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Maximum Force Technique for the Measurement of the Surface Tension of a Small Droplet by AFM

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An atomic force microscope (AFM) is used to measure the meniscus force on a vertical quartz rod as the rod is pulled through an air/liquid interface. A fluid bridge forms between the liquid and the base of the rod as the rod is withdrawn from the liquid. The force reaches a maximum as the bridge necks down and finally detaches from the rod. The maximum force on the rod is independent of the material of the rod and can be used to calculate the surface tension of the liquid. Alternately, if the surface tension of the liquid is known, the maximum force of the meniscus can be used to calibrate the spring constant of the AFM cantilever. The contact angle of the liquid on the rod was calculated as the rod was inserted into the liquid droplet. Contact angle hysteresis was observed. Results are presented of the measurement of the meniscus force of water, 10^{-3} M cetyl trimethyl ammonium bromide (CTAB) and tetradecane as the rod is withdrawn from the liquid.

Keywords: AFM; Contact angle; Hysteresis; Nanoscale; Surface tension; Wetting

INTRODUCTION

The advance of nanotechnology has led to the dramatic decrease in the dimensions of materials. As the size of materials shrink, the surface to

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volume ratio dramatically increases and the properties of the surface become increasingly important. New methods, both experimental and theoretical, are needed to measure the properties of nanoscale materials. For example, biological materials, such as lung epithelial fluid, tears, and synovial fluid, are only available in small volumes. What methods can be used to measure the surface tension of small volumes of liquids? The surface energy of a solid material gives information regarding miscibility and solvent interactions. Both of these parameters are important in determining the stability of nanocomposite materials. Can macroscopic wetting theories be used at this small scale, especially when the material dimension is much less than the capillary length?

Macroscopic measurements of the surface tension of a liquid can be determined by a variety of techniques including pendant drop, sessile drop, du Nuoy ring, capillary rise, and Wilhelmy plate [1–3]. The value of the surface tension is considered to be a property of the interface and should be independent of the measurement technique. Dynamic methods, however, such as detachment methods, often give higher values than those measured with static methods. This is especially true for liquid mixtures, such as surfactant solutions.

The Wilhelmy plate method is a well known technique that measures the force on a plate as it is inserted or removed from liquid [4]. The excess force on the plate in the liquid is given as the meniscus force minus the buoyancy correction. From this force balance the contact angle or surface tension can be determined.

The rod-in-free-surface technique is similar to the Wilhelmy plate technique [5,6]. In the rod-in-free-surface method a rod with a flat end at the base is hung from a balance. A liquid is brought into contact with the base of the rod causing an increase in the force on the rod due to the meniscus. Then, the level of the liquid is slowly lowered while continuously monitoring the force on the rod. The force of the meniscus on the rod reaches a maximum and falls before detachment of the meniscus from the rod occurs. The force maximum is a function of the volume of the liquid bridge and is independent of the material of the rod. The contact angle of a liquid against the rod can also be measured if the meniscus force as a function of depth of immersion of the rod into the liquid is known. Typically, the contact angle is determined by measuring the force of the meniscus when the base of the rod is even with the free surface of the liquid.

The macroscopic measurements such as the du Nouy ring, Wilhelmy plate, and rod-in-free surface calculate the surface tension or contact angle from the measured force on the probe. The surface tension or contact angle can be determined when the base of the probe

is: even with the free surface of the liquid, partially immersed in the liquid, above the free surface of the liquid and a stable meniscus has formed, or where the meniscus detaches from the probe. Frequently, the entire force-distance curve is measured, *i.e.*, the force on the probe as it is pushed into and withdrawn from a solution. The contact angle or surface tension can then be calculated from a particular point or set of points on the force-distance curve, such as the force at detachment.

Recently, the static wetting force of single microspheres and nanotubes have been measured by AFM [7–10]. In the microsphere measurements the meniscus force is only measured at zero total force, *i.e.*, where the buoyancy force equals the capillary force. In the nanotube experiments the force-distance curve is measured as the nanotube touches and is removed from a solution. The contact angle of the liquid next to the microsphere or nanotube is then calculated from the immersion depth at zero force. If the macroscopic theories can be applied to these microscopic measurements, then measurement of the entire force curve should give additional information, as has been suggested [11].

The rod-in-free-surface technique has been used to measure the surface tension of surfactant solutions using rods with 1-mm diameter, a dimension comparable with the capillary length [6]. In this article we extend the rod-in-free-surface measurements by investigating the wetting of a 97- μm diameter rod using an atomic force microscope (AFM). Because the capillary length is a few mm we are measuring the wetting force on a material whose dimension is much less than the capillary length. The entire force-distance curve is measured as the rod is immersed into a droplet and removed from the droplet. We then calculate the surface tension of the liquid and the contact angle of the liquid against the rod surface from the measured forces. The surface tension is determined from the maximum excess force, not where the force is zero.

An accurate measure of the meniscus force by AFM demands an accurate measure of the cantilever spring constant. The cantilever spring constant is often calibrated by noting the thermal resonance frequency, but, once a particle or probe has been attached to the cantilever, the effective spring constant will change depending on the point of attachment [12]. The maximum force method, in which the maximum force required to pull a rod from contact with a liquid is measured, provides a method of calibrating the effective cantilever spring constant with a mass attached if the surface tension of the liquid is known. Alternately, if the effective spring constant of the cantilever is known, the maximum force method can be used to determine the surface tension of a liquid.

EXPERIMENTAL

An atomic force microscope (Dimension 3100, Veeco Metrology, Santa Barbara, CA, USA) was used for the measurements. A quartz rod was drawn to $97\ \mu\text{m} \pm 2\ \mu\text{m}$ diameter. Unless otherwise noted, the \pm refers to the standard uncertainty in the measurements and is taken as one standard deviation of the observed values. The quartz rod was broken into approximately 300- μm lengths and a small rod was attached to an AFM cantilever using fast setting epoxy, as shown in Figure 1. The specific rod used was found to be at a 30° angle to the cantilever. The cantilever is angled approximately 10° to the measurement surface. Therefore, the rod was at a 20° angle to the liquid surface. The rod was cleaned for 10 minutes in an ultraviolet ozone cleaner prior to measurement. The bare cantilever (Tap 525, Veeco Metrology, Santa Barbara, CA, USA) had a manufacturer's listed spring constant of $200\ \text{N/m} \pm 150\ \text{N/m}$.

The AFM photodiode was calibrated by pressing the rod on a rigid Si sample and noting the deflection and also by pressing the rod

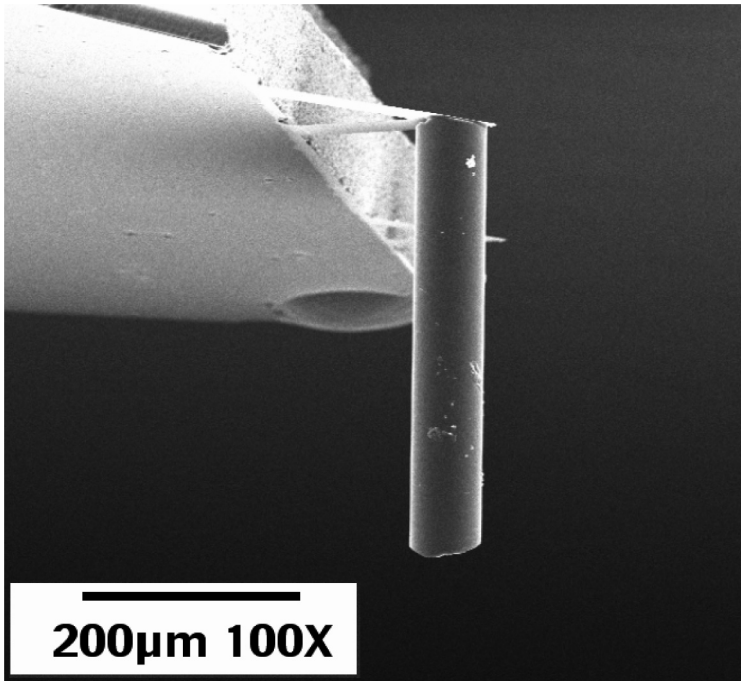


FIGURE 1 SEM micrograph of a $68\ \mu\text{m}$ quartz rod bonded to an AFM cantilever.

against an oscillating rigid Si sample that is translated using a previously calibrated low voltage piezoelectric stack (TS18-H5-202, Piezo Systems, Inc, Cambridge, MA, USA). When the rod is in contact with the hard sample, the cantilever moves with the sample and the response of the photodiode signal is measured. The photodiode calibration will depend on the specific angle of the cantilever to the surface, the placement of the laser on the cantilever, and the position of the laser on the photodiode. For these measurements, the photodiode calibration was $50 \text{ nm/V} \pm 3 \text{ nm/V}$. The height step size calibration of the AFM stepper motor was measured to be within 1% of the value given by the manufacturer. However, because we are mainly interested in accurate measurement of the forces and not the height of the meniscus bridge we are presenting the data as a function of time for a constant step rate.

A 0.5-ml liquid droplet was placed on a Teflon[®] sheet that had been cleaned in concentrated NaOH solution and rinsed in water. The rod was slowly lowered onto the droplet using the stepper motor on the AFM. Once contact between the droplet and the rod occurred, the AFM cantilever was raised in a stepwise fashion using the AFM stepper motor at a rate of approximately $3 \mu\text{m/step}$ and 1 step/s . During the measurement the laser signal was focused near the center of the photodiode where the photodiode was calibrated. The photodiode signal was sampled at 250 points/s and stored on a computer. After the measurement the AFM cantilever was examined under a microscope to ensure that the cantilever was not wet during the measurement.

Deionized water, 10^{-3} M cetyltrimethyl ammonium bromide (CTAB), and tetradecane were used as the wetting liquids. The CTAB and tetradecane were obtained from Fisher Scientific (Pittsburgh, PA, USA), and used as received. The literature values of the surface tensions of water, 10^{-3} M CTAB and tetradecane are 72 mN/m , 37 mN/m , and 27 mN/m , respectively [13–15]. The experiments were performed at $23^\circ\text{C} \pm 1^\circ\text{C}$.

RESULTS AND DISCUSSION

When the quartz rod is lowered to touch the surface of the droplet and contact between the droplet and the rod occurs, the meniscus rapidly advances up the side of the rod as shown in Figure 2a. The excess force measured on the rod is the meniscus force and acts to pull the rod into the liquid. As the rod is withdrawn from the solution the meniscus retracts and finally reaches the end of the rod. The meniscus remains pinned at the edge of the rod as the rod is being withdrawn until the meniscus breaks (Figure 2b).

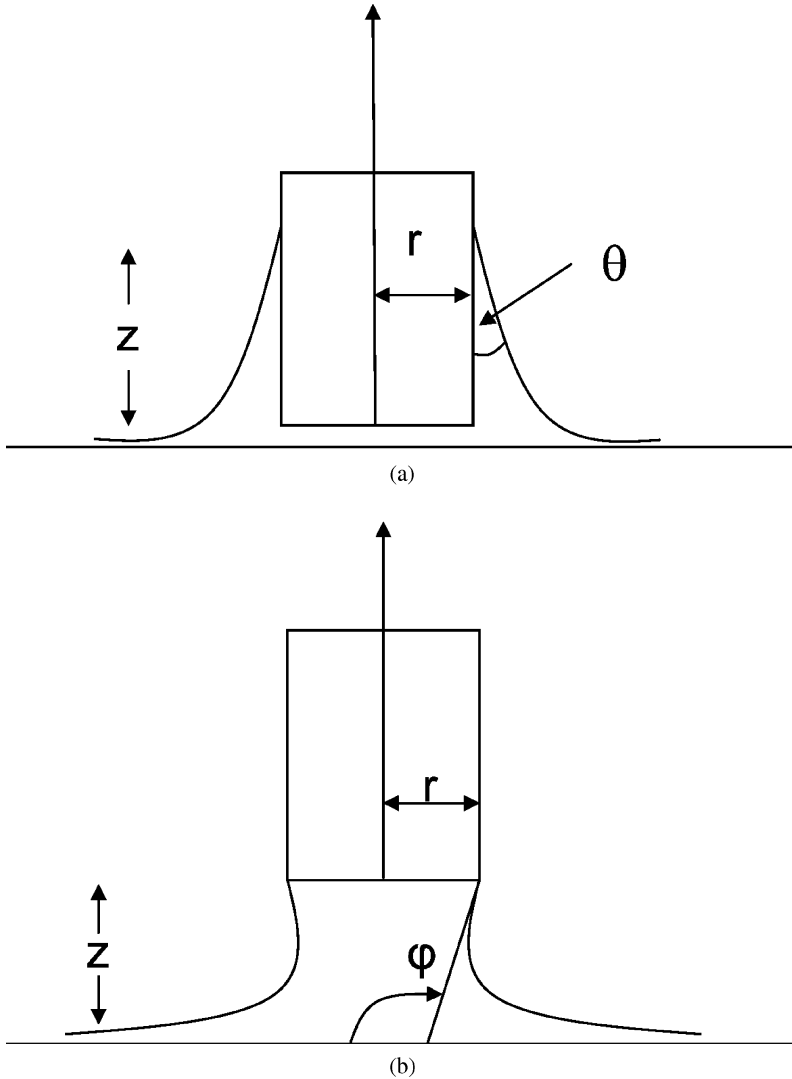


FIGURE 2 Schematic diagram of the base of a rod (a) inserted into a liquid droplet and (b) being pulled from the free surface of a liquid.

The total force F exerted by a meniscus on a rod of radius r can be described by [5,16,17]:

$$F = \Delta\rho g v = 2\pi r \gamma_{lv} \sin \phi + \Delta\rho g \pi r^2 z \quad (1)$$

where v is the volume and z is the height of the liquid meniscus above the undisturbed liquid surface, γ_{lv} is the liquid/vapor surface tension, $\Delta\rho$ is the density difference across the liquid-vapor interface, g is the acceleration due to gravity, and φ is defined as in Figure 2b. Note that when the meniscus is wetting the sides of the rod and is not pinned at the edge of the rod, as shown in Figure 2a, $\varphi = 90^\circ - \theta$, where θ is the contact angle.

When the capillary length exceeds the diameter of the rod, the buoyancy force can be ignored and the force on the rod is given by: [6,16]

$$F \approx 2\pi r \gamma_{lv} \cos \theta. \quad (2)$$

The maximum force on the rod occurs when the volume of the meniscus is maximum. This occurs when the meniscus is pinned at the edge of the rod and $\varphi \sim 90^\circ$, giving [5,6]

$$F_{\max} \approx 2\pi r \gamma_{lv}. \quad (3)$$

It should be noted that the maximum force is independent of the contact angle of the liquid on the rod, *i.e.*, is independent of the material of the rod. This is because the meniscus is pinned at the edge of the rod. More rigorous equations for the maximum force on a rod have also been published, but Equation (3) has been found to be accurate to better than $\pm 1\%$ for small diameter rods ($r < 1$ mm) [6].

The height of the meniscus, measured from the undeformed liquid surface, is given by [16,17]:

$$z \approx r \sin \varphi \left(\ln \frac{4}{(l + \cos \varphi)R} \right) - \gamma_E \quad (4)$$

where γ_E is Euler's constant ($\gamma_E = 0.577215\dots$) and $R = r/c$, where the capillary length c is defined as $c = (\gamma_{lv}/\Delta\rho g)^{1/2}$ and is the ratio of the surface tension to gravitational effects. At the force maximum $z = 234 \mu\text{m}$, $218 \mu\text{m}$, and $217 \mu\text{m}$ for water, 10^{-3} M CTAB, and tetradecane, respectively. The capillary lengths are 2.7 mm, 1.9 mm, and 1.9 mm for water, 10^{-3} M CTAB, and tetradecane, respectively. It should be noted that we are measuring in a regime where the diameter of the probe ($97 \mu\text{m} \pm 2 \mu\text{m}$) is much less than the capillary length.

Figure 3 shows the force, measured as cantilever deflection, as a function of time as a rod contacts the free surface of a 10^{-3} M CTAB solution and is slowly removed from the solution. Due to the meniscus force the cantilever deflection, x , increases from zero to 31 nm as the rod touches the liquid surface. The force on the cantilever is stable and no change in the measured deflection is detected unless the rod

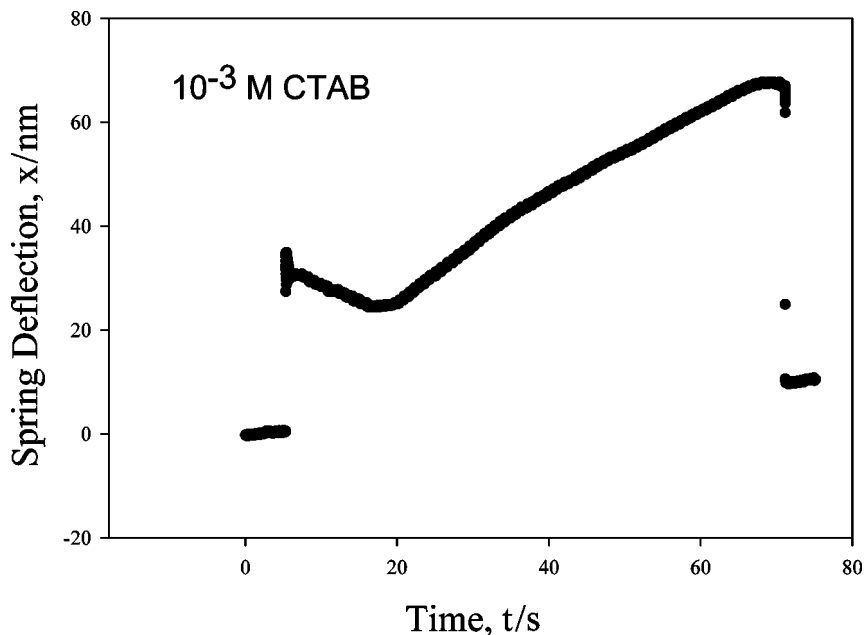


FIGURE 3 Measured cantilever spring deflection as a function of time for a quartz rod contacting a 10^{-3} M CTAB solution.

is pushed into or pulled out of the solution. As shown in Figure 3, at a time of $t \approx 8$ s, the rod is pushed into the liquid and the cantilever deflection decreases.

At $t \approx 18$ s the rod is pulled from the liquid at a rate of approximately $3 \mu\text{m}/\text{step}$ and $1 \text{ step}/\text{s}$. The cantilever deflection increases and reaches a maximum at $x_{\text{max}} = 68 \text{ nm}$. As the pulling continues the cantilever deflection falls slightly as the fluid necks down and then abruptly drops to near zero as the droplet detaches from the rod. The value of the maximum of the cantilever deflection was found to be very reproducible with repeat measurements giving $x_{\text{max}} = 70 \text{ nm} \pm 4 \text{ nm}$. Note that the cantilever deflection is not the height of meniscus.

According to Hooke's Law, $F = kx$, where x is the cantilever deflection and k is the cantilever spring constant. The maximum cantilever spring deflection $x = 70 \text{ nm} \pm 4 \text{ nm}$ gives $F_{\text{max}} = 14 \mu\text{N} \pm 0.8 \mu\text{N}$ assuming $k = 200 \text{ N/m}$, the manufacturer's value of the spring constant of the bare cantilever. The surface tension of the liquid can be determined from the measured maximum force and Equation (3), giving $\gamma_{\text{lv}} = 46 \text{ mN/m} \pm 3 \text{ mN/m}$. This value of γ_{lv} is significantly greater than the literature value of 37 mN/m [15]. In the case that

the rod is not perpendicular to the surface or if the base of the rod is rough, both of which exist here, a smaller force would be measured resulting in a lower calculated surface tension. Because a higher value of the surface tension was calculated we believe the initial estimate of the spring constant was too high. In addition, even if the spring constant of the bare cantilever is accurately known, once a small rod is attached onto the end of the cantilever, the exact placement of the fiber on the cantilever dramatically affects the value of the spring constant. We, therefore, use the literature value of the surface tension together with the reproducible maximum force measurement to obtain the spring constant of this cantilever-rod configuration. Once the spring constant is known, we use this value to measure the surface tension of other liquids. Therefore, if $\gamma_{lv} = F_{\max}/2\pi r = 37 \text{ mN/m}$, then $F_{\max} = 11.3 \mu\text{N}$, giving $k = 161 \text{ N/m}$. A revised force curve using $k = 161 \text{ N/m}$ is shown in Figure 4.

The measured force abruptly increases when the rod touches the liquid. At this force the height of the meniscus is calculated to be

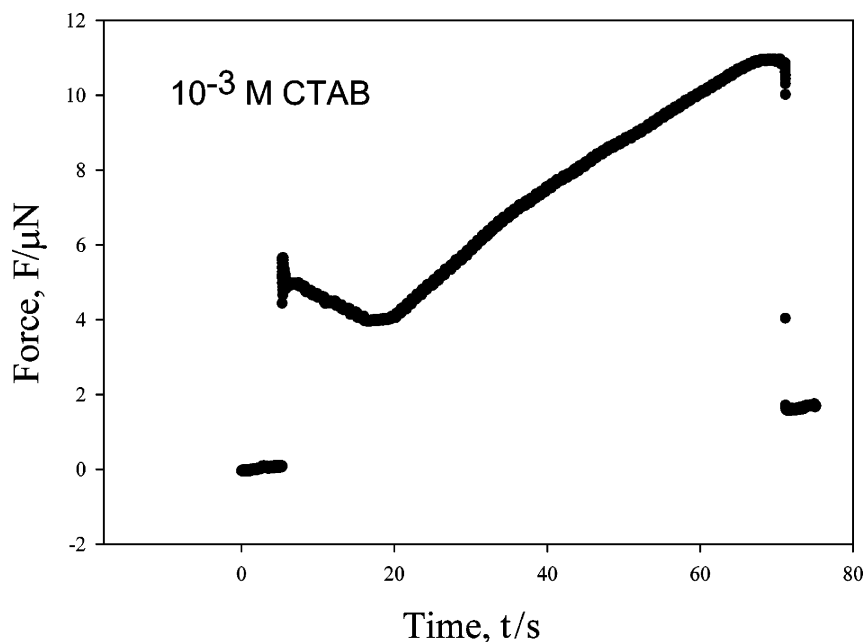


FIGURE 4 Measured force as a function of time for a quartz rod contacting a 10^{-3} M CTAB solution. The cantilever spring constant was calibrated using the expected surface tension of this solution.

37 μm (the calculation is discussed later). Because we are collecting 250 data points per second and no data were collected while the meniscus was advancing along the rod, the meniscus must wet the rod at an average speed of at least 9 mm/s. At the other end of the force curve the meniscus detaches from the rod at a force approximately (85 to 90)% of F_{max} .

Figure 5 shows measurements of the meniscus force on a rod in three solutions: water, 10^{-3}M CTAB, and tetradecane. The same rod and cantilever were used for all the measurements, with the rod cleaned between measurements. The spring constant ($k = 161\text{N/m}$) was calibrated previously using the surface tension of 10^{-3}M CTAB = 37 mN/m as the calibration. In all cases the force abruptly increases when the rod touches the liquid. The contact angle of the liquids next to the rod can be calculated from this initial force measurement using Equation (2). When the rod initially touches the liquid, the wetting is similar to that shown in Figure 2a. The base of the rod is assumed to be at a height approximately equal to the surface of the undeformed droplet; although, as previously mentioned, the buoyancy force is negligible. The measured forces are $F = 9.8\ \mu\text{N} \pm 0.8\ \mu\text{N}$, $5.2\ \mu\text{N} \pm 0.6\ \mu\text{N}$, and $8.4\ \mu\text{N} \pm 0.8\ \mu\text{N}$ for water, 10^{-3}M CTAB, and tetradecane, respectively. Using Equation (2) to calculate the contact angle, $\theta = 63^\circ \pm 2^\circ$, $63^\circ \pm 4^\circ$, and $0^\circ \pm 20^\circ$ for water, 10^{-3}M CTAB, and tetradecane, respectively. Clearly, the rod is slightly hydrophobic and tetradecane wets the quartz rod.

As the rod is pulled from liquid the force increases to $F_{\text{max}} = 15.3\ \mu\text{N} \pm 0.4\ \mu\text{N}$, $11.3\ \mu\text{N} \pm 0.6\ \mu\text{N}$, and $9.5\ \mu\text{N} \pm 0.2\ \mu\text{N}$, for water, 10^{-3}M CTAB, and tetradecane giving $\gamma_{\text{lv}} = F_{\text{max}}/2\pi r = 50\text{mN/m} \pm 2\text{mN/m}$, $37\text{mN/m} \pm 2\text{mN/m}$, and $31\text{mN/m} \pm 7\text{mN/m}$, respectively. The measured force maximum is greatest for water and least for tetradecane, as expected from the surface tension values. The results are summarized in Table 1 and compared with previously published values of the surface tension. The calculated surface tension of tetradecane is within 15% of the literature value, but the AFM measurement underestimates the surface tension of water by 44% [13].

A number of experimental variables could affect the maximum force measurement. The end of the rod is slightly rough and at a slight angle ($\sim 20^\circ$) from normal to the surface. Presumably, the angle would decrease the measured force and a smaller surface tension would be calculated. Surface roughness at the end of the rod would also be expected to decrease the measured force. Also, it is notoriously difficult to obtain a correct surface tension of water as contaminants readily adsorb at the interface. Bulk measurements of the surface tension of water are readily available, but the small $\sim 0.5\text{ml}$ water droplet used

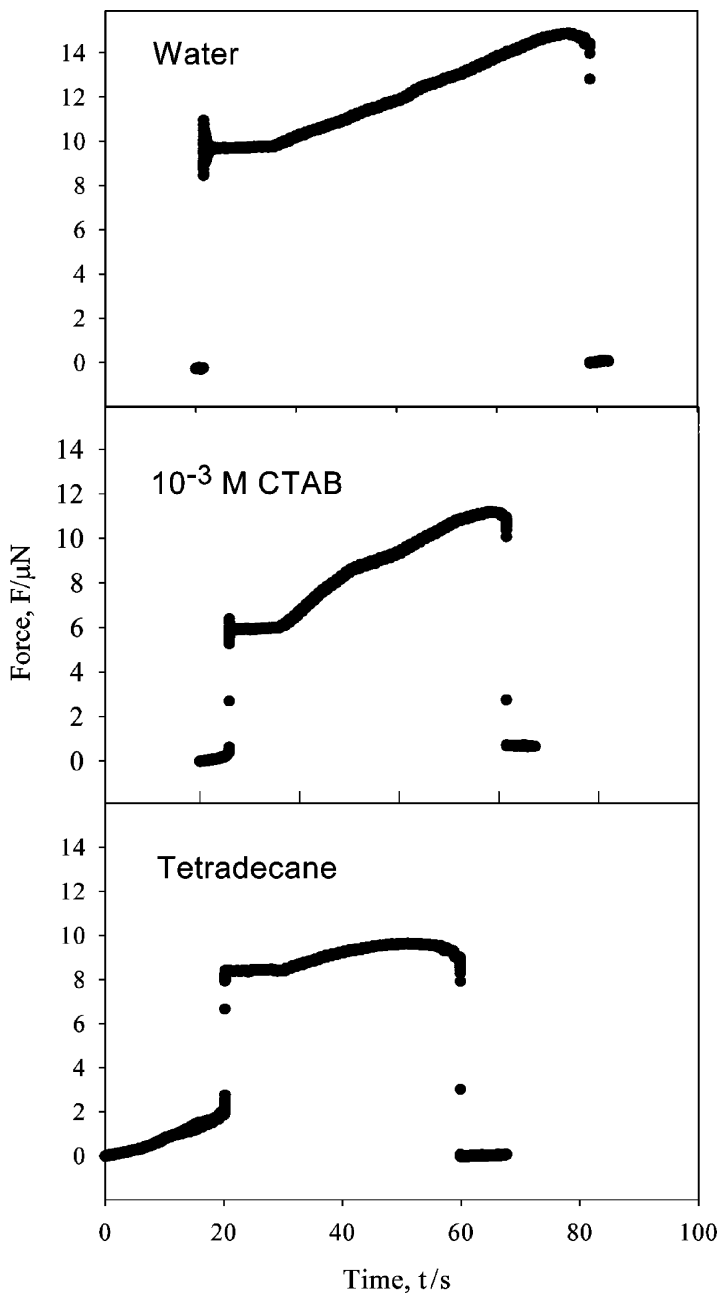


FIGURE 5 Measured force as a function of time for a quartz rod contacting water, 10^{-3} M CTAB, and tetradecane. The cantilever spring constant was calibrated from the measurement in Figure 3.

TABLE 1 Comparison of AFM Results to Macroscopic Measurements

Liquid	Surface tension measured by macroscopic measurements	Surface tension measured by AFM
Water	72 mN/m	50 mN/m
10^{-3} M CTAB	37 mN/m [15]	37 mN/m
Tetradecane	27 mN/m [14]	31 mN/m

in these experiments will likely quickly adsorb contaminants from laboratory air or trace impurities on contacting solid surfaces [14].

Because the buoyancy force is negligible for small rods it is surprising that the force shown in Figure 4 decreases as the rod is pushed into the solution. The decreased force on the cantilever can be attributed to contact angle hysteresis. As previously mentioned the contact angle calculated for the 10^{-3} M CTAB solution against the quartz rod is 63° . Using Equation (4) the height of the meniscus is calculated to be $z \approx 37 \mu\text{m}$. The lower part of the rod is surrounded by the liquid meniscus, as shown in Figure 2a. If the rod is further lowered into the solution, the decrease in the force due to buoyancy is calculated to be $F_b = \rho(\pi r^2) \Delta x'$ where ρ is the density of the quartz rod (assumed to be 2.2 g/cm^3) and $\Delta x'$ is the length of the rod lowered into the solution. Figure 4 shows the meniscus force decreases from $9.8 \mu\text{N}$ to $4 \mu\text{N}$ as the rod is lowered $30 \mu\text{m}$. For $\Delta x' = 30 \mu\text{m}$, $F_b = 0.0048 \mu\text{N}$. Clearly, buoyancy force cannot account for the decrease in the measured force. According to Equation (2), at $F = 4 \mu\text{N}$, $\theta = 69^\circ$. Thus, a 6° increase in the contact angle decreases the meniscus force by approximately $5 \mu\text{N}$. The change in the meniscus force is quantitatively consistent with a fixed contact line on the rod as it is pushed down $30 \mu\text{m}$. Therefore, the interface does not move but remains pinned until the contact angle exceeds the advancing contact angle. The presence of contact angle hysteresis means that there is not a unique contact angle measured, but that the interface can be stable at more than one contact angle. Contact angle hysteresis has also been observed for many macroscopic systems and for micron sized spherical particles [9].

Recently, the static wetting force of a 20-nm diameter multiwalled carbon nanotube and a 40-nm diameter boron nitride nanotube was measured [8,10]. Although the maximum force as the nanotube was pulled from the liquid was measured, the surface tension derived using the maximum force [Equation (3)] was not analyzed. Using the published values of wetting of the carbon nanotube by polyethylene glycol (PEG), glycerol, and water, the maximum wetting force is $F_{\text{max}} = 1.9 \text{ nN}$, 2 nN , and 2.3 nN , respectively. Using Equation (3) the

surface tension is calculated to be 30 mN/m, 32 mN/m, and 37 mN/m for PEG, glycerol, and water, respectively. The corresponding literature values of the surface tension of 48 mN/m, 64 mN/m, and 72 mN/m, measured by traditional methods, are approximately 100% higher than these values. Similar differences between measured and literature values are found for boron nitride nanotubes. The source of these discrepancies is unclear, but could be due to the assumption of a flat base at the end of the nanotube. If the end were rounded as opposed to flat, a different maximum wetting force would likely result.

The results indicate that more studies, both experimental and theoretical, are needed to be able to determine accurately the surface tension of liquids using AFM. Experimentally, ideal probes are needed where the roughness is minimized and the orientation with respect to the liquid surface is known. Theoretically, we would like to understand better the meniscus force for various geometries and surface roughnesses.

These measurements demonstrate that the maximum force method can be used even in the limit where the capillary length is much greater than the probe radius. The AFM method is suitable for measuring the relative interfacial and surface properties of small volumes, such as biological materials, which are only available in small amounts [18]. Microfluidic applications also depend on interfacial properties and this method could be incorporated into a microfluidic platform. In addition, this method can be used to measure the surface energy (via the contact angle) of individual small structures.

The AFM has been shown to be a versatile tool in the measurement of mechanical properties. For example, friction, adhesion, and elastic and viscoelastic properties have all been quantitatively measured by AFM [19–22]. Critical in each of these measurements is the determination of the spring constant of the cantilever with a probe attached. The maximum force method gives a way of calibrating the cantilever with a mass attached if the surface tension of the liquid is known.

CONCLUSION

We demonstrate the feasibility of using an AFM to measure the meniscus force on a 97- μm diameter rod at the free surface of a liquid droplet by the rod-in-free-surface technique. The meniscus force on the rod as it is pushed into and pulled out of the liquid is measured and was used to determine the surface tension of a droplet and the contact angle of a liquid next to the rod. The change in the meniscus force, measured as the rod is pushed into the droplet, is quantitatively consistent with a fixed position of the contact line. Therefore, the contact

angle was found to show contact angle hysteresis. Because of this, the measured contact angle was not unique for each solution against the quartz rod since the interface was stable at more than one contact angle. The force maximum, measured as the rod is pulled out of the liquid, is very reproducible and is an intrinsic property of the system. Distinct differences in the maximum force were measured for water, 10^{-3} M CTAB, and tetradecane. The surface tension, calculated from the force maximum, was within 15% of the literature value for tetradecane, but the AFM underestimated the surface tension of water. The technique can also be used to calibrate the spring constant of the AFM cantilever containing an attached probe, if the surface tension is known.

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