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Surface Tension of Several Liquid-Crystal Compounds in the Smectic-A or Smectic-A_d Phase

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Abstract. — After implementing a computer-enhanced imaging system in our newly established apparatus, we have achieved much higher resolution in measuring the surface tension of free-standing films in the smectic-A or smectic-A_d phase of seven different liquid-crystal compounds. The experimental results reveal two salient features: the relation of surface tension to thickness and the difference in surface tension between the smectic-A and smectic-A_d phases

1. Introduction

One of the important classes of liquid-crystal mesophases is that of the smectic phases which exist as layered structures with relatively weak interlayer interaction [1]. Much like a soap film on a ring, free-standing smectic liquid-crystal films [2] can be prepared and suspended over a hole cut into a film plate, provided that appropriate compounds are chosen [3]. In recent years, free-standing liquid-crystal films have been the focus of an intensive experimental, as well as theoretical research effort. These substrate-free films are extremely intriguing and may be characterized as a stack of 2D layers separated by roughly the length of the highly anisotropic liquid-crystal molecules (≈ 25 Å long and ≈ 5 Å in diameter). In free-standing films, the layer normals are parallel to the film normal. Because uniform free-standing films can be created from two to several hundred layers in thickness, they are uniquely suited to study the evolution from two-dimensional to three-dimensional behavior, effectively two-dimensional systems, the properties and effect of free surfaces and reduced dimensionality, etc. Moreover, because there are more than 15 different smectic phases, these free-standing films offer unique opportunities to study a variety of phase transitions in single smectic domain samples using a number of experimental probes. In an effort to more fully understand the films and their free surfaces, Pieranski *et al.* [4] and Stoebe *et al.* [5] have established relatively straightforward methods to determine the surface tension of free-standing films. Since the initial report of our effort

[5], significant improvement in the experimental resolution (approximately 5-fold) has been achieved. In this paper, we will present and discuss our measured surface tension data from seven different liquid-crystal compounds exhibiting smectic-A (SmA) or smectic-A_d (SmA_d) phases. In the SmA phase, the layer spacing (d) is approximately equal to the length of the molecule (l). In the SmA_d phase, the molecules form a bilayer structure and $l < d < 2l$. The salient features found in these experimental studies are the following:

- (i) within our experimental resolution ($\pm 1\%$), the surface tension is independent of film thickness [6]. If, however, the surface tension is assumed to be linearly dependent on the film thickness, then the coefficient (α) of the linear term obtained from our free-standing films is $< 3 \times 10^{-3}$ dyn/cm-molecular layer [7], consistent with the previously reported results of Pieranski *et al.* [4];
- (ii) despite the antiferroelectric bilayer ordering, the SmA_d phase exhibits a much larger value of the surface tension than the SmA phase, most likely due to the large dipole moment associated with the cyano group.

Because of the asymmetry in the binding at virtually all solid/vapor interfaces, the particles in the vicinity of the interface tend to be less ordered. A similar situation is encountered in ordinary liquid/vapor interfaces. In contrast, however, at the liquid-crystal/vapor interface the smectic ordering is enhanced since the centers of mass are fixed and the molecules are orientationally ordered. Thus the molecules at the "surface layer" tend to be more ordered than those in the bulk. This surface-enhanced ordering is responsible for an unusual phenomenon observed in liquid-crystal free-standing films. Upon heating, the melting of most ordinary materials starts at free surfaces. *However, in the case of liquid-crystal films, the melting originates at the interior layers* [8]. The surface tension is clearly an important quantity necessary to characterize this behavior, and many other physical phenomena related to the liquid-crystal/vapor interface. For example: i) de Gennes [9] discussed the lenticular fracture of a smectic liquid crystal in which knowledge of the surface tension is critical; ii) Lejcek and Oswald [10] presented theoretical calculations to illustrate the influence of surface tension on the stability of edge dislocations in SmA liquid crystals; iii) The surface tension constitutes an important fitting parameter for the X-ray scattering profile from thin SmA free-standing films [11, 12]. Thus numerous methods have been utilized to directly [4, 5, 13, 14] or indirectly [15, 16] measure the surface tension of liquid crystals

2. Measurement Technique

The experimental system consists of a temperature-regulated oven, a specially-designed film plate to support the liquid-crystal free-standing film, and a high-resolution imaging system. To implement our new imaging system and achieve higher sample temperature stability, we have constructed a new oven with two sets of windows (see Fig. 1). The details of our experimental principle have been reported in reference [5]. The basic idea of our measurement technique is that a rectangular free-standing film in a vertical orientation is created between a film plate and an extremely flexible string guided by a set of fine v-grooves cut into the film plate. The top end of the string (#8-0, 40- μ m-thick silk suture) is fastened to the film plate and a weight (M) is attached to the lower end of the string (see Fig. 1b). Surface tension causes the film to minimize its surface area. As a result, the string will be deformed into an arc with a radius of curvature dependent on the surface tension of the film and the mass of the suspended weight. A typical set of photos with and without a film present in the right half of the opening is shown in Figure 2.

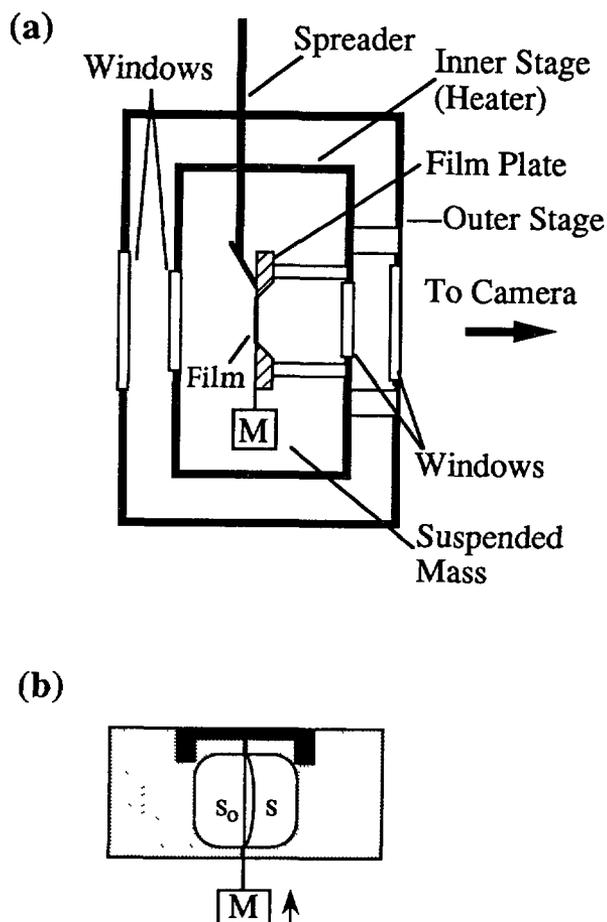


Fig. 1. — Schematic of the sample oven side view (a) and film plate front view (b). For ease of imaging the string, two sets of windows are utilized in this new oven design. When a film is present, the string is deformed from its straight configuration (s_0) into the arc (s), thereby elevating the mass (M).

In equilibrium, the film surface tension (γ_s) is directly related to the radius (R) of the curvature of the string and the mass (m) of the weight,

$$2\gamma_s R = mg + f_f. \quad (1)$$

Here f_f accounts for any frictional force between the string and the lower v-groove. The factor of 2 accounts for the two free surfaces of the film. At a given temperature and for four different masses of the weight, we prepared four 4-layer films and measured the respective dependence of R on m . A linear relation between R and m with a zero intercept (within our resolution) leads us to conclude that the friction f_f can be neglected [5]. The flexibility of the #8-0 string has also been checked by comparison with larger diameter sutures [5]. In this experimental approach, the ability to measure the radius of curvature (R) with sufficiently high resolution is the determining factor of the accuracy of the surface tension. Significant improvements in the resolution (by about a factor of five) of measuring R have been achieved by designing a new imaging and data analysis scheme. After spreading, the film and resulting string deflection are

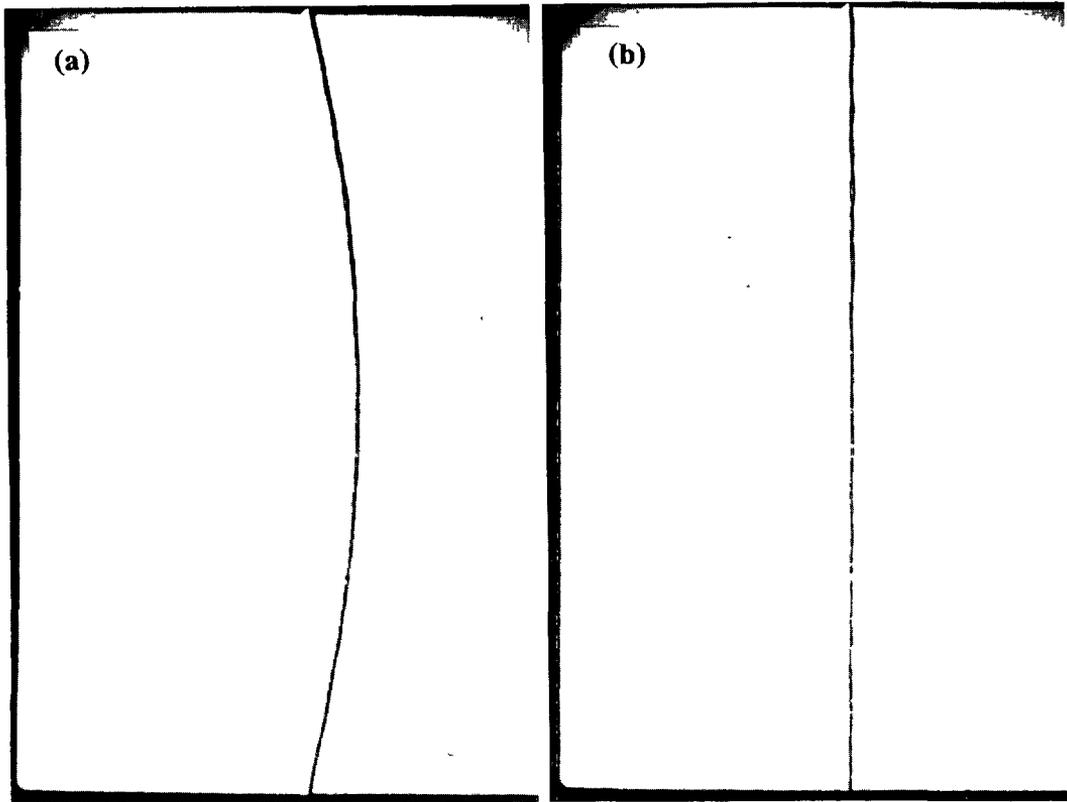


Fig. 2. — Silhouette of the film with (a) and without (b) a film present. The film is approximately 1.76 cm by 0.65 cm of a 11-layer 65OBC film. Because of the strong interference effects, the film in (a) is invisible.

photographed by a 35 mm camera. A macro- and teleconverter-lens assembly magnifies the image by a factor of five. Backlighting is used to produce a sharp silhouette image for ease of image analysis. The processed black and white photos are then scanned into a computer. Imaging software is then used to “skeletonize” the string to a width of one pixel by a consistent algorithm. A series of points is then obtained from the shape of the string. Distances are converted from pixels to real distance by comparing the known span of the film plate to the same length in the scanned images. It is then straightforward to fit the points to an expression for a circular arc, which yields a value for the radius of curvature of the string. Then Equation (1) without the friction term (f_f) allows us to determine the film surface tension from the measured values of R and m .

This novel and simple experimental technique has an obvious inherent limitation. It requires a free-standing film. Consequently, it is impossible to measure the surface tension of either the isotropic or nematic phase of liquid crystals. The conventional methods, namely, the suspended pendant drop, the Wilhelmy slide, light scattering from surface capillary waves, etc., have been utilized to measure the surface tension in the isotropic, nematic and/or smectic phases of various liquid-crystal compounds. Besides the highly consistent nature of our experimental results, the excellent agreement between our surface tension data and those obtained from these conventional methods gives us great confidence in our experimental approach.

3. Experimental Results and Discussions

Employing this remarkable experimental technique, we have measured the surface tension of the following three liquid-crystal compounds in their SmA or SmA_d phase in the form of free-standing films as a function of film thickness. The results are shown in Figures 3-5 for CBOOA (p-cyano-benzylidene p'-n-octyloxyaniline) at 76.5 °C (in the SmA_d phase), 12CB (4-cyano-4'-n-dodecylbiphenyl) at 54.0 °C (in the SmA_d phase), and 65OBC (n-hexyl-4'-n-pentyloxy-biphenyl-4-carboxylate) at 75 °C (in the SmA phase), respectively. Over relatively wide ranges of film thickness, these three sets of data clearly demonstrate that the surface tension is independent of the film thickness down to two-layer films. Thus, within our resolution, the source of the surface tension is highly localized, and only the two outermost layers contribute. Although a one-layer film has been reported and characterized in one liquid-crystal compound [17], we have been unable to prepare any one-layer films for surface tension measurements.

It is relatively difficult to prepare uniform, thick CBOOA free-standing films as these films tend to spontaneously thicken. Nevertheless, we have successfully prepared uniform, thin CBOOA films. The surface tension obtained from 2-, 3-, 4-, and 5-layer films ($\gamma_s = 26.8 \pm 0.3$ dyne/cm) in the SmA_d phase is found to be independent of the film thickness and agrees very well with those of Krishnaswamy and Shashidhar [13], who found $\gamma_s \approx 26$ dyn/cm at the sample-vapor interface of a suspended pendant drop of CBOOA. Similarly, the surface tension of 12CB (Fig. 4) ($\gamma_s = 27.2 \pm 0.3$ dyne/cm) with $2 \leq N \leq 80$ is in reasonably good agreement with the value ($\gamma_s = 26 \pm 0.8$ dyn/cm) obtained from the SmA_d phase of thick 8CB films ($N \approx 40$) using light scattering techniques. Here N is the thickness of the film in units of molecular layers. Finally, the surface tension ($\gamma_s = 20.8 \pm 0.3$ dyne/cm) from 65OBC films (Fig. 5) in the SmA phase with $3 \leq N \leq 25$ is also found to be independent of the film thickness and is significantly smaller than the previous two cases.

These three sets of experimental data obtained in the SmA or SmA_d phase are found to be independent of film thickness within our resolution of approximately $\pm 1\%$. Recently, Pieranski *et al.* [4] have measured the total film tension in the SmA_d phase of S2 (a cyano-biphenyl-

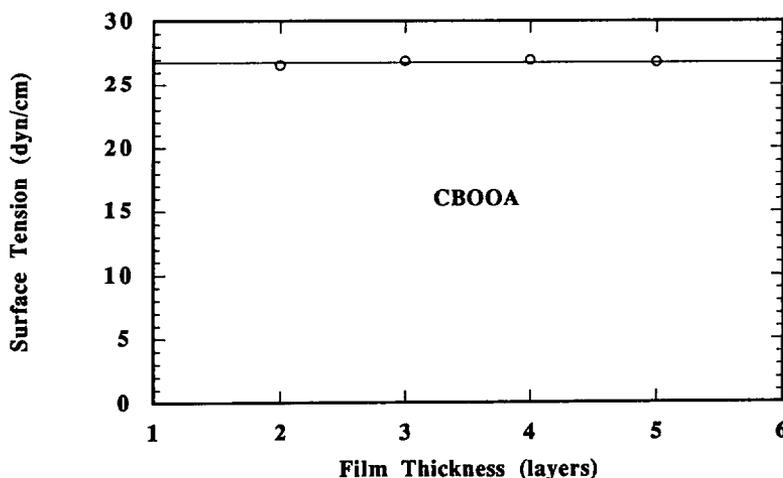


Fig. 3. — Surface tension as a function of film thickness for thin CBOOA free-standing films. The data were taken at 76.5 °C.

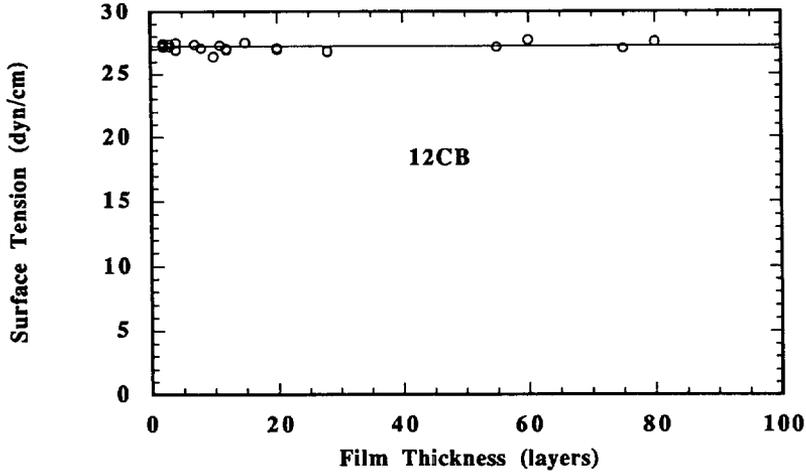


Fig. 4 — Surface tension *versus* film thickness for 12CB free-standing films. The sample temperature was at 54 °C.

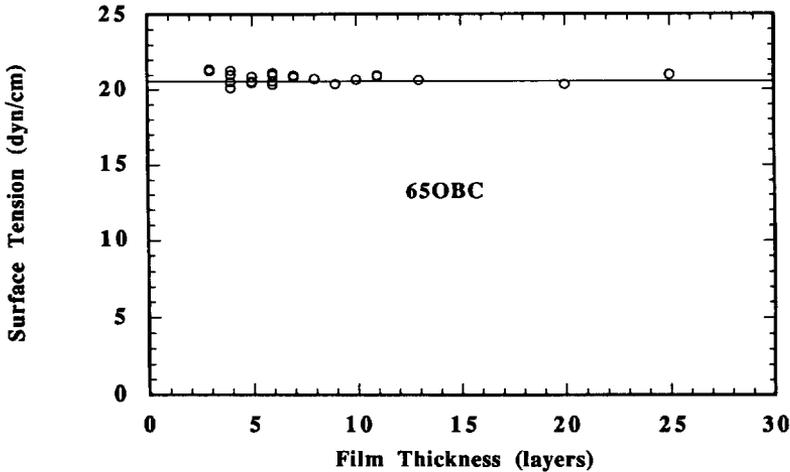


Fig. 5 — Thickness variation of surface tension for 65OBC free-standing films. The measurements were conducted at 75 °C.

mixture from BDH Chemicals Ltd). The following linear relation was found among the results from one thin film and three very thick films (3300-, 4800-, and 6400-layer films).

$$\gamma_s = \gamma_{so} + \alpha N.$$

with $\gamma_{so} = 57.8$ dyn/cm and linear coefficient $\alpha = 3.81 \times 10^{-4}$ dyn/cm. Thus in the limit of thin films, the surface tension is 28.9 dyn/cm. Without a reliable method to determine the thickness of extremely thick films ($N > 200$), we were unable to characterize the surface tension in this regime. Otherwise, in order to determine the small value of the linear coefficient (α), it requires a much better resolution (approximately one part in 10^3) for an experimental range of only one hundred layers. Thus, we do not currently have sufficient resolution to determine the value of the linear coefficient. On the other hand, the excellent agreement between our

thin film results and the bulk measurements, namely, suspended pendant drop investigations of CBOOA, strongly suggests that the coefficient α is practically zero.

In addition to the data presented in Figures 3-5, we have also measured the surface tension of 8OCB (4-cyano-4'-n-octyloxy-biphenyl) at 56.5 °C, 3(10)OBC (n-hexyl-4'-n-pentyloxybiphenyl-4-carboxylate) at 76.0 °C, 7O.7 (4-n-heptyloxybenzylidene-4-n-heptylaniline) at 72.5 °C, and 4O.8 (4-n-butyloxybenzylidene-4-n-octylaniline) at 61.9 °C in their SmA_d or SmA phase. On the basis of our surface tension results, these seven different liquid-crystal compounds can be grouped into two categories. The first one (3(10)OBC, 65OBC, 7O.7, and 4O.8) exhibits the ordinary SmA phase. The surface tension of these compounds is about 21 dyn/cm. Our values of surface tension are slightly lower than the critical surface tensions (γ_c) of hydrocarbon surfaces containing a -CH₃ group in either the crystal form (22 dyn/cm at 20 °C) or the monolayer (24 dyn/cm at 20 °C) [18]. In comparison, the hydrocarbon surface consisting of a -CH₂-group has a much higher value of γ_c (\approx 31 dyn/cm at 20 °C) [18]. The *principle of independent surface action*, proposed by Langmuir [19], qualitatively states that one could suppose each part of a molecule to possess a *local* surface free energy. Numerous other systems have been employed to test this important principle and provided significant insight to its validity [18]. However, because of their well-organized molecular layer structure, thermotropic smectic liquid-crystal free-standing films offer a unique opportunity to perform a critical test of this fundamental principle. In the ordinary SmA phase, to minimize the surface free energy, each molecule prefers to have the molecular group with the lowest surface free energy exposed to the outermost surface. Moreover, our measured surface tension is slightly lower than γ_c of the hydrocarbon surface containing -CH₃ groups in the crystal form. This leads us to believe that the "almost perfect" smectic layer structure in free-standing films allows the -CH₃ terminal groups to pack very tightly at the surface.

The molecules in the second group (CBOOA, 8OCB, and 12CB) possess a large dipole moment associated with the cyano group. As a result, the smectic phase exhibits a bi-layer antiferroelectric phase (the SmA_d phase) wherein cyano groups form pairs and constitute the center of the bi-layer structure. The alkyl-chains point outward. The surface tension of about 27 dyn/cm is approximately 25% higher than the first group. It has been argued that the surface tension is directly related to the polarizability of the molecule [20]. Thus, a possible explanation for the larger surface tension exhibited by the second group could involve the strong dipole moment associated with the cyano group, which has a high polarizability even in the antiferroelectric arrangement. Since the dipolar interaction is long-ranged, however, one would expect the above mechanism to induce substantial thickness dependence of the surface tension. Perhaps the antiferroelectric coupling between the molecular dipoles in the bi-layer structure makes the interaction quadrupolar, thereby greatly decreasing the range of the interaction and reducing the impact of the strong dipole moment associated with the cyano groups.

In conclusion, we have developed and further improved a very simple and straightforward method to investigate the surface tension of free-standing films. Currently, the resolution is about $\pm 1\%$. The system has been employed to measure the surface tension of seven different liquid-crystal compounds in their SmA or SmA_d phase. Our experimental results for the thickness dependence of surface tension indicate that the mechanism responsible for the surface tension is *highly localized* in the two outermost surface layers. Furthermore, a large enhancement in the surface tension of SmA_d phases has been observed. Additional experimental investigation is necessary to address the relation between this enhancement and the electric dipole moment associated with the cyano group which is responsible for the formation of the SmA_d phase. Further measurements on other liquid-crystal compounds are in progress.

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References

- [1] de Gennes P.G. and Prost J., *The Physics of Liquid Crystals* (Clarendon Press, Oxford,1993); Chandrasekhar S., *Liquid Crystals* (Cambridge University Press, 1992); Vertogen G. and de Jeu W.H., *Thermotropic Liquid Crystals, Fundamentals*, Springer Series in Chemical Physics **45** (Springer, Heidelberg, 1988); Gray G. W. and Goodby J. W. , *Smectic Liquid Crystals*, (Leonard Hill, Glasgow, 1984)
- [2] Young C. Y., Pindak R., Clark N. A. and Meyer R. B., *Phys. Rev. Lett.* **40** (1978) 773.
- [3] Huang C. C. and Stoebe T., *Adv. Phys.* **42** (1993) 343
- [4] Pieranski P., Beliard L., Tournellec J. Ph., Leoncini X., Furtlehner C., Dumoulin H , Riou E., Jouvin B., Fenerol J. P , Palaric Ph., Heuving J., Cartier B. and Kraus I., *Physica A* **194** (1993) 364.
- [5] Stoebe T., Mach P. and Huang C. C , *Phys. Rev. E* **49** (1994) R3587.
- [6] To achieve our experimental goals, only "appropriate" liquid-crystal compounds (those which readily yield uniform films) are utilized. Few experiments are successful on films that spontaneously thicken so the compounds that produce such films are justifiably bypassed. However, our experience indicates that a number of compounds do, in fact, fail to expel thicker regions and do not readily produce uniform films. For example, the compound CBOOA forms films which tend to spontaneously thicken if the initial thickness is greater than roughly 5 layers. This is the primary reason why we could only successfully obtain surface tension data from the films with $N \leq 5$ Moreover, in the early stages of designing an ac free-standing film calorimeter, we consistently experienced film thickening upon heating from the hexatic-B phase into the SmA phase of 65OBC. In this case, however, by significantly reducing the amount of the liquid-crystal material loaded onto the film holder, we have been able to eliminate this behavior. Meanwhile, by closely examining the molecules located at the edge between the N -layer and $N + 1$ -layer regions, there exists a force imbalance acting on the molecules at the edge. This net attractive force would reduce the $N + 1$ -layer region of the film. Of course, the line energy must also be considered. Thus experimentally, it is not true that thicker regions of the free-standing film *always* recede. To the best of our knowledge, these macroscopic phenomena remain to be carefully investigated.
- [7] In our laboratory, without the proper apparatus necessary to measure film thicknesses greater than roughly 200 layers, our current resolution in determining the linear coefficient α (Eq. (1)) is about 3×10^{-3} dyn/cm-layer However, the agreement between our value of surface tension of 2-, 3-, 4-, and 5-layer CBOOA films and that of the pendant drop (bulk sample) leads us to conclude that the linear coefficient is practically zero, unless one can convincingly argue that the surface tension of thick smectic free-standing films differs from that of bulk samples without well-organized layer structure in the interior
- [8] Jerome B., *Rep. Prog. Phys.* **54** (1991) 391, Jin A. J., Stoebe T. and Huang C. C., *Phys. Rev. E* **49** (1994) R4791 and references found therein.
- [9] de Gennes P. G., *Europhys. Lett.* **13** (1990) 709.

- [10] Lejcek L. and Oswald P., *J. Phys. II France* **1** (1991) 931.
- [11] Tweet D. J., Holyst R., Swanson B. D., Stragier H. and Sorensen L. B., *Phys. Rev. Lett.* **65** (1990) 2157;
Holyst R., Tweet D. J. and Sorensen L. B., *ibid.* **65** (1990) 2153.
- [12] Shindler J. D., Mol E. A. L., Shalaginov A. and de Jeu W. H (preprint).
- [13] Krishnaswamy S. and Shashidhar R., *Mol. Cryst. Liq. Cryst.* **38** (1977) 353.
- [14] Gannon M. G. J. and Faber T. E., *Philos. Mag. A* **37** (1978) 117 and references found therein.
- [15] Sohl C. H., Miyano K. and Ketterson J. B., *Rev. Sci. Instrum.* **49** (1978) 1464.
- [16] Bottger A. and Joosten J. G. H., *Europhys. Lett.* **4** (1987) 1297.
- [17] Rosenblatt C., Pindak R., Clark N. A. and Meyer R. B., *Phys. Rev. Lett.* **42** (1979) 1220.
- [18] Zisman W. A., in Contact Angle, Wettability and Adhesion, F. M. Fowkes Ed., *Advances in Chemistry Series*, No. 43, (American Chemical Society, Washington, D.C. 1964) p. 1.
- [19] Langmuir I., *Colloid Symposium Monograph* (The Chemical Catalog Company, New York, 1925) p. 48.
- [20] de Gennes P. G., *Rev. Mod. Phys.* **57** (1985) 827.