and a video camera and frame grabber to facilitate the data acquisition. The film plate is located within the inner stage resistive heater of the oven [see Fig. 1(a)]. The temperature of the film plate is measured with a YSI 44011 thermistor and has been found to be stable to better than 10 mK. O-rings have been used to create a vacuum tight outer stage and ordinary plate glass windows allow optical access. A very flexible, and uniformly thin string (#8-0 surgical silk suture, 40 μm in diameter) is suspended between two small v grooves spaced 1.64 cm apart across the knife-edged hole cut into the center of the film plate. One end of the string is fixed to the plate and the other is attached to a mass that hangs freely so the string is straight when

no film is present [see Fig. 1(b)]. The sample is initially loaded around the right side of the film plate aperture and onto the string. The oven can then be evacuated and backfilled with $\frac{1}{4}$ atm of pure argon gas to provide a nonreactive thermal link between the heater and film plate.

The free-standing films are created by the motion of a spring-loaded cover glass slip across the opening in the film plate, roughly parallel to the suspended string. Because no sample is loaded to the left of the string, films were created only on the right side, suspended between the string and the edge of the film plate. At least 20 films could typically be created before breaking vacuum to replace the string, clean the oven with acetone, and load a fresh sample around the perimeter of the film plate and onto the string. Once the film had been spread, its thickness could be determined through a combination of methods. For films thinner than 12 molecular layers, the thickness could be determined exactly by employing a standard optical technique [1]. Thicker films display characteristic colors due to the interference effects of reflected white light and the thickness of these films can be determined to within 10% [2].

As mentioned above, the films are very stable and can be maintained for days, largely due to the existence of the surface tension generated by the film-vapor interfaces. While the surface tension stabilizes the film, it also acts to minimize the film area by deforming the string into the arc shown in Fig. 2. The deformation of the string is related to the strength of the surface tension. While

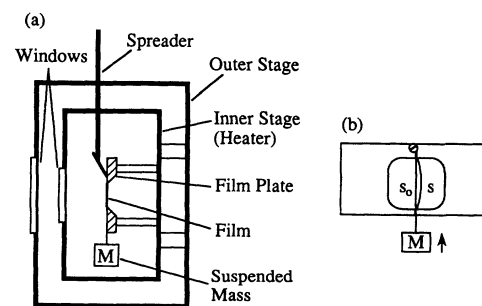


FIG. 1. Schematic of the sample oven side view (a) and film plate front view (b). When a film is present, the string is deformed from its straight configuration (s_0) into the arc (s), thereby elevating the mass.

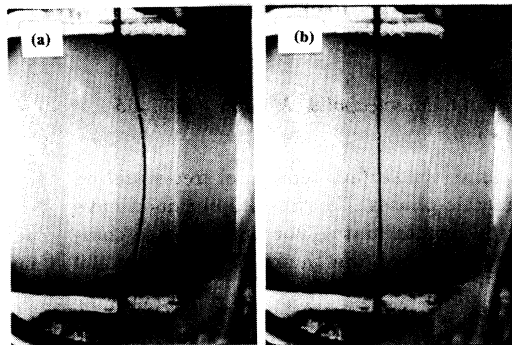


FIG. 2. Picture of the film plate with (a) and without (b) a film present. The film is approximately 1.64 cm by 0.75 cm by 100 Å. Because of the strong interference effects, the film in (a) appears transparent.

the deformation proved to be independent of relaxation time, to be consistent, each film was allowed to equilibrate for at least 15 min before the arc was captured on videotape. With the video system still in operation, the film was then ruptured by a sudden jerk of the spreader and the string was observed to immediately return to its relaxed, straight configuration. The geometry of the video system was checked by imaging a uniform grid and a small correction factor was included in our data analysis.

Once the deformed and straight string configurations have been captured on videotape, the determination of the film surface tension is straightforward. As the string is pulled inward, the suspended mass is elevated until equilibrium is achieved. The force balance equation describing this situation for a segment of the string arc with length $\delta l = R\delta\phi$ (see Fig. 3) may be written as $2\sigma_s R\delta\phi = 2T \sin(\delta\phi/2)$, where σ_s is the surface tension and T is the tension in the string. Because the film has two free surfaces, the total film tension is twice the surface tension. Since the mass of both the string and the film are negligible compared to the mass of the weights used (m_w), the string tension can be expressed as $T = m_w g + f_f$, where f_f accounts for any friction between the string and the lower v groove. Furthermore, since $\delta\phi$ can be taken to be small, the force balance equation can be written as $2\sigma_s R = m_w g + f_f$. The radius of curvature, R , can be easily determined from the videotape record using the geometrical relation $s_0/2R = \sin(s/2R)$, where s is the total arclength of the deformed string and s_0 is

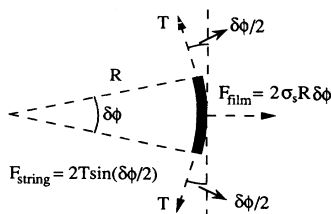


FIG. 3. Force diagram (not to scale) of a segment of the string with length $\delta l = R\delta\phi$.

the height of the film plate aperture ($s_0 = 1.64$ cm). The two remaining unknowns in the force balance equation are then the surface tension and the frictional force.

The importance of the frictional force was determined by measuring s and obtaining the radius of curvature for a series of four-layer-thick 65OBC smectic-A (Sm-A) films as a function of the mass of the suspended weight [3,4]. 65OBC is a member of the n -alkyl-4'- n -alkoxybiphenyl-4-carboxylate, nm OBC, homologous series. The four-layer films were all spread and maintained at 74.5 °C, roughly in the middle of the 65OBC Sm-A phase range. The radius of curvature versus mass results are plotted in Fig. 4. Since the force balance equation may be rewritten as $R = m_w g / 2\sigma_s + f_f / 2\sigma_s$, the linearity of this plot confirms the expected functional dependence on m_w . Fitting the data to a straight line yields values for the slope, $g/2\sigma_s = 23.9 \pm 0.6$ cm/g, and y intercept, $y_{int} = f_f / 2\sigma_s = 0.09 \pm 0.14$ cm. Taking $g = 980$ cm/sec², this fit therefore gives the surface tension $\sigma_s = 20.5 \pm 0.5$ dyn/cm. Moreover, the small value of the y intercept is consistent with the hypothesis that the frictional force is relatively unimportant. In fact, if friction is assumed to be negligible, the force balance equation reduces to $\sigma_s = m_w g / 2R$ resulting in the values σ_s (in dyn/cm) = 19.6, 20.4, 19.7, 20.4 for m_w (in g) = 0.0939, 0.1613, 0.2523, 0.3453, respectively. Since the reproducibility in the determination of σ_s for seven different four-layer-thick films was found to $\pm 5\%$, these results indicate that the frictional force can be ignored up to the error of this technique. The procedure can then be simplified considerably by requiring the use of only a single mass.

The argument for low friction is further supported by the fact that the results were unchanged as the film plate design evolved and the contact length between the lower v groove and the string was reduced by more than a factor of 3. Another check was performed when the #8-0, 40- μ m-thick suture was replaced with #6-0, 70- μ m-thick suture and the results were found to differ by less than our 5% experimental resolution. Because the bend and stretch elastic constants of the string should increase at least linearly with diameter, this suggests that little en-

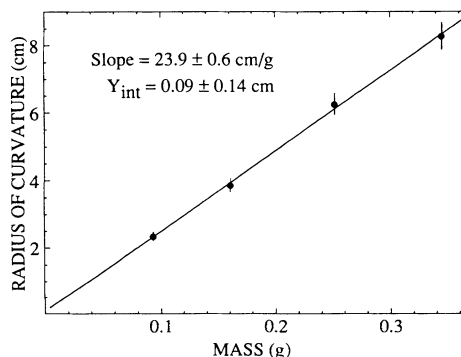


FIG. 4. Plot of R as a function of the mass of the suspended weight (solid circles). The data were fit to a straight line. The linearity of the data and the small value of the y intercept support the use of the simplified force balance equation: $R\sigma_s = m_w g / 2$.

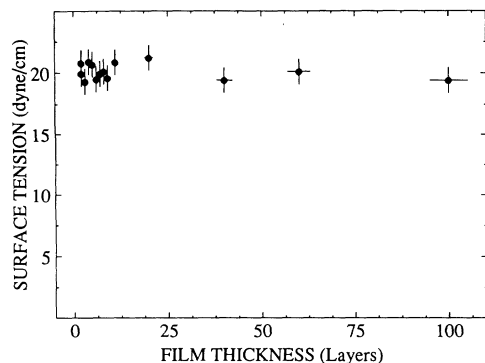


FIG. 5. Plot of surface tension versus film thickness showing that the surface tension is independent of film thickness to within our present experimental resolution ($\pm 5\%$).

ergy is involved in deforming the string itself, further confirming our experimental results.

Once the simplified relation, $\sigma_s = m_w g / 2R$, had been established, the system could be easily extended to measure the surface tension of Sm-A films of 65OBC as a function of film thickness. The results of such an experiment are plotted in Fig. 5. It is apparent that the values obtained are constant to within our experimental resolution ($\sigma_s = 20.3 \pm 1$ dyn/cm). This is a surprising result since, as the film thickness is reduced, the surface regions would be expected to overlap. Their interaction would presumably lead to larger values of the surface tension for the thinner films. On the other hand, the film tension and surface tension should be equivalent in an idealized two-dimensional film, and it is not clear what results would be expected from a film only a single molecular layer in thickness. The lack of any significant change for even the two-layer-thick films suggests that the mechanism responsible for the creation of the surface tension is very strongly localized at the film-vapor interfaces and therefore independent of film thickness.

This conclusion is supported by a recent low angle x-ray study on free-standing films of the liquid-crystal compound 70.7 (4-*n*-heptyloxybenzylidene-4-*n*-heptylaniline) [5]. The fluctuation amplitudes determined by the authors were found to sharply decrease (because of the surface tension) within one layer of the outermost surface layers. Because no measured values of the surface tension were then available, it was included as an important fitting parameter in their analysis. The value that was obtained through their fitting, $\sigma_s = 25 \pm 2$ dyn/cm, was also found to be independent of film thickness for the range of thicknesses studied (3–40 layers)

[6]. We have subsequently measured the surface tension of 70.7 near 72.5°C (in the surface stabilized Sm-*I*, interior Sm-*C* phase). Our results ($\sigma_s = 21 \pm 1$ dyn/cm) are in reasonably good agreement with those quoted above, obtained indirectly as fitting parameters. Moreover, since the value of σ_s was found to be very sensitive to the theoretical model used in the fitting of the x-ray data, our results should aid in the further analysis of this data and help to determine which of the theoretical models is most appropriate.

Using the method presented in this paper, we have also obtained values for the surface tension of Sm-A films of the compound CBOOA (*p*-cyanobenzylidene *p*'-*n*-octyloxyaniline). Our result, $\sigma_s = 28 \pm 1.5$ dyn/cm, compares well with those of Krishnaswamy and Shashidhar, who found $\sigma_s \approx 26$ dyn/cm at the sample-vapor interface of a suspended pendant drop of CBOOA [7]. Both this result and the agreement between our data on 70.7 and the presently available published data strongly support this measurement technique and instill confidence in our results on 65OBC.

In conclusion, we have developed a very simple method of directly measuring the surface tension of free-standing films to better than 5% and the details of the measurement have been presented. The system has been used to determine the surface tension of 65OBC, CBOOA, and 70.7 liquid-crystal films. The values obtained have been shown to be in good agreement with the available data to which they can best be compared. Studies as a function of film thickness have also been performed. Up to our 5% resolution, the surface tension of the 65OBC Sm-A phase has been found to be independent of film thickness, indicating that the mechanism responsible for the surface tension is highly localized. Finally, the experimental apparatus may also serve as a useful tool to gain knowledge about the surface tension and interfacial properties of a number of other physical systems in which free-standing films can be created.

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mined; if the mass is too small, the string has a tendency to be pulled out of the lower v groove and the reproducibility of the very large deformation is diminished. The masses discussed therefore roughly span the experimentally accessible range.

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It should be noted that, unlike the method presented in this paper, the pendant drop method does not require the creation of a free-standing film. The pendant drop method may, therefore, be used to obtain the surface tension in the nematic and isotropic liquid-crystal phases (phases in which free-standing films are not stable).

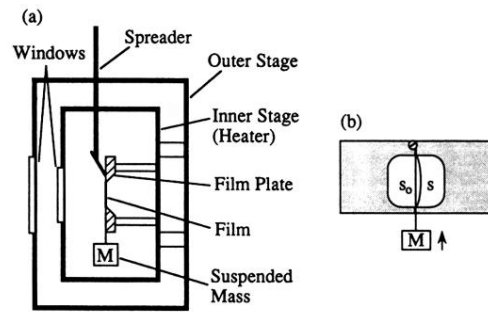


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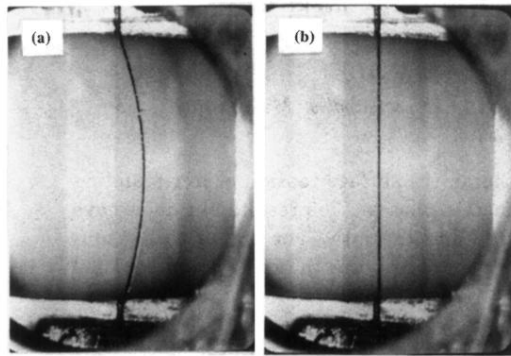


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