Temperature variation of film tension measured by a vibrating membrane tensiometer

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We have constructed a vibrating membrane tensiometer that utilizes a phase lock-in technique to track a resonant peak. This experimental apparatus enables us to obtain the temperature variation of the film tension in a continuous manner. The film tension of two different liquid crystal compounds has been measured with resolution better than 0.2%. The results from a 126 nm-thick film in the crystal-*B* phase of one compound yield a bulk tension value of 2.5 dyn/cm. We interpret several reproducible features of our tensiometer data in the context of surface and bulk phase transitions.

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One of the fundamental goals of surface science is to correlate macroscopic surface phenomena, e.g., adhesion, detergency, friction, and wetting, with the relevant molecular structure of the surface involved. To effectively address this issue, knowledge about surface tension is of importance. Recently, employing our flexible-string tensiometer, we have found [1] a dramatic effect of single-atom replacement on the surface tension of liquid-crystal free-standing films. The experimental results demonstrate that the molecular origin of surface tension is localized at the terminal chemical group situated at the film/vapor interface. However, because of its resolution limit (only about 2%) [2], it is impractical to use the string tensiometer to study the temperature variation of surface tension in the vicinity of a phase transition.

In the past decade, several tensiometers have been built by various research groups to acquire surface tension data from liquid crystal films [2–6]. In order to achieve much higher relative resolution in film tension measurements, we have constructed a tensiometer combining two experimental techniques. The first, introduced by Miyano [3], involves electrically vibrating a free-standing liquid-crystal film and measuring the resonant frequencies of vibration. The second, employed by Agnolet *et al.* [7], uses a feedback loop to allow an oscillator to drive itself at resonance. Our experiment applies this feedback approach to the technique of Miyano, allowing us to track the evolution of the film's resonant vibration frequency as temperature is varied. In this Rapid Communication we report our use of this approach with much improved resolution to studies on two compounds, *n*-pentyl-4′-*n*-pentanoyloxy-biphenyl-4-carboxylate (54COOBC) [8] and 4-hexyloxyphenyl-4′-decyloxybenzoate (HOPDOB) [9]. HOPDOB is one of few compounds on which temperature variation of surface tension has been previously reported [9]. The data display a broad anomaly around 53 °C. In the case of 54COOBC, our results enable us to estimate mass density change through the smectic-*A* (Sm-*A*)–hexatic-*B*(Hex-*B*) transition as well as the film tension in the crystal-*B* (Cry-*B*) phase. Also, previous heat

capacity data [8] from thick free-standing films allow us to identify a broad hump to be related to the surface hexatic order.

Our basic experimental approach is the following. The film is prepared across a circular hole (0.635 cm in radius) in an electrically grounded stainless steel plate. The plate is contained inside a sealed, two-stage temperature-regulated oven in a helium environment of about 100 mTorr. By employing a feedback system, the pressure is regulated to within 1 mTorr. Reducing the helium pressure will decrease its contribution to the total effective mass per unit area of the film. Some helium exchange gas, however, is needed to provide a sufficient thermal link between the free-standing film and the heating wall. An electrode, placed roughly 5 mm below the film, is driven with a sinusoidal voltage (frequency ω) of approximately 75 V rms. The film, which is dielectric in nature, responds to the oscillatory field and vibrates. A laser beam reflected from the film is aimed at a position sensitive detector. The amplitude of the signal from this detector is a measure of the amplitude of oscillation of the film. Miyano [3] demonstrated that such a film could be effectively modeled as the classic vibrating membrane. The solution to the equation of displacement perpendicular to the film plane is $z(r,\phi) = J_n(kr)\exp(in\phi)$. Here (r,ϕ,z) are the cylindrical coordinates of the film. $J_n(kr)$ is the Bessel function of order n and $k = \omega(m_A/\gamma)^{1/2}$. For a film of radius R, of mass per area m_A and under tension γ, the resonant frequency, ω_r, is given by the mth zero point of the J_n's (denoted here as $\alpha_{n,m}$) such that

$$R\omega_r(m_A/\gamma)^{1/2} = \alpha_{n,m}. \qquad (1)$$

By measuring the amplitude of vibration as a function of the driving frequency, the positions of the resonant peaks can be determined. Figure 1 shows two such scans that we made with the compound 54COOBC in the bulk Sm-*A* (a) and Cry-*B* (b). The first three resonant peaks, designated by (n,m), are shown. Knowing the radius of the film, one can then easily determine the ratio m_A/γ from Eq. (1). We will assume that the tension is the sum of two terms,

$$\gamma = \gamma_B + 2\sigma, \qquad (2)$$

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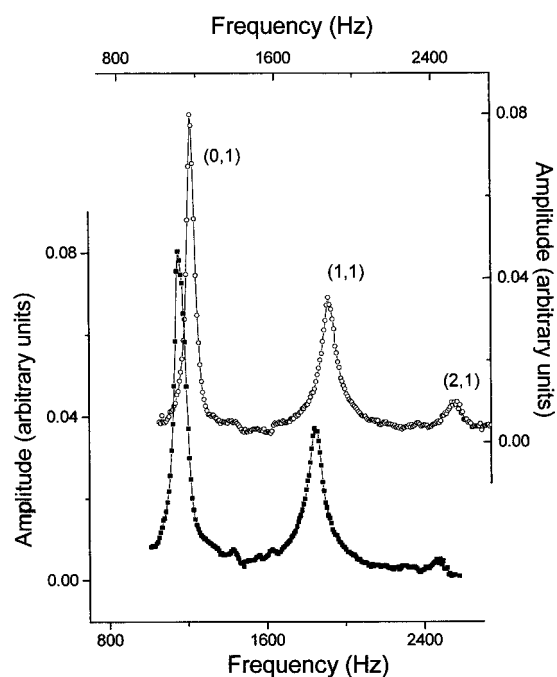
FIG. 1. The first three drumhead vibration modes in a free-standing 54COOBC film (thickness$=112$ nm, radius$=0.635$ cm, and pressure$=100$ mTorr). (a) $T=61.3$ °C (closed squares) and (b) 50.1 °C (open circles). The numbers in the parentheses (n,m) designate the mth zero point of the Bessel function of nth order.

FIG. 2. Schematic of the electronic feedback circuit which tracks and drives the vibrating membrane on resonance.

where γ_B is the bulk tension, σ is the surface tension of the film, and the factor of 2 is included due to the two free surfaces. Notice that a measurement of resonant frequency as a function of temperature for a given film is sensitive to changes in the surface tension, bulk tension, and density of the material. Also notice that in a fluid phase, the bulk tension is zero and the sole source of film tension is the surface tension.

One concern with our experimental approach is any damping effect the helium might have. Miyano [3] studied this effect as a function of helium pressure from 40 mTorr to 1 Torr and found that the resonant frequencies were insensitive to pressure at 100 mTorr and below. We also confirmed this observation; as will be seen, our measurement gives no indication that the helium at 100 mTorr is significantly affecting the measured frequencies. By identifying resonant peaks, Miyano measured the change in the ratio γ/m_A as a function of temperature in the compound butyloxybenzylidene octylaniline (4O.8). Despite the elegance of this measurement, the temperature resolution of such an approach is seriously limited by the time necessary to make a frequency scan. Usually it took about 5 min to complete a scan of a single resonant peak Under this circumstance, even a modest temperature-variation study can be prohibitively cumbersome. For instance, simply gathering frequency data over a temperature range of 10 K with 100 mK resolution would take more than 8 h.

To deal with this drawback and improve experimental resolution, we employed phase sensitive feedback loop techniques. Figure 2 displays a schematic of the circuit. This configuration allows the system to drive and track itself at resonance. After a current to voltage converter, the signal from the position sensitive detector is fed to the differential
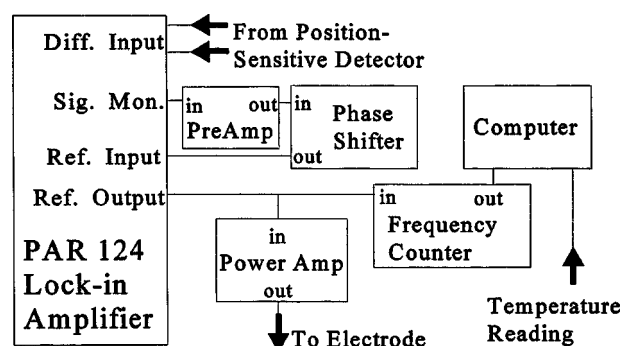
preamplifier of a Princeton Applied Research (PAR) 124 lock-in amplifier (LIA). The signal monitor of the LIA, which outputs a sine wave at the film's vibrational frequency, is used to trigger the reference channel of the same lock-in amplifier. The reference channel outputs a constant amplitude sinusoidal wave at this trigger frequency. The reference output signal is then, in turn, used to drive a bipolar operational power amplifier that provides the driving electric field to the electrode. This reference signal is also fed to a frequency counter from which a computer takes the reading. Notice in the schematic that the signal monitor output is both amplified and phase shifted. It is amplified with a low-noise band-pass amplifier because the LIA's maximum output for this channel (~ 200 mV) is not large enough to effectively trigger the reference channel. It is phase shifted because, theoretically, the driving signal and the film's vibration are 90° out of phase at resonance. For the feedback loop to work properly, the reference channel must respond to the film's vibration with a signal that is in phase with that vibration. An adjustable phase shifter is used to account for the 90° shift as well as any other lags associated with the circuitry. Also note that the band-pass filter of the LIA's input channel is set to a small Q value ($=5$) to avoid additional phase shifts in the feedback loop as the resonant frequency changes.

In our experiments, we tracked and measured the (0,1) (see Fig. 1) resonant frequency as a function of temperature for a given film. The following approach was chosen. After preparing a uniform film, the peak (0,1) was identified using a scan similar to Fig. 1. Four consecutive scans were performed and the data fit to a Lorentzian in order to determine the resonant frequency with resolution better than 2 Hz. The feedback loop was then implemented and the phase shifter was adjusted so that the system was locked on the resonant frequency. We then simply recorded the frequency of vibration and the temperature of the film plate while ramping the temperature of the oven's inner stage. The response of the feedback loop was sufficiently fast and did not impose any limitation in the rate of gathering data. To give our experiment a critical test, we made measurements on a compound in which a distinct feature in surface tension had been established through another technique. Thieme *et al.* [9] measured the surface tension as a function of temperature in bubbles of the compound HOPDOB from 45 °C to 75 °C in the bulk smectic-C (Sm-C) phase. Their data show a noticeable change in the sign of the slope at around 53 °C. Based on the bulk transition temperatures [9] of this compound, we do not
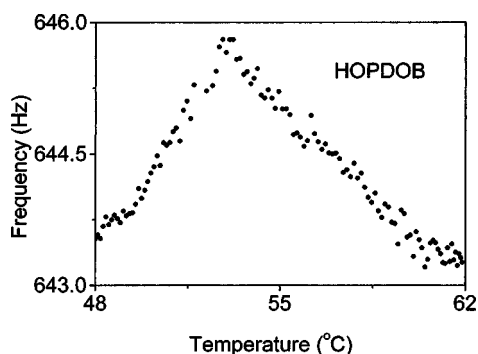
FIG. 3. Temperature variation of resonance frequency obtained from a HOPDOB film. The film thickness is 354 nm. The slope change in the vicinity of 53 °C suggests a surface transition, as discussed in the text.
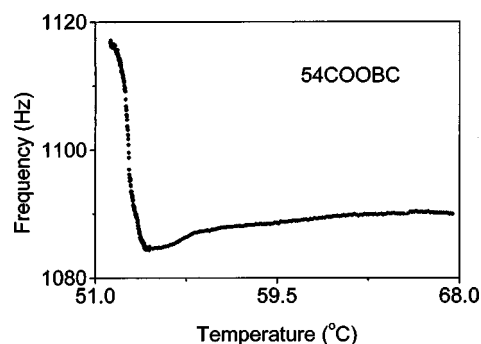

FIG. 4. Temperature dependence of resonant frequency obtained from a 54COOBC film. The film thickness is 126 nm. The smooth change in the vicinity of 55 °C and an abrupt change near 52 °C indicate the bulk Sm-A–Hex-B and Hex-B-Cry-B transitions, respectively.

expect there to be any bulk tension (i.e., the compound is in a fluid state) nor any anomalous changes in density at that temperature. Therefore, from Eqs. (1) and (2) a measurement of the (0,1) resonant frequency should effectively be a measure of the surface tension. Figure 3 shows our measurement for an HOPDOB film of purple color. Qualitatively, we have a similar change in slope at the same temperature as Thieme *et al.* To assure ourselves that these two data sets are also quantitatively consistent, we checked two things. First, using Thieme's value of surface tension, our value of frequency, a nominal density of 1.0 g/cm^3, and a nominal ordinary index of refraction of 1.5, we calculated the optical thickness of the film from Eq. (1). The calculated value of 530 nm (optical thickness) is consistent with the observed purple color of the film. The corresponding film thickness is about 350 nm. The second check was to compare the percent change in surface tension per degree between 55 °C and 60 °C in the two measurements. The two were consistent to well within the data scatter. The consistency between these two very dissimilar measurements of surface tension is also an indication that the frequencies we measure are not significantly affected by damping from the helium exchange gas in our reduced pressure regime. Besides being an assurance of the validity of our method, our study of HOPDOB also demonstrates the dramatic improvement in resolution that this experiment brings to the measurement of surface tension as a function of temperature in free-standing films. The data scatter on the vertical axis in Thieme's data is roughly 2%. From Fig. 3, our scatter is smaller than 0.2%. We can also make one additional comment about the HOPDOB data. Usually the surface tension will decrease as temperature increases. The increase found between 48 °C and 54 °C (Fig. 3) indicates surface enhanced order. Even though the film is in the bulk Sm-C temperature range, we believe that there is an onset of surface Cry-B order near 54 °C. Other experimental probes (e.g., x-ray scattering) are required to characterize the nature of this transition.

After establishing the resolution of our tensiometer, we also made measurements on the 54COOBC compound. We have identified three reproducible features in runs from three different 54COOBC films. Figure 4 displays one of these data runs. Again, the data scatter is better than 0.2%. We interpret the data features based mainly upon comparisons to our previous heat-capacity measurement from a thick

54COOBC-film [8]. The first feature is a broad step near 55 °C. Heat-capacity data indicates the bulk of the film undergoes the Sm-A–Hex-B transition at this temperature. Since both the Sm-A and Hex-B phases lack long-range positional order, we believe our data are showing the change in density of the material associated with this transition. As the temperature decreases and the film becomes more ordered, the molecular packing becomes more efficient. Thus, the mass density (m_A) increases and from Eq. (1) the resonant frequency decreases. Using the measured value of 54COOBC's surface tension (20.5 dyn/cm [2]), we estimate that the density of the film increases by 0.6%. A comparable change in density was previously obtained from x-ray [10] and optical reflectivity [11] measurements through the Sm-A–Hex-B transition in thin free-standing films of other compounds. The second feature is the pronounced increase in frequency at roughly 52.5 °C. Although we do not show data below 51.5 °C in this particular run due to a film rupture, we have several data sets which show that the resonant frequency levels off at this temperature. We believe this overall increase in frequency is due to the bulk Hex-B–Cry-B transition. A transition from a noncrystal phase to a crystal phase introduces a contribution to the bulk tension in Eq. (2) and thus a significant increase in resonant frequency. Again taking $\sigma = 20.5$ dyn/cm and assuming that the density remains the same through this Hex-B–Cry-B transition [12], we estimate the bulk tension to be 2.5 dyn/cm. Third, around 63 °C, and similar to the result shown in Fig. 3, the slope of the resonant frequency curve shows a sign-change from positive to negative. This is a clear indication of the onset of surface order. By comparison, our previous heat capacity data from thick free-standing films showed a surface Sm-A–Hex-B transition at 63.5 °C [8].

We can also point out that the data acquired in Fig. 4 via continuous feedback loop are in fact consistent with discrete spectral scans collected at different temperatures. Figure 1 exhibits three resonance-peaks in a 54COOBC film at one temperature above and at one below the bulk Hex-B–Cry-B transition. As was the case with the temperature data, the positions of the resonance peaks are increased at the lower temperature, further substantiating the effectiveness of the feedback loop.

In summary, we have constructed a vibrating membrane tensiometer capable of measuring changes in tension of a free-standing liquid-crystal film with relative resolution of 0.2%. In addition, the feedback approach reduces the time associated with finding a resonant frequency to practically zero, allowing greatly improved temperature resolution. We first tested the system on HOPDOB, a compound that had been studied thoroughly by another technique. The results were consistent with each other. We then made measurements on 54COOBC, revealing three distinct features associated with various phase transitions in the film.

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