

## Mechanical Measurements of the Smectic-*B*-*A* Transition in Liquid-Crystal Films

R. Pindak, D. J. Bishop, and W. O. Sprenger  
*Bell Laboratories, Murray Hill, New Jersey 07974*  
 (Received 27 February 1980)

A low-frequency torsional oscillator has been used to measure the temperature dependence of the in-plane shear modulus and dissipation of freely suspended films of butyloxybenzylidene octylaniline. It has been observed that smectic-*B* films have a solidlike shear modulus and that the smectic-*B*-*A* transition proceeds in at least two separate steps. The lower-temperature transition is the bulk melting while the higher-temperature transition is tentatively identified as surface melting.

PACS numbers: 64.70.Ew

Freely suspended films of smectic liquid crystals with thicknesses from two to hundreds of molecular layers are proving to be important both in characterizing bulk smectic phases and as systems for studying phase transitions in two dimensions.<sup>1,2</sup> In this Letter we report the first mechanical measurements of the smectic-*B*-*A* transition in such films. We have used a low-frequency torsional oscillator to measure the temperature dependence of the in-plane shear modulus and dissipation of freely suspended films of butyloxybenzylidene octylaniline (4O.8) as a function of the number of molecular layers. This experiment was motivated by the possibility of studying melting (i.e., the smectic-*B*-*A* transition) as it evolved from two to three dimensions. We have made three new observations: (a) Smectic-*B* films of all thicknesses have a solidlike response. (b) The smectic-*B*-*A* transition proceeds in at least two separate steps. The lower-temperature transition is the bulk melting and is accompanied by a sharply changing shear modulus and a dissipation peak. The higher-temperature transition, which we tentatively identify as surface melting, shows a slowly changing shear modulus and a shoulder in the dissipation. (c) Finally, both the shear modulus and dissipation show additional structure at temperatures below the smectic-*B*-*A* transition for which we have no explanation.

The nature of two-dimensional (2D) melting and the behavior of the 2D shear modulus  $\mu$  was recently studied by Halperin and Nelson.<sup>3</sup> Building on ideas due to Kosterlitz and Thouless,<sup>4</sup> they constructed a dislocation mediated theory of melting. As in the Kosterlitz-Thouless theory, at the 2D melting temperature  $T_m$  they predict a universal jump involving the two Lamé constants,  $\mu$  and  $\lambda$ , which characterize the elastic properties of the 2D crystal. The shear modulus  $\mu$  itself will undergo a discontinuous jump at  $T_m$ . In the limit

that the unmeasured Lamé constant  $\lambda \gg \mu$ , this jump will be of magnitude  $\mu_D = 4\pi k_B T_m / a_0^2$ , where  $a_0$  is the lattice spacing. In 4O.8,  $a_0 = 5 \times 10^{-8}$  cm which gives a predicted jump  $\mu_D = 220$  ergs/cm<sup>2</sup>. This value can be at most a factor of 2 higher if the limit  $\lambda \gg \mu$  is not satisfied. In addition Halperin and Nelson make the observation that if a 2D crystal melts by the appearance of a small density of free dislocations, then it should first melt into the intermediate hexatic phase and then into a 2D liquid. The hexatic phase would have only short-range positional order but quasi long-range bond orientational order. It would then be expected to support a shear.

To measure the shear modulus in liquid-crystal films we constructed the apparatus shown in Fig. 1. The main element is a high-*Q* BeCu torsional oscillator. It has a disk-shaped top of radius  $R_1 = 0.59$  cm supported by a 1-mm-diam torsional rod. Attached to the oscillator is a metal plate that forms part of the pickup and drive capacitors. In operation a quantity of 4O.8, in its smectic-*A* phase, was placed around the hole in the support ring and then, with a glass spreader, a freely suspended film of the liquid crystal was drawn across the hole (radius  $R_2 = 0.70$  cm). The film's thickness was determined by measuring its optical reflectivity. In this fashion it was possible to produce uniform films from two to hundreds of layers in thickness. After a film was formed the movable oscillator base was raised by pressurizing a set of three bellows until the oscillator, wet with liquid crystal, touched the film. The liquid-crystal film then formed an annular region between the torsional oscillator and the support ring. A pair of concentric cylinders with viewing ports (not shown) enclosed the oscillator to control its temperature and environment. A set of shutters closed the viewing ports to minimize thermal gradients due to radiation losses.

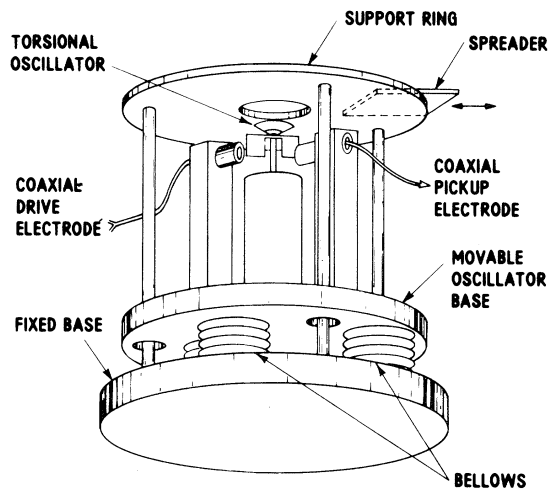


FIG. 1. The experimental cell. The liquid-crystal film to be measured is supported between the support ring and the torsional oscillator.

The oven temperature was regulated to better than  $\pm 0.01^\circ\text{C}$ . The oscillator was phase locked in the standard way with the high- $Q$  mechanical oscillator serving as the frequency-determining element of a feedback loop consisting of an amplifier, a phase shifter, and a zero-crossing detector. The total perturbation to the oscillator frequency and dissipation due to the liquid-crystal film was small and the oscillator remained phase locked throughout the entire measurement. In order to enhance the stability of the oscillator the measurements were performed at a reduced pressure of 5 mm Hg of dry  $\text{N}_2$ . During the course of a temperature scan ( $\sim 24$  h) the films remained stable and constant in thickness.

The resonant period of the oscillator could be resolved to 1 part in  $10^5$  and the amplitude to 1 part in  $10^3$ . The oscillator torsional spring constant  $K_0$  was calibrated to an absolute accuracy of 5% by placing known masses on the oscillator and measuring the shift in period. At  $T_0 = 56^\circ\text{C}$ , the resonant frequency of the oscillator was 524 Hz and  $K_0 = 4.9 \times 10^6$  ergs. The dissipation  $Q_0^{-1}$  of the unloaded oscillator was determined at  $T_0$  by measuring the  $1/e$  ringdown time with the result that  $Q_0(T_0) = 770$ . In the high- $Q$  limit the amplitude  $A$  is proportional to the  $Q$ . The amplitude scale could then be calibrated in terms of the dissipation by use of  $Q^{-1}(T) = Q_0^{-1}(T_0)A_0(T_0)/A(T)$ , where  $A_0$  is the amplitude of the unloaded oscillator. At the outer edge of the disk  $A_0 = 7 \text{ \AA}$  giving a shear angle of  $7 \times 10^{-7}$  rad. This was well with-

in the linear response regime that was found to extend up to  $A = 200 \text{ \AA}$ .<sup>5</sup>

With the calibrated oscillator, changes in its mechanical properties due to an applied film can be related to the material parameters of the film. In particular, the torsional elastic constant of the film  $K_F$  is related to the resonant period  $P$  of the oscillator-film system by the equation

$$P = 2\pi [I_0 / (K_0 + K_F)]^{1/2}, \quad (1)$$

where  $I_0$  is the moment of inertia of the oscillator. The moment of inertia of the film  $I_F$  has been neglected since  $I_F/I_0 < 10^{-6}$  for the films studied. The 2D shear modulus  $\mu$  of the film is related to  $K_F$  by

$$\mu = CK_F = \frac{R_2^2 - R_1^2}{4\pi R_1^2 R_2^2} K_F, \quad (2)$$

where the geometrical constant  $C$  has the value  $0.065 \text{ cm}^{-2}$ . Combining Eqs. (1) and (2) we can express the shear modulus in terms of the decrease in period as

$$\mu \approx 2CK_0(\Delta P/P_0), \quad (3)$$

where  $P_0$  is the period of the oscillator alone and  $\Delta P = P_0 - P$ . The predicted jump  $\mu_D$  would give a change in period  $\Delta P/P_0 = \mu_D/2CK_0 = 4 \times 10^{-4}$  which is within the instrument's resolution. It should be stressed that the oscillator is not sensitive to the presence of a liquidlike phase. The added inertia of a liquidlike phase would increase the period of the oscillatory but because  $I_F \ll I_0$  its effect would be negligible. For this reason our measurement would not be sensitive to the hexatic phase which is expected to have a liquidlike response at low frequencies.

The temperature dependence of the oscillator's period  $P_0$  and dissipation  $Q_0^{-1}$  are shown in Fig. 2. Coupling a 24-layer film of 40.8 to the oscillator leads to a new resonant period  $P$  and dissipation  $Q^{-1}$  for the oscillator-film system (Fig. 2). Above  $56^\circ\text{C}$ , the oscillator's period and dissipation are unaffected by the presence of the film. As discussed above, this implies a liquidlike response and is the expected result for the smectic- $A$  phase. The surprising result is that this behavior does not continue down to the bulk  $B$ - $A$  transition temperature at  $49^\circ\text{C}$ . Instead, just below  $56^\circ\text{C}$ , a solidlike response (decrease in period) is observed indicating that the film has a finite shear modulus at this temperature. As the temperature is lowered, the shear modulus continues to increase until it reaches a value  $\mu \sim 750$  ergs/cm<sup>2</sup>. These changes are accompanied by an

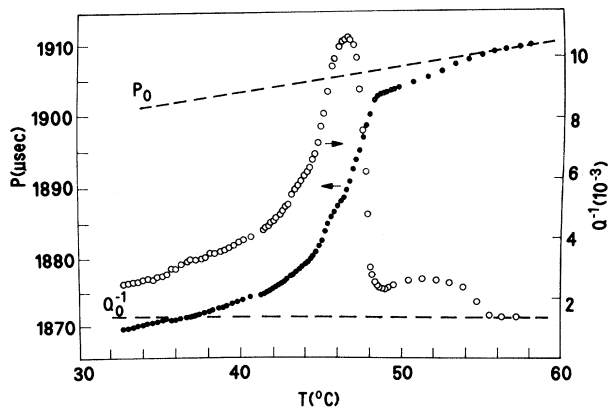


FIG. 2. The period ( $P$ ) and the dissipation ( $Q^{-1}$ ) as functions of temperature for a 24-layer film.  $P_0$  and  $Q_0^{-1}$  are the background period and dissipation of the empty cell.

increase in the dissipation of the system. At  $49^\circ\text{C}$  (the bulk  $B$ - $A$  transition temperature), there then occurred a sharp increase in the shear modulus accompanied by a peak in the dissipation. Referring to Fig. 3, we have labeled the temperature associated with the onset of the shear modulus by  $T_1$  and the temperature associated with the sharp increase by  $T_2$ . For  $T \ll T_2$ , within the smectic- $B$  phase, the shear modulus saturated at a value per layer  $\mu_L = 420$  ergs/cm $^2$ . This gives a value for the bulk shear modulus  $\mu_B = \mu_L/h = 1.5 \times 10^9$  ergs/cm $^3$  where  $h$  is the layer thickness (28.6 Å). The value for  $\mu_B$  is consistent with the value obtained by ultrasonic measurements on bulk samples ( $\mu_B = 1.2 \times 10^9$  ergs/cm $^3$ ).<sup>6</sup>

To understand better the nature of these transitions at  $T_1$  and  $T_2$ , the temperature dependence of  $P$  and  $Q^{-1}$  was measured as a function of film thickness (Fig. 3). The thinnest film that remained stable enough to be carefully measured was four layers and we studied films from 4 to 24 layers. For thin films the curves were reproducible on heating and cooling; thick films tended to thin on heating so that hysteresis effects could not be checked. For the lower-temperature transition, it was found that both the total period change and the dissipation maximum scaled with the number of layers. This is what would be expected for the elastic response of a crystal of increasing thickness. Such solidlike response even for thin smectic- $B$  films supports recent x-ray measurements on 4O.8 which demonstrated that thick smectic- $B$  films are 3D crystals and thin smectic- $B$  films are best characterized as 2D

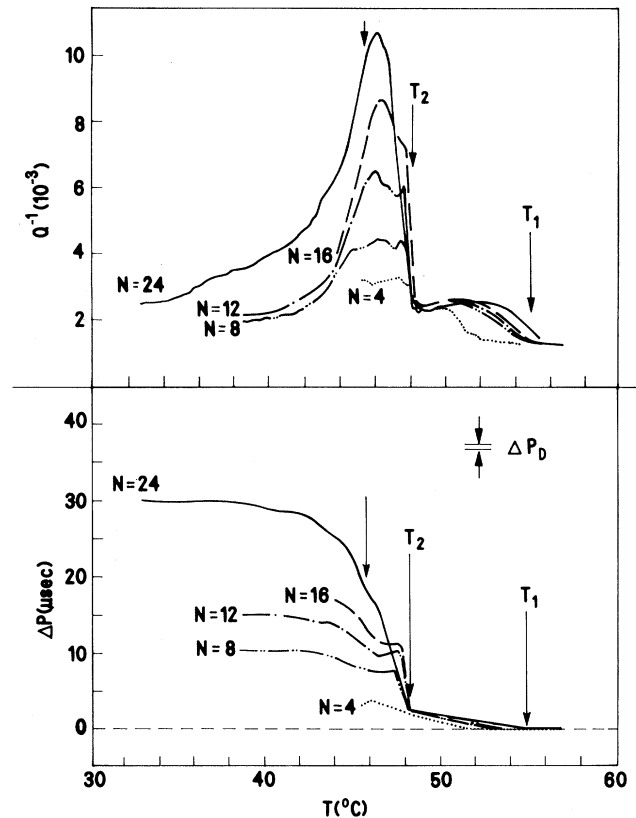


FIG. 3. The dissipation (upper) and period shift (lower) as functions of temperature for different numbers of molecular layers ( $N$ ).  $\Delta P_D$  is the expected size of the period shift corresponding to the discontinuous jump in shear modulus  $\mu_D$ . The curves for  $N < 24$  have been shifted down in temperature such that the feature at  $T_2$  coincides for all the curves.

crystals.<sup>2</sup>

For the higher-temperature transition both the total period change and dissipation increase were found to be *independent* of film thickness. The fact that it was independent of film thickness, a solidlike response, and of magnitude approximately twice the response per layer in the smectic- $B$  phase [i.e.,  $\mu(T_2) \approx 2\mu_L(T \ll T_2)$ ] implied that this feature was a surface transition involving the outer layers of the film which remain crystalline to a higher temperature than the bulk.<sup>7</sup> The polar nature of the free surface would tend to orient the asymmetric molecules preferentially with respect to their long axes (random in the bulk).<sup>1</sup> Also, the layer (smectic- $A$ ) order parameter would be higher at a free surface as evidenced by an increase in the smectic- $A$ -nematic transition temperature in thin films. A coupling between either

of these order parameters and the in-plane positional order could have resulted in its surface enhancement.

Other features we observed in going from 24 to 4 molecular layers were an increase in  $T_2$  of 2 deg and a 1-deg decrease in  $T_1$ . Also, there appeared to be a third feature (indicated by the unlabeled arrow in Fig. 3) which is not understood. At this temperature both the period change and dissipation leveled off before decreasing at  $T_2$ .

In summary, we have developed an apparatus capable of measuring the in-plane shear modulus and dissipation of thin-smectic films. We have observed that smectic-*B* films have a solidlike shear modulus and that smectic-*A* films have a liquidlike response giving further support to the conclusion that the smectic-*B* phase, even in thin films, is a crystalline phase. We have further observed that the smectic-*B*-*A* transition proceeds in two steps. The lower-temperature feature is associated with the bulk melting and the upper feature with an enhancement in the surface melting temperature. Finally, we did not find any evidence for a discontinuous jump in  $\mu$  at either of the transitions. For the four-layer film (see Fig. 3) this should have been a 10% effect and was not observed. Possible explanations include the finite frequency effects of our measurement or

impurities in our samples which can cause a coexistence of the smectic-*A* and -*B* phases. To minimize these problems, dc shear-modulus measurements<sup>5</sup> and further measurements on more stable compounds are in progress.

The authors would like to acknowledge any helpful discussions with W. F. Brinkman, R. C. Dynes, D. S. Fisher, D. E. Moncton, and D. D. Osheroff, and thank E. Benick for technical assistance.

---

<sup>1</sup>C. Rosenblatt, R. Pindak, N. A. Clark, and R. B. Meyer, *Phys. Rev. Lett.* **42**, 1220 (1979).

<sup>2</sup>D. E. Moncton and R. Pindak, *Phys. Rev. Lett.* **43**, 701 (1979).

<sup>3</sup>B. I. Halperin and D. R. Nelson, *Phys. Rev. Lett.* **41**, 121 (1978); D. R. Nelson and B. I. Halperin, *Phys. Rev. B* **19**, 2457 (1979).

<sup>4</sup>J. M. Kosterlitz and D. J. Thouless, *J. Phys. C* **6**, 1181 (1973).

<sup>5</sup>W. O. Sprenger, D. Osheroff, and R. Pindak, to be published.

<sup>6</sup>S. Bhattacharya and S. V. Letcher, to be published.

<sup>7</sup>A continuation of the x-ray experiments discussed in Ref. 2 gave results consistent with this conclusion. Above 49°C, thin films of 4O.8 had a two-component scattering profile: a sharp solidlike peak on top of a broad liquidlike maximum. D. E. Moncton and R. Pindak, to be published.