

**Surface tension measured by vibrating membranes:
An application to smectic-*A* and -*B* phases**

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A technique is proposed to measure the surface tension of nonfluid materials by monitoring the resonance frequencies of drumhead vibrations of freely suspended films. It has been applied to the smectic-*A* and -*B* phases of a liquid-crystal BBOA (butyloxybenzylidene octylaniline). The anomalous temperature dependence of the surface tension is in accordance with that previously suggested surface ordering above the bulk *A*-*B* transition temperature.

Measurement of surface tension¹ (or, alternatively, surface energy) of a material in other than the liquid phase is difficult because, under ordinary circumstances, the surface energy is negligibly small compared with that associated with a deformation of the bulk. The bulk moduli are many orders of magnitude larger than the surface tension in a solid; thus a solid does not spontaneously assume that shape which would minimize surface energy. Consequently, direct measurements of surface tension of solids by surface deformation (a common method in liquid surface tension measurements) are rare.²

In this Communication, I propose a new technique

which would allow direct measurements of surface tension of solids by monitoring the resonant frequencies of drumhead vibration modes of freely suspended films. The feasibility of the technique is demonstrated using a smectic-*B* phase of BBOA (butyloxybenzylidene octylaniline) which is known to be a three-dimensionally ordered solid [so-called crystal *B* (Ref. 3)]. I also report the effect of the anomalous surface ordering in this material found earlier in the course of shear measurements.^{4,5}

Let us picture a solid film of radius R and thickness h (inset in Fig. 1) clamped on the rim. The equation of motion for the drumhead vibration of a

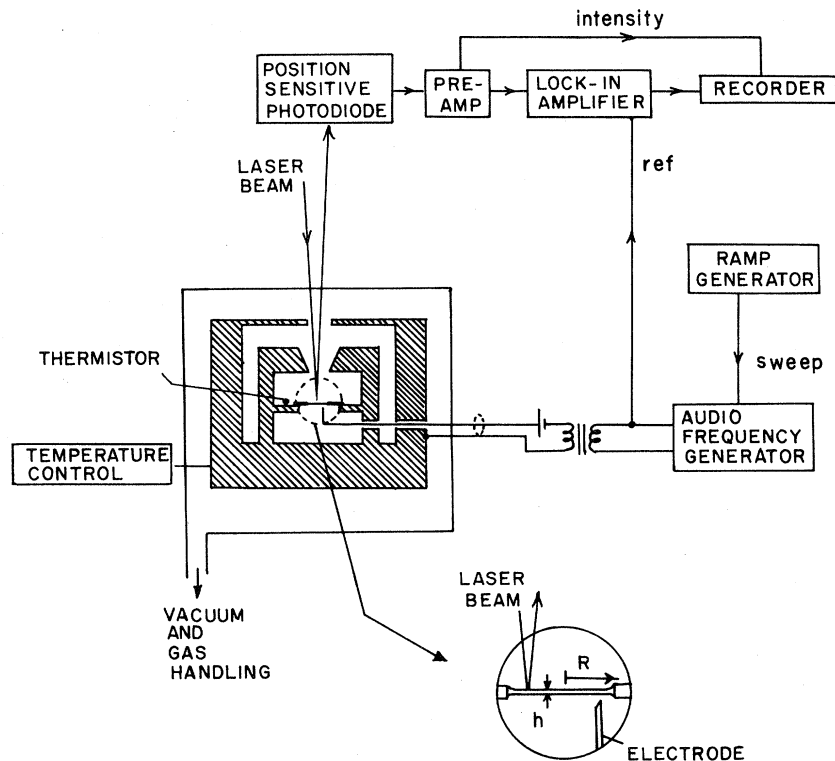


FIG. 1. Schematic diagram of the experiment.

solid membrane under a tension τ is given by⁶

$$\frac{Eh^3}{12(1-\sigma^2)}\Delta^2\zeta - \tau\Delta\zeta + m_A\ddot{\zeta} = 0, \quad (1)$$

where E is Young's modulus, σ is Poisson's ratio, m_A is the mass per unit area ($m_A = \rho h$, ρ : density), and ζ is the displacement of the film from the equilibrium position. It is understood that the bulk is isotropic, although Eq. (1) can be easily generalized for an anisotropic solid.⁷ Let us assume that the tension τ can be split into two parts:

$$\tau = \tau_B + 2\gamma, \quad (2)$$

where τ_B is the bulk stress and γ is the surface tension. The factor of 2 in front of γ accounts for the two surfaces of the film. If the film is annealed completely, the bulk stress should relax to zero ($\tau = 2\gamma$) and one has a freely suspended film. In this case of vanishing bulk stress, the drumhead vibrations of the film are solely determined by the surface tension. This is seen as follows. In Eq. (1) with $\tau = 2\gamma$, let us assume $E = 10^{12}$ dyn/cm² (typical for a metal), $\sigma = 0.3$, $h = 10^3$ Å, $\gamma = 25$ dyn/cm, and $k = 10$ /cm (the wave number). Then the ratio of the first term to the second is 1.5×10^{-6} . Therefore, for all practical purposes, the first term can be neglected leaving only the surface-tension contribution. Clearly, this technique can be used to measure the surface tension of any solid if a stress-free freely suspended thin film can be grown.

The solution to Eq. (1) (neglecting the first term) is given by

$$\zeta(r, \phi) = J_n(kr) e^{in\phi} \quad (n: \text{integer}), \quad (3)$$

where J_n is the Bessel function of order n , $k = \omega\sqrt{m_A/2\gamma}$, and (r, ϕ) are the cylindrical coordinates of the film. The boundary condition at the rim requires

$$J_n(Rk_{n,m}) = 0, \quad (4)$$

where $Rk_{n,m}$ is the m th zero point of J_n . The damping of the film vibration is caused by two mechanisms: internal friction (or viscosity) and coupling to the surrounding gas. The latter is evaluated as⁸

$$\delta \sim P/m_A\bar{u}\omega, \quad (5)$$

where P is the pressure and \bar{u} is the average molecular velocity of the gas.

The experimental setup is shown in Fig. 1. A freely suspended film was drawn in an evacuated cell backfilled with He gas. Helium was chosen because, for a given P , \bar{u} is larger and hence the damping is smaller. The drumhead vibration was generated electrostatically and detected by specularly reflecting a laser light.⁹

A typical vibrational spectrum of a smectic- B film is shown in Fig. 2. The mode assignment was con-

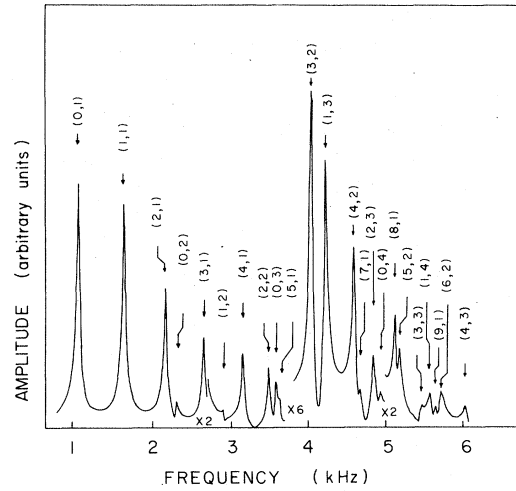


FIG. 2. Drumhead vibration modes in a freely suspended BBOA film ($h = 4850$ Å, $R = 0.40$ cm, $T = 45^\circ\text{C}$, and $P = 40$ mTorr). The numerals in the parentheses (n, m) designate the m th zero point of the Bessel function of order n . Arrows indicate the calculated resonant frequencies with a single adjustable parameter $\gamma = 27.0$ dyn/cm assuming $\rho = 1$ g/cm³.

firmed up to the fifth mode by a direct observation of the nodal structure by moving the laser beam across the film. For a higher mode (i.e., larger k), the contribution from the first term in Eq. (1) becomes more important. However, the peak frequencies all agreed with the expected series given by Eq. (4) within $\pm 0.5\%$ and no systematic deviation was observed. Hence the omission of the first term is justified.

The effect of the damping due to the gas was studied with a 13-layer film for the (2,2) and (0,3) vibration modes (~ 13 kHz) at 45°C . As the pressure was lowered from 1 Torr to 40 mTorr, the Q factor increased dramatically; even at 40 mTorr, the gas effect was still considerable. The peak position, however, did not change for a pressure range of 40 \sim 500 mTorr and was shifted down by only 1.4×10^{-3} at 800 mTorr. From Eq. (5), it is clear that resonance frequencies are measured correctly even for a two-layer film if the pressure was less than 100 mTorr.

Measurements at a pressure lower than the vapor pressure were not practical because of evaporation. The temperature uniformity of the film is also questionable at a lower pressure because the film is thermally connected to the surrounding only through radiation and the conduction in the gas. As a compromise, most of the data were taken with films of small (hence higher ω) radius ($R = 0.238$ cm) and large thickness ($h = 1000 \sim 5000$ Å) at a relatively high total (vapor pressure plus He) pressure of 150 \sim 200 mTorr. For convenience, the (1,1) mode was monitored as a function of the temperature. The

amplitude of the vibration was $\sim 10 \text{ \AA}$.

The temperature dependence of γ/m_A is shown in Fig. 3. The temperature dependence of m_A in BBOA is expected to be small.¹⁰ Thus Fig. 3 reflects the temperature dependence of the surface tension. Two salient features of Fig. 3 are the steady decline of γ as the temperature is lowered and the lack of a singularity at the bulk A - B transition T_{AB} . These observations are in accordance with the surface layer solidification above T_{AB} found in the shear modulus^{4,5} and x-ray studies.³

The temperature dependence of the surface tension is related to the surface excess entropy per unit area S_A by²

$$S_A = - \frac{\partial \gamma}{\partial T}, \quad (6)$$

provided that the molecular diffusion is fast enough so that the surface achieves thermal equilibrium with the bulk within the time scale of surface deformation. Usually the surface is more disordered than the bulk; S_A is positive for all common liquids. Therefore $\partial \gamma / \partial T > 0$ in Fig. 3 implies anomalous surface ordering. This type of behavior has previously been seen in liquid crystals in narrow temperature regions around the isotropic-nematic transition¹¹ and the nematic-smectic- A transition.¹² It should be noted, however, that $\partial \gamma / \partial T > 0$ for only $T \geq 55^\circ \text{C}$, i.e., above the temperature where a solidlike shear modulus appeared.^{4,5} On the one hand, this indicates that the surface solidification is accompanied by a pretransitional ordering at least several degrees wide in contrast to the sudden bulk solidification process. On the other hand, because S_A must still be negative below $T \sim 55^\circ \text{C}$, leveling of γ vs T seems to imply that, at this temperature, the surface solidification becomes complete to such a degree that fast diffusion of molecules is no longer possible and hence Eq. (6) is not applicable. Once the surface layer is ordered, no further change in γ is expected. Thus at T_{AB} no singularity appears even though the bulk undergoes the phase transition. The only feature associated with T_{AB} is the reduction of the damping. This is probably due to the decrease of the bulk viscosity accompanying the bulk solidification.

Because of the limited stability, detailed studies of thin films were not possible. However, all γ values measured down to three-layer films fall in the range $27 \pm 2 \text{ dyn/cm}$. The surface tension is thus indeed governed by the outermost single layer, although the thermodynamical meaning (in Gibbsian sense) of the

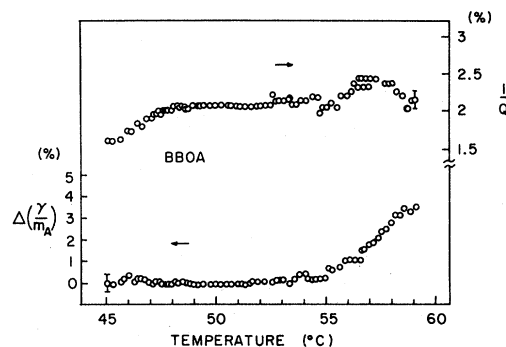


FIG. 3. Change in γ/m_A and $1/Q$ vs temperature. The base line [0% in $\Delta(\gamma/m_A)$] corresponds to $\gamma = 27.3 \text{ dyn/cm}$ assuming $\rho = 1 \text{ g/cm}^3$. $1/Q$ at 45°C was dominated by the damping due to the gas. The bulk A to B transition was 49.5°C .

surface tension of a three-layer film is not clear.

In order to further support the idea behind Eq. (2), the following observation was made. The temperature coefficient of γ in the smectic- B phase is very small and is nearly constant. However, when a smectic- B film was heated by a stepwise temperature rise, the resonance frequency suddenly dropped dramatically. It slowly recovered to the original value in 10–15 min. It is clear that the sudden thermal expansion created a dilational stress in the bulk [negative τ_B in Eq. (2)] which reduces τ . The bulk stress, however, appeared to be relieved relatively easily as evidenced by the recovery of the resonance frequency. Thus the dislocations and other defects have to be highly mobile in this material. A similar conclusion can be drawn from the extraordinarily small shear modulus at low frequencies.⁵

In conclusion, it is shown that the drumhead vibration of a solid membrane is governed only by the surface tension if the film is completely annealed. This idea is applied to smectic- A and - B films of BBOA. The surface solidification process in these films seems to be continuous, which is interesting in the context of the recent development of the theory of melting in two dimensions.¹³ Further study of the surface layers, e.g., heat-capacity measurements, will be of great value.

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¹Subtle distinctions among surface tension, surface energy, and surface stress for a solid surface are not addressed here. See, for example, Ref. 2.

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