

## Unique approach to measuring temperature variation of surface tension in smectic liquid crystals

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# Unique approach to measuring temperature variation of surface tension in smectic liquid crystals

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We have measured the temperature variation of surface tension,  $\sigma$ , in freestanding films of three liquid-crystal compounds. To do so, we have constructed a curvature-pressure tensiometer that uses a feedback loop to hold constant the curvature of a film while the temperature of the system is smoothly ramped. The apparatus enables us to obtain the temperature variation of  $\sigma$  in a continuous manner with resolution in  $\sigma$  of  $\sim 0.2\%$ . We interpret reproducible features of our data in terms of phase transitions. © 2003 American Institute of Physics. [DOI: 10.1063/1.1623629]

## I. INTRODUCTION

The study of surface tension is fundamental to the understanding of adhesion, detergency, wetting, etc. The remarkably high surface area to volume ratios of freestanding liquid-crystal films allow unique opportunities to probe the surface properties of these materials. In recent years, a variety of tensiometers have been developed in order to measure the surface tension of freestanding liquid-crystal films.<sup>1–5</sup> These efforts have provided a wealth of information, such as the role of molecular and physical structure in determining the value of surface tension.<sup>6,7</sup> Studying the temperature variation of surface tension is also of great interest because it allows the investigation of surface ordering as the free surface undergoes a phase transition from one molecular arrangement to another. Unfortunately, obtaining high-resolution data has proven to be a difficult task. There are two recurring problems that can arise in the techniques referenced above. First, the scatter in data for a given temperature is greater than 1% in most cases. Second, obtaining a single data point is too time consuming to allow for high-resolution measurements with respect to temperature. The techniques referenced have at least one of these problems if not both. One notable success in dealing with both complications simultaneously was our construction of a vibrating drumhead tensiometer.<sup>8</sup> In this apparatus, the film is vibrated using electric fields. A phase-locked feedback loop ensures that the film vibrates at resonance while the temperature is ramped. Recording the resonance frequency and temperature provides a relative measure of surface tension versus temperature. The data scatter with respect to surface tension was reduced to roughly 0.2%. The temperature resolution was practically continuous. Despite the elegance of the experiment and the lovely data it can produce, this technique has

complications making interpretation of data less than straightforward. For instance, since the entire film vibrates and the mass per area of the film is one determining factor in the resonant frequency, the meniscus can easily play an important role in determining the resonant frequency. Furthermore, any changes in the meniscus during data collection can then introduce shifts in the resonant frequency causing complications in data analysis. In addition, such an experiment is dynamic by design. As the film oscillates, material must flow in and out of the film if the film is to maintain a constant density. How the flow rates of a material affect the resonant frequency of vibration is not clear and may not be a simple issue. At a technical level, this experiment is extremely sensitive to acoustical vibrations because the resonant frequencies tend to be on the order of 1 kHz. Thus, data collection is easily interrupted by very ordinary events such as the sound of a person's voice. As a result, obtaining the desired temperature scans has proven much more elusive than our preliminary studies indicated.

We have constructed a new tensiometer to address the shortcomings of the drumhead experiment. Our new tensiometer has comparable data scatter and temperature resolution as the drumhead experiment. We have measured the temperature variation of surface tension for three liquid-crystal compounds to demonstrate the effectiveness of this new experimental setup.

## II. THEORY BEHIND THE EXPERIMENT

Consider a freestanding film with a surface tension that varies with temperature,  $\sigma(T)$ . It has been established by Stannarius *et al.*<sup>4</sup> that a pressure difference between two sides of a smectic film will induce spherical curvature in a freestanding film (like blowing up a soap bubble on a ring).

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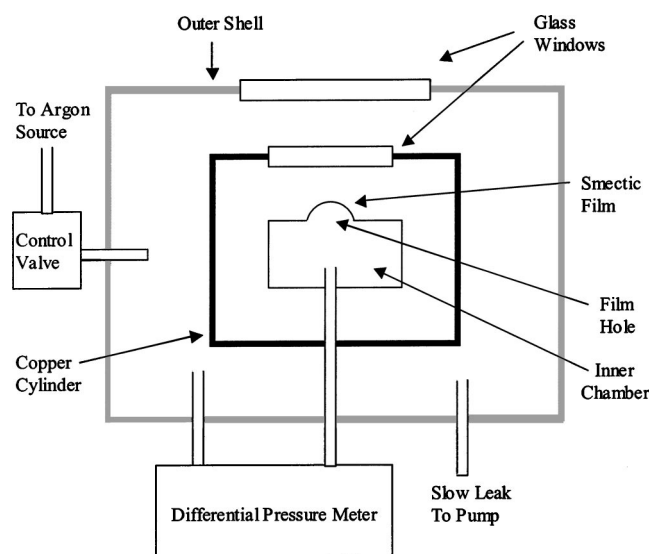


FIG. 1. Three-staged oven that houses the smectic films. The inner and outer chambers are sealed from one another when a film is prepared in the film hole. The pressure in the outer stages is manipulated by means of a control valve. The film is inflated by slightly closing the control valve to decrease the pressure in outer stages. A differential pressure meter measures the pressure difference between the inner and outer stages. The intermediate stage is the heater.

The pressure difference in the radial direction across the film,  $\Delta P$ , and the radius of curvature,  $R$ , are simply related through the surface tension of the film.

$$\Delta P = 4\sigma(T)/R. \quad (1)$$

At a given temperature, the pressure difference required to inflate a film to a given radius of curvature is simply proportional to the surface tension of the film. Thus, if  $R$  is held constant while  $T$  is varied, then  $\Delta P$  will vary in direct proportion to  $\sigma$ . By recording the  $\Delta P$  required to hold  $R$  constant versus  $T$ , one obtains the temperature variation of  $\sigma$ . This is precisely the idea behind our experimental apparatus.

### III. EXPERIMENT

#### A. Making a bubble and controlling the pressure difference

The freestanding films are prepared in a three-staged oven as depicted in Fig. 1. The outer shell is an airtight aluminum cylinder so that the film can be contained in a pressure-controlled environment of argon. With the exception of a circular hole (diameter of 0.95 cm), the inner stage is an airtight stainless-steel chamber. The liquid-crystal films are prepared across the circular opening in the inner stage. When a film is prepared, the inner chamber becomes sealed from the outer stages. The intermediate stage is a temperature-controlled copper cylinder (not airtight) allowing smooth ramping of the ambient temperature of the film. The oven is weakly coupled to a mechanical pump, causing a slow evacuation. The oven is also coupled to an argon source through a control valve (MKS Type-148C).<sup>9</sup> A pressure controller (MKS Type-250) manipulates the control valve in order to regulate the pressure of the outer stages. Since the inner stage is sealed by the film, the controller regulates the

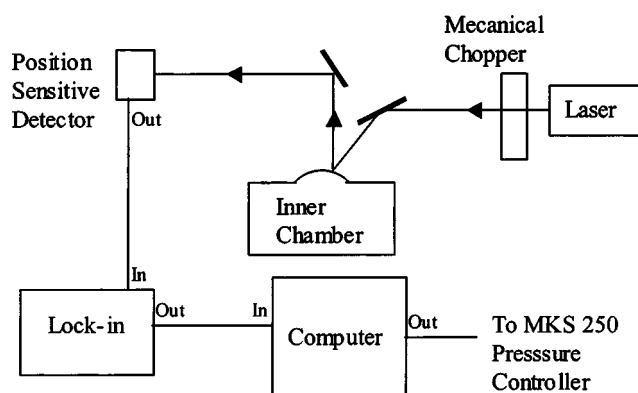


FIG. 2. System used to hold bubble radius constant. A mechanically chopped laser beam is reflected from the film to the center of a position-sensitive detector. A lock-in amplifier reads the detector signal and is output to the computer. The computer drives the pressure controller in order to keep the laser beam centered on the detector.

pressure difference between the inner and outer stages. Our tests indicate that the permeability of argon molecules through the film is very low. An MKS Type-223b differential capacitance manometer (0.2 Torr full scale, resolution of  $2 \times 10^{-5}$  Torr) measures the pressure difference. The signal from the manometer (a voltage proportional to the pressure difference) provides feedback to the pressure controller. The set point of the controller is simply manipulated by an external dc voltage, referred to as the “control voltage.” For our setup, the radius of curvature of a bubble is roughly 1 cm and the pressure difference is stable to within  $\pm 3 \times 10^{-5}$  Torr. The key thing to notice is that the pressure difference is effectively manipulated and easily recorded to high resolution, since it is only a matter of providing and recording a dc voltage.

#### B. Holding the bubble radius constant

Figure 2 shows a schematic of the system used to hold  $R$  constant. A chopped intensity-stabilized He-Ne laser beam is reflected from the bubble to a position-sensitive photodiode (UDT type SC-10D).<sup>10</sup> Since the path of the reflected ray is determined by the radius of the bubble, holding  $R$  constant is then simply a matter of keeping the reflected beam spot at the same position on the photodiode. This was accomplished by constructing a proportional-integral-differential feedback system that interfaces the signal from the photodiode with the pressure-control system. The photodiode is designed to have a null signal when the beam spot is centered on the detector. As shown in Fig. 2, the output of the photodiode is input to a lock-in amplifier that is tuned to the chopping frequency. The computer reads the signal of the lock-in amplifier and accordingly outputs a voltage to drive the pressure controller (i.e., the control voltage). If the signal of the lock-in amplifier wanders from zero (i.e., if the beam spot moves from the center of the photodiode), the computer adjusts the control voltage to bring the signal back to zero (i.e., bring the beam spot back to the center of the photodiode). With the feedback system operating, the computer simultaneously records the control voltage and the film-plate temperature as the temperature of the oven is ramped. The con-

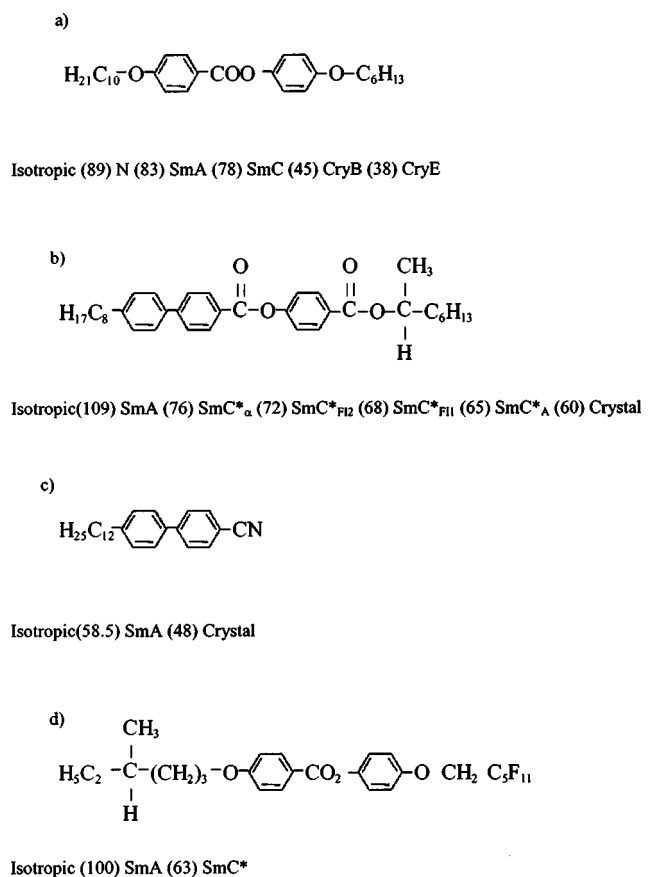


FIG. 3. (a)–(d) The molecular structures of HOPDOB, MHPBC, 12CB, and 4M6OBF5MOP, respectively. Transition temperatures are in degrees centigrade.

trol voltage is then scaled into absolute units by measuring surface tension with our flexible-string tensiometer.<sup>2</sup>

#### IV. RESULTS AND DISCUSSION

We measured the temperature variation of  $\sigma$  for three compounds, HOPDOB, MHPBC, and 12CB. The chemical structures and phase sequences are shown in Fig. 3.

In order to give our system a critical test, we made measurements on the liquid-crystal compound HOPDOB. In two distinct experiments, the temperature variation of  $\sigma$  has been studied for this material.<sup>8,11</sup> Upon cooling, both previous experiments show a sharp slope change from negative to positive near  $T=53^\circ\text{C}$ . This feature is explained by recalling that the temperature derivative of  $\sigma$  is directly related to the excess surface entropy per unit area,  $s$ :

$$d\sigma/dT = -s. \quad (2)$$

As the surface undergoes an ordering transition,  $s$  can change from positive to negative. A slope change as seen in the HOPDOB data is indicative of a surface ordering transition. Our system reproducibly shows the same slope change as previously seen. Figure 4 shows one such data run. First, notice that the scatter in the data is roughly 0.2%, comparable to the results of our drumhead experiment. Additionally, the temperature resolution is also practically continuous by nature of the experimental design. Analyzing a 3 K temperature window just below the anomalous change in slope,

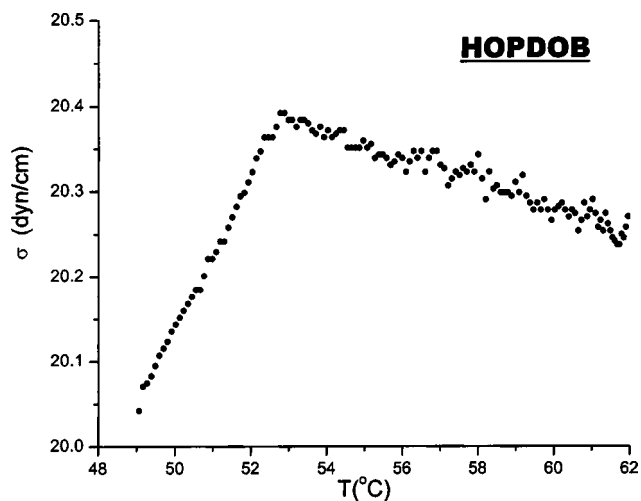


FIG. 4. Temperature variation of surface tension obtained from an HOPDOB film. The slope change in the vicinity of  $53^\circ\text{C}$  suggests a surface transition. The units on the vertical axis were scaled from surface-tension data (in Ref. 11).

our data indicate that the surface tension changes by  $(0.452 \pm 0.002)\%$  per K over this range. Analyzing the surface tension data reported in Ref. 11 within the same temperature window, we get a slope of  $(0.44 \pm 0.09)\%$  per K, assuring us that the two data sets are quantitatively consistent.

We also made measurements on the compound MHPBC. In doing so, we found some surprising results. Differential optical reflectivity (DOR) measurements show a surface transition from SmA to SmC\*<sub>α</sub> near  $T=101.5^\circ\text{C}$ .<sup>12</sup> We carefully scanned a wide temperature window ( $67$  to  $109^\circ\text{C}$ ) but were not able to detect any anomalies in our data associated with surface or bulk phase transitions in MHPBC. Unlike with HOPDOB, it seems that the change in excess surface entropy for the  $101.5^\circ\text{C}$  surface transition in MHPBC is too small to be resolved by our probe. Understanding the reasons behind this will require further study. An unexpected reproducible feature, however, does show up near the bulk SmA to isotropic transition near  $T=109^\circ\text{C}$  (see Fig. 5). The slope,  $d\sigma/dT$ , changes from positive to negative upon cooling. It would be naïve to claim that this anomalous change in the surface tension is simply due to a surface transition as in HOPDOB. One problem is that the slope change is the reverse of what one expects for surface enhanced ordering as predicted by Eq. (2). Additionally, as far as we know, there is not any reason to expect a surface transition at this particular temperature. The surface layer is already in the SmA phase, so a transition to an intermediate phase before melting to isotropic is not logical. Incidentally, this feature showed up in an optically pure sample as well as in a racemic mixture of the compound.

To understand the origin of this feature, we needed to rule out mechanisms that are not due to the surface tension itself. It is natural to speculate that as the reservoir of material on the film plate melts, the anchoring position of the bubble will shift due to the flow of material as it more fully spreads out on the plate. Such a process would be irreversible. Figure 5 shows a cooling run and a subsequent heating

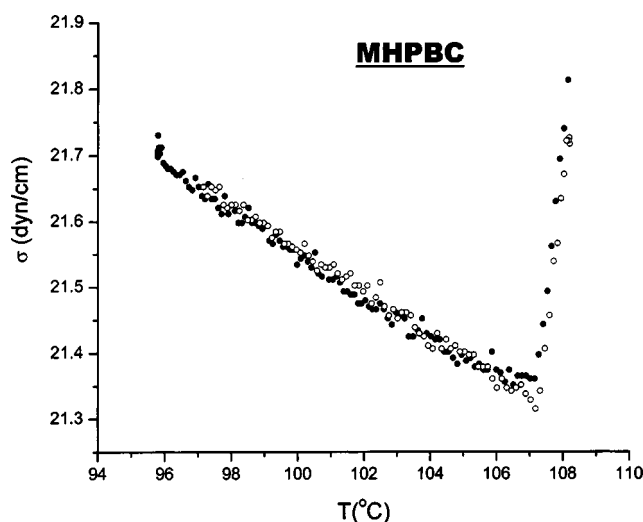


FIG. 5. Subsequent cooling (open circles) and heating runs, showing temperature variation of surface tension obtained from an MHPBC film. The slope change in the vicinity of 107 °C is the opposite of what is expected for a surface ordering transition. The units on the vertical axis were scaled from surface tension values obtained with our flexible-string tensiometer.

run. As one can see in Fig. 5, the feature is reversible upon cooling and heating, ruling out this first possibility. The reproducibility shown near the SmA–isotropic transition gives assurance that once the anchoring position of a film is established, that position is robust. This important issue will be addressed again later in the article.

A second possibility is that upon approaching the isotropic phase, the material undergoes a change in optical properties that shifts the path of the reflected ray, mimicking a change in surface tension. DOR measurements, however, show no dramatic changes in the optical properties of the material upon approaching the isotropic transition. The DOR probe is designed specifically to probe optical changes. It is highly improbable that the tensiometer is more sensitive to optical changes than the DOR experiment, particularly when considering the fact that the tensiometer shows no anomalies for the many transitions clearly observed by DOR.

Having ruled out these possibilities, we will speculate upon how the surface tension itself might be responsible. It has been definitively shown that the value of surface tension for a freestanding liquid-crystal film is determined by the molecular group exposed at the free surfaces of the film.<sup>6,7</sup> A surface composed of —CH<sub>3</sub> groups will have a surface tension of roughly 21 dyn/cm, whereas surface composed of —CH<sub>2</sub>— groups will have surface tension of roughly 31 dyn/cm. A surface composed partially of —CH<sub>3</sub>'s and —CH<sub>2</sub>—'s will have some weighted average of these values. The molecular structure of MHPBC is typical to many smectic liquid crystals in that it has flexible hydroalkyl tails on each end of the molecule (see Fig. 3). A closely packed SmA surface layer with such a compound will yield a value of  $\sigma \sim 21$  dyn/cm since only the —CH<sub>3</sub> end group will be exposed. Using our flexible-string tensiometer,<sup>2</sup> we have measured a value of 21.4 dyn/cm at 104 °C, indicating a closely packed surface at this temperature. In contrast, it has been seen that if these flexible tails have space to conformationally explore, then the surface tension will be increased

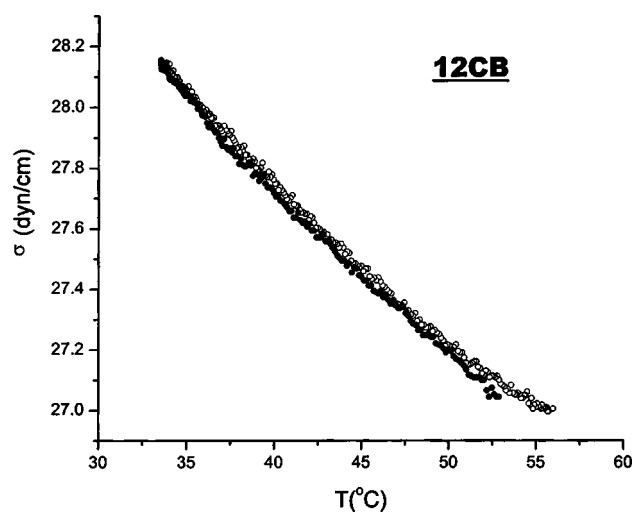


FIG. 6. Subsequent cooling (open circles) and heating runs, showing temperature variation of surface tension obtained from a 12CB film. The units on the vertical axis were scaled from surface tension values obtained with our flexible-string tensiometer.

because some fraction of the tails will fold over and expose —CH<sub>2</sub>— groups at the surface. This effect has been seen in two separate cases.<sup>6,13</sup> In the case of 12CB, the bilayer structure leads to the exposure of —CH<sub>2</sub>— groups at the film surfaces and a measured surface tension of 27.1 dyn/cm (see Ref. 6 for further discussion).

These ideas lead to a plausible explanation for our data. As the film approaches the SmA–isotropic transition, fluctuations in the layer structure become more pronounced. The flexible tails then have more space to conformationally explore, exposing more —CH<sub>2</sub>—'s and increasing the average surface tension of the film. The observed increase in surface tension above 107 °C is about the resolution of our flexible-string tensiometer. Further investigations are necessary to confirm or reject this speculation.

We also made measurements on the compound 12CB. Figure 6 shows such a run. Upon heating, the crystal–SmA transition temperature occurs at 48 °C, the bubble can be supercooled and remains stable far below this temperature. Notice that the subsequent cooling and heating runs very nearly overlap. We believe the small offset is due to slight adjustment of the anchoring position of the bubble to the meniscus during the long temperature ramp. From the reproducibility over such a wide temperature window, we are again assured that once the anchoring position of a bubble is established, that position is robust. Schneider used a double-ring tensiometer to measure  $\sigma$  versus  $T$  on the compound 8CB.<sup>5</sup> Although 8CB and 12CB most likely should not have exactly the same slope, we thought a comparison would give a further sense of the reliability of our data. Comparing the average slope over a 15 K window, we find that the values are within 5% of one another (−0.21% per K for 12CB and −0.20% per K for 8CB). The consistency between these two very different experimental techniques gives further evidence that our probe reliably records the relative values of surface tension as a function of temperature. Schneider's apparatus provides significantly better resolution with respect to  $\sigma$  than ours ( $2 \times 10^{-5}$  and  $2 \times 10^{-3}$ , respectively), but acquiring

TABLE I. Comparison of the ratio of control voltages to that of measured surface tensions for two sets of compounds. The compounds were chosen for their wide range of surface tension values. Within experimental resolutions of both probes, the ratios are in good agreement. The uncertainty for the control voltage ratios is probably underestimated because they are based on the spread in data from film to film for a single compound and do not take into account any uncertainty introduced by removing the windows to clean the oven.

Compounds	Control voltage ratio	Surface tension ratio
MHPBC:4M6OBF5MOP	$1.46 \pm 0.9:1$	$1.52 \pm 0.6:1$
12CB:MHPBC	$1.37 \pm 0.8:1$	$1.27 \pm 0.5:1$

temperature data with the two-ring experiment is very cumbersome.

In addition to comparing our temperature scans to those of other research groups, we also compared recorded control voltages from compound to compound. Ideally, one can simply compare the ratio of the control voltages for two compounds and compare this to the ratio of surface tensions measured by other means. In order to make such a comparison meaningful, it is crucial that the optical components are not moved since even a slight adjustment of a single mirror, lens, or window can lead to a noticeable change in the control voltage necessary to center the laser beam on the photodiode. This is practically impossible to accomplish from sample loading to sample loading because cleaning the chamber necessarily means removing two of the windows through which the laser beam travels. Additionally, it is also practically impossible to ensure that the anchoring of the bubble to the meniscus will remain the same from film to film, let alone from one compound to the next. Our studies indicate that from film to film with a single compound, there is a spread in the control voltages of roughly  $\pm 3\%$ . Recall, however, that the anchoring position for any given bubble is robust, as evidenced by the reproducibility upon cooling and heating in Figs. 5 and 6. Despite these complications, we felt it important to run this additional test of our system. For three compounds loaded in succession (4M6OBF5MOP, MHPBC, and 12CB), we recorded the control voltages necessary to center

the laser beam on the photodiode without making any adjustments to the optical components other than those necessary to clean the oven. 4M6OBF5MOP, MHPBC, and 12CB were chosen because they provide a wide range of surface tensions due to their varied chemical structures. We measured the surface tension of each using a flexible-string tensiometer<sup>2</sup> to be  $14.1 \pm 0.3$ ,  $21.4 \pm 0.4$ , and  $27.1 \pm 0.5$  dyn/cm, respectively. Due to the order of sample loadings, it makes the most sense to compare MHPBC to the other two. The results are given in Table I. Within our experimental resolutions, the ratios agree with each other. This yields further confidence in the reliability of our probe.

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