Contact Angle Measurements Using the Drop Shape Method

By Roger P. Woodward, Ph.D.

First Ten Angstroms, 465 Dinwiddie Street, Portsmouth, VA 23704
Tel: 1.757.393.1584 Fax: 1.757.393.3708 email: sales@firsttenangstroms.com

Drop shape analysis is a convenient way to measure contact angles and thereby determine surface energy. The principal assumptions are

- The drop is symmetric about a central vertical axis: this means it is irrelevant from which direction the drop is viewed.
- The drop is not in motion in the sense that viscosity or inertia are playing a role in determining its shape: this means that interfacial tension and gravity are the only forces shaping the drop.

Calibration is straightforward in that only optical magnification is needed. This can be measured with high accuracy and is easy to trace to national standards.

Contact angles are measured by fitting a mathematical expression to the shape of the drop and then calculating the slope of the tangent to the drop at the liquid-solid-vapor (LSV) interface line. We will now lead the reader through the process of making real measurements.

Step 1. Determine Drop Orientation. There are two choices:

- Sessile drop. This is a sitting drop, as in a drop of water resting on a table.
- Sessile bubble. The bubble (drop) is floating in fluid up against the sample bottom. The positions of liquid and vapor have been interchanged.

FTÅ instruments can make both kinds of measurements when equipped with the appropriate chambers. Note that liquid-liquid-solid (LLS) and liquid-vapor-liquid (LVL) measurements are also possible in some cases.

Step 2. Setup Instrument. This involves several steps:

- Mount sample on holder so it may be held flat and moved about. Double-sided foam tape (e.g., Scotch brand Cat. #114) is useful.
- Choose test fluid and place in syringe. Start with water even though other fluids may be required for surface energy analysis. Water is a good starting place because it is safe and forms a high, easily observed, contact angle on most materials. If the test fluid is difficult to clean, e.g., an ink, use disposable plastic syringes. The dispense needles are normally disposable. If the test fluid is valuable, or dangerous, load a minimal amount (say 50µl) by drawing it into the syringe through the needle.
- Obtain an initial live video image of the sample. Adjust lighting and focus. Adjust the pump or needle location so the tip is visible in the image. Adjustment of the camera viewing angle is so important the entire next section is devoted to it.

Step 3. Adjust Camera Angle. We will use the FTA calibration standard to illustrate this process. Figure 1 shows a photo of the standard, which consists of a sapphire ball embedded in an aluminum holder. The protruding height is nominally the radius, so the contact angle is 90°. The ball diameter is an even millimeter number, such as 4 or 6mm, with a tolerance of ±2.5µm.

You can verify the angle if you have a micrometer accurate to 1µm. Measure the height of the base next to the ball and measure the height of the ball plus base. For the standard illustrated, we measure base=5.628mm and base+ball=7.628mm. Subtraction then gives a protruding height, h, of

2.000mm and a diameter, d, of 4.000mm. The contact angle, θ, is given by geometry:

$\theta = 2 \tan^{-1} 2h/d = 2 \tan^{-1} 4/4 = 2 \times 45° = 90°$

Figure 1. Calibration standard.

The sapphire ball standard is more useful than, say, a photographic film standard because it is a 3D object that requires proper lighting and camera angle. Even more importantly, it demands finding the baseline accurately, which is the difficult part of contact angle measurements.

The camera may be placed to either look exactly horizontally at the drop or look down at, say, 3°. The camera angle does not, per se, affect the reading but it does profoundly affect finding the baseline and the baseline affects the reading. Baseline inaccuracy is the primary contributor to contact angle inaccuracy. Both the horizontal, 0°, and look down, 3°, methods will be illustrated.

Camera angle is set by the height of the camera relative to the specimen and by the tilt of the camera stage. Adjust height and then trim tilt to bring the drop vertically into the image. Observe the angle of a line through the centerline of the microscope lens; this is the camera angle. If not satisfactory, readjust the camera height and repeat.

Figure 2 shows the video image with a 0° camera angle and Figure 3 shows a 3° angle. In both cases the standard was oriented as in Figure 1, i.e., with the base long axis across the image. A small amount of "reflection image" can be seen below the baseline in Figure 3 because the camera can "see" the top surface when looking down.

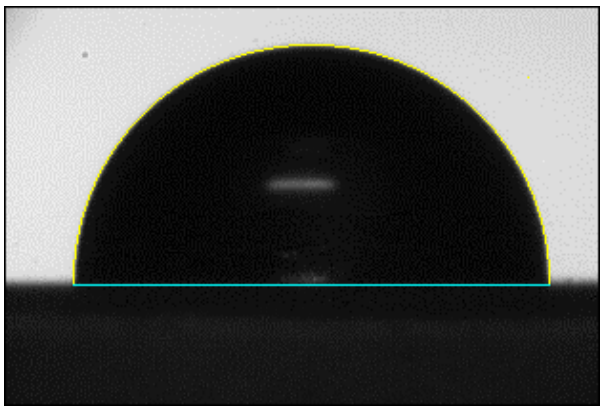

Figure 2. 4mm sapphire ball at 0° camera.

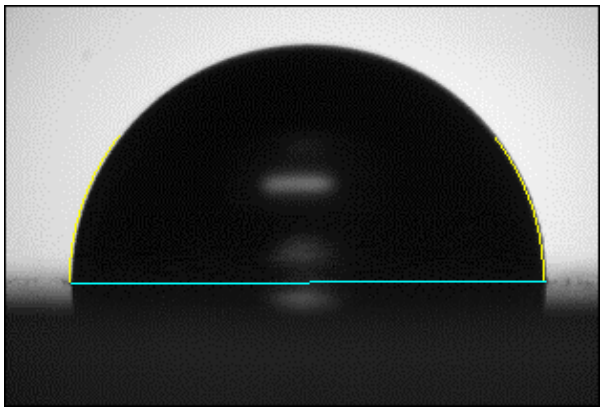

Figure 3. 4mm sapphire ball at 3° camera.

The horizontal method of Figure 2 provides a substitute for the LS baseline with the "horizon" that stretches across the image at the SV interface. This is now coincident with the LS baseline because of the horizontal geometry.

The horizon is easy to establish and should be used when possible. It can be selected in the Auto C.A. tab by the Use Horizon as Baseline checkbox. To be useful it must be in sharp focus, which in turn depends on the depth of focus of the microscope and the size of the specimen. Figures 2 and 3 were taken with the aperture set at 1/8 open, i.e., not quite closed. The magnification is ×1.4 with a 1/2″ camera (6.4mm × 4.8mm CCD). Figure 3 would still be useful with the smaller depth of focus an open aperture because the LS interface is actually in the focal plane, but Figure 2 would not be useful because the horizon formed

by the front "corner" of the holder is not actually in the focal plane of the drop--it is in front of the focal plane.

The 3° look down method should be used whenever the horizon can not be brought into sharp focus. If the drop can not be placed within ≈5mm of the edge of the specimen, then it should be used because of this depth of focus issue. Additionally, the camera angle should not be an intermediate value, such as 1 or 2°, because then the horizon will not be in focus and neither will it be below the true LS baseline in the image, with the result being a clouded baseline.

The question of when the camera is exactly horizontal is sometimes difficult. An easy answer is to open and close the aperture and note whether the horizon appears to move vertically. If it does, the camera not horizontal. Estimate the "center" of the horizon when it is fuzzy (because of an open aperture and small depth of field). The vertical movement should not be more than about 1-2mm on the computer screen as the aperture is varied.

The following table summarizes geometry, baseline, and aperture settings.

Geometry	Baseline	Aperture
Horizontal: 0° camera angle	Horizon (SV line): coincident with true LS baseline	Near closed: to obtain depth of focus
Look Down: 3° camera angle	LS Interface: locate at LSV line at drop edge	Open: to obtain clarity, adjust for light

Figure 4 shows the same sapphire standard with the long axis of the base towards the camera. The camera can now see a substantial amount of "top" surface in the image, so the reflection image is clear to the frame bottom. Compare this to Figure 3. In this mode, check Reflection Image Present and uncheck Use Horizon as Baseline in Auto C.A. Sometimes the algorithm will find the baseline better if neither are checked—it depends on the clarity of the baseline. Some experimentation is necessary. Check Use Previous Baseline to keep the same throughout a movie.

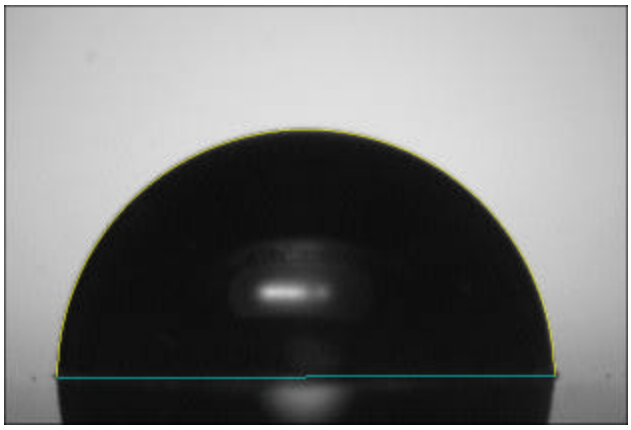

Figure 4. 3° over wide surface.

The examples of Figures 2 and 4 used Drop Shape Fitting/Spherical in the Contact Angle tab and Figure 3 used Non-Spherical. Use Non-Spherical when the dispense needle is embedded in the drop or when the drop is unusually large so gravity is distorting it. Non-spherical mode fits only at the corners of the drop and does not use the shape at the top. This means it has fewer pixels in the image to work with, so it will be more noisy, but the algorithm can fit more general shapes correctly. Gravity will make spherical mode read low. Try both analysis modes and see the difference.

This particular sapphire ball standard was measured with a micrometer to be 90.0°. Figures 2, 3, and 4 reported, respectively,

- 90.28°
- 90.36°
- 89.71°

Notice none of these are exactly 90.0°. This is to be expected and is the consequence of electronic noise in the image and baseline uncertainty.

The user can always set the baseline manually. This feature can be used to explore the sensitivity to the vertical baseline position. When the baseline is moved down one pixel in Figure 2, the measured contact angle increases from 90.28° to 90.74°. An error like this of 0.5° per pixel is not unusual. The above set has an average error of 0.31°.

With care, contact angle measurements on the 90° standard will be traceably accurate to ±1°.

This is small compared to the variances from spot to spot on most surfaces, and it is also small compared to the uncertainties in current theory for converting contact angles to surface energies. The good news is that 90° is the most difficult angle to determine the baseline, so generally speaking your real measurements will be easier and better. Most importantly, you control the accuracy by your care in setting up the camera and baseline clarity.

Step 4. Calibration. Once camera angle and aperture are set, calibrate magnification by measuring a standard and entering the known and measured values on the Calibration tab. You can use the measured base width of the 90° standard or measure the diameter of the dispense needle. Approximate values for needle diameters are given in Help/Reference Data.

If you average data over a movie, the standard length will typically show a coefficient of variance, COV, of about .05%, or about 10 times better than the COV we expect for a sequence of contact angles measurements (where COV might be, say, 0.5%). This emphasizes the point that contact angle measurement uncertainty is almost entirely due to baseline uncertainty.

Notice there is no way to "calibrate" contact angle data. There is no knob to turn or coefficient to multiply by. Instead, you must satisfy yourself that you have correctly setup and focused the instrument. The purpose of the 90° standard is to give you a known, unvarying image of a drop with which to work. So what you calibrate is your setup: camera angle, focus, and lighting.

Finally, the software gives you the alternative of independently determining the vertical position of the SV surface and entering it as the baseline. Capture an image of the SV surface, obtain a baseline at the correct level (perhaps by manually drawing it), and then check Store and Reuse this Baseline on the Auto C.A. tab.

Step 5. Fluid Loading. You must tell the software the syringe internal diameter so the pump will be calibrated. This is done on the Pump tab.

Syringe and needle sizes are selected on the basis of how much fluid is to be handled and what size drops are needed. Plastic syringes are convenient and disposable, but fluid should not be left in them over a period of days because some contamination of the fluid may result.

Most of the time we will load fluid in the syringe (but not always, because you can perform a bubble up measurement with the syringe controlling the vapor bubble). If you wish to fill a small syringe, the best way is to use a *second* syringe. Fill it in the normal way by drawing fluid up through its attached needle. Then dispense this into the first syringe with its needle removed and the syringe held upside down. In this fashion fluid flows down into the syringe and will displace all of the air, if one is careful. Once the syringe is absolutely full, attach the needle. Now you may turn the syringe over if you wish. Dispense enough fluid to displace the air in the needle. This is one reason to use a larger capacity syringe, because the needle body will hold 25µl or so and this will use up most of a 50µl syringe.

If you wish to use only a very small amount of fluid, you will not want to fill a syringe. Instead, you may leave air in the syringe and draw only a small amount of fluid up into the needle body. It is practical to make measurements with at little as 20µl total fluid in this fashion. (You need to keep some fluid in the needle while the drop is formed, so 20µl would support a 10µl drop.) Another technique is to fill the syringe with a *working fluid*, but keep an airgap between it and the fluid being tested. Fill the syringe as before, but expel air from only the visible part of the Luer hub (you can see into the plastic hub on most needles). Then draw test fluid back up into the needle portion. Use the syringe scale to precisely draw, say, 20µl. Experiment to see how much you can pick up without the test fluid infringing on the area previously wetted by the working fluid.

Step 6. Drop Dispense. When you pump more viscous fluids, the pumping rate must be slowed to accommodate the pressure drop across the

needle. Unless you have specific need to form the drop in a second or so, pump at 1µl/s or less. If fluid keeps on coming after the pump is stopped, this is a sign the rate is too high. Glass syringes are better in this regard than plastic ones, because they will stretch less under pressure.

Make sure the syringe plunger is firmly attached to the push plate using the clip provided (do not leave it off).

You want to place the drop on the surface with it falling as little as possible so kinetic energy does not spread it. There are two approaches to this:

- Form a pendant drop, then raise the specimen until it touches the bottom of the drop. If the drop is large enough, the adhesion to the surface will pull it off the tip.
- Position the tip above the surface at such a height that the growing pendant drop will touch the surface and detach before it falls free of its own weight.

The alternative is to place the needle down close to the surface and pump the drop out with fluid in contact with both the needle and the surface. This is the captive needle/captive drop approach.

Figure 5, 6, and 7 illustrate the drop touching off onto a PTFE film surface. The drop is near the edge so the sample holder is in focus. The contact angle, which is the advancing angle, is 116°.

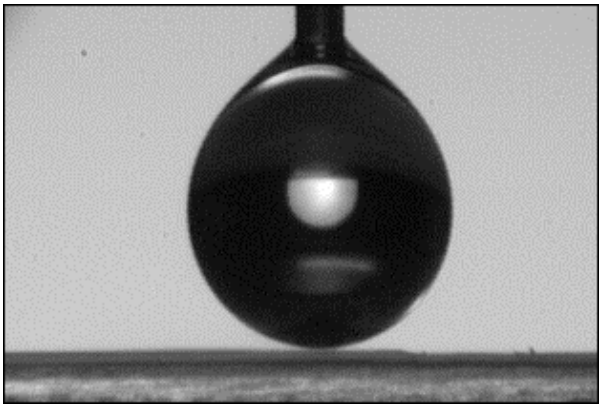

Figure 5. Drop just above surface.

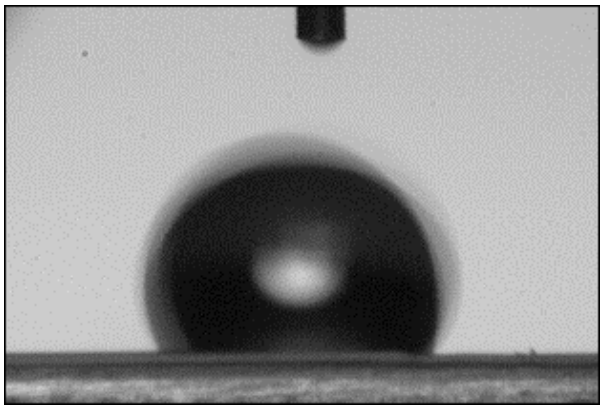

Figure 6. Drop at touch-off. Notice motion.

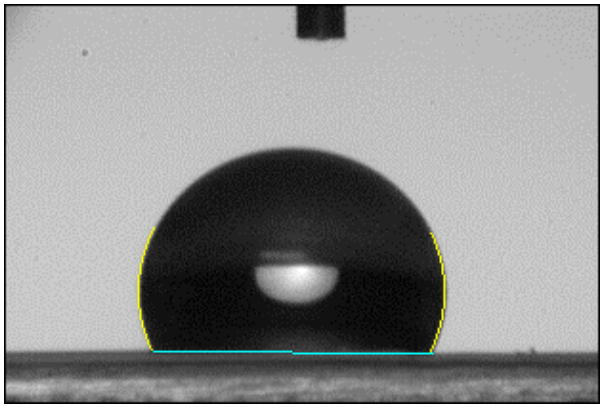

Figure 7. ½ second later drop is motionless.

Figures 8 and 9 illustrate the captive needle approach on the same material.

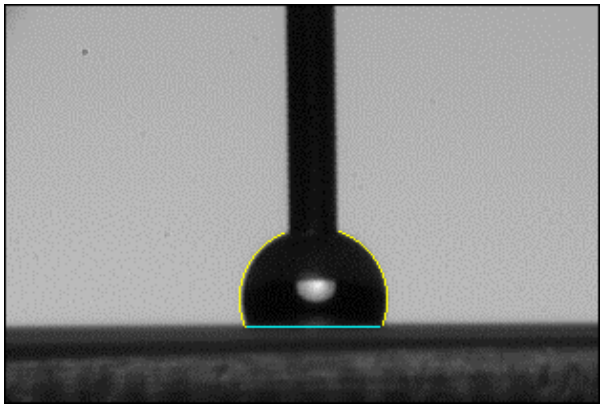

Figure 8. Small captive needle drop.

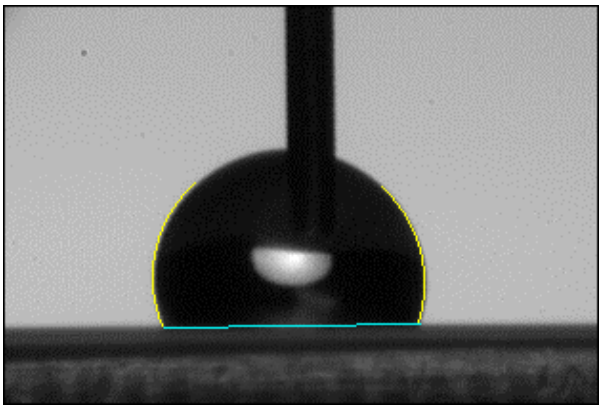

Figure 9. Captive needle drop 10 seconds later.

The disadvantages of the captive needle mode are that non-spherical analysis must be used and sometimes the drop will not grow evenly around the needle because of surface energy variations, as can be seen in Figure 9. However, the advantages are that a large number of data points can be obtained quickly and this is a true advancing contact angle measurement.

For comparable surfaces, Berg (see References of this paper) reports advancing contact angles of 115-126° and receding angles of 98-102° using the Wilhelmy balance.

Advancing and Receding Angles with Captive Needle. The captive needle approach offers the possibility of advancing and receding angle measurements in the same experiment. The pump can be programmed under Tools/Pump Program to both dispense and pick up. Berg discusses the technique in his first chapter. There are two salient conditions to meet:

- The needle tip must be small compared to the drop so fluid adhesion does not distort the drop shape.
- The expansion or contraction of volume must be slow enough that equilibrium conditions prevail.

It will turn out these are much easier to meet for an expanding drop than for a receding drop. There is a simple test described by both Berg and E. Vogler (private communication): the same value will be obtained for a sequence of measurements when equilibrium conditions prevail. Therefore, when viewing the contact angles as a time series, we expect a plateau at the advancing and receding values. Figure 10 shows a graph of the contact angles from the run shown in Figures 8 and 9.

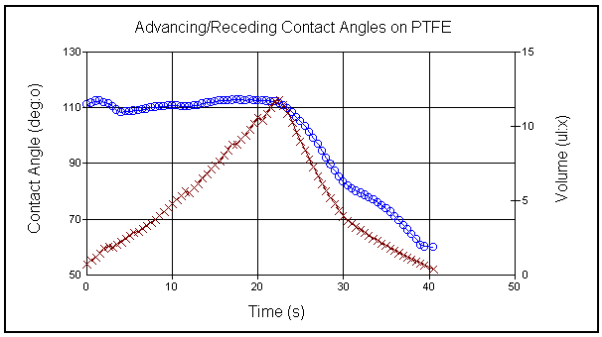

Figure 10. Advancing/receding experiment.

The advancing angle plateau is clearly seen from t=0 to t=22s. It has an average value of 112°. The pump reversed at 22s. When the drop contracts, however, there is no clear equilibrium value—the contact angle seems to keep getting smaller. No correct receding angle measurement is available.

To improve this situation, FTA offers glass capillary needles with small tips (e.g., 30µm OD and 5µm ID) and Luer fittings. These were used for the experiment of Figure 11.

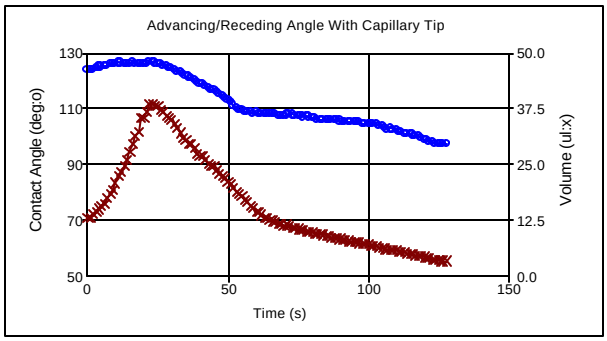

Figure 11. Capillary tip angle plot.

The advancing contact angle is 126°. At first glance the receding portion appears similar to Figure 10, but there are differences. Careful inspection reveals a plateau at the end of the receding angle period. This is shown in the expanded scale, time shifted plot of Figure 12, which shows the last 18s of Figure 11 data.

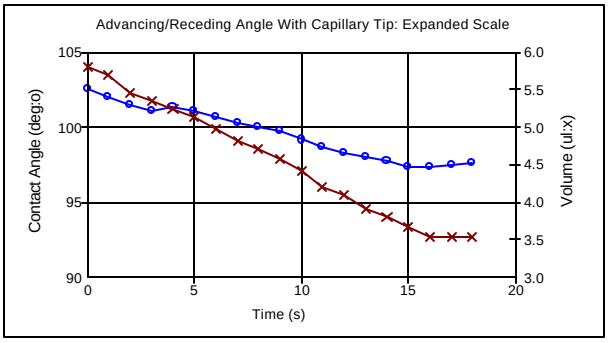

Figure 12. Expanded scale data of Figure 11.

The asymptotic receding angle value is 98°, which is consistent with Wilhelmy plate data presented in Berg. The 60° inferred from Figure 10 is far too low. The last 5 seconds of data from Figure 12, listed below, shows a plateau. Volume decreases in time but contact angle doesn't. After the last entry, the drop detached from the needle.

Time (s)	Contact Angle (°)	Volume (µl)
14	97.72	3.799
15	97.38	3.675
16	97.31	3.555
17	97.50	3.536
18	97.64	3.524

Remembering that a picture is worth a thousand words, Figures 13 and 14 show the drop just before detachment for these two different tips.

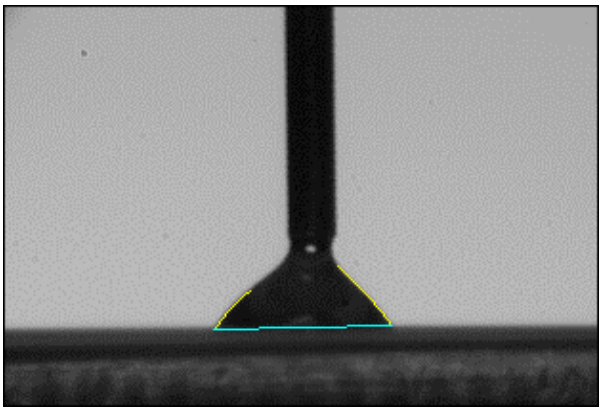

Figure 13. Just before detachment for Figure 10.

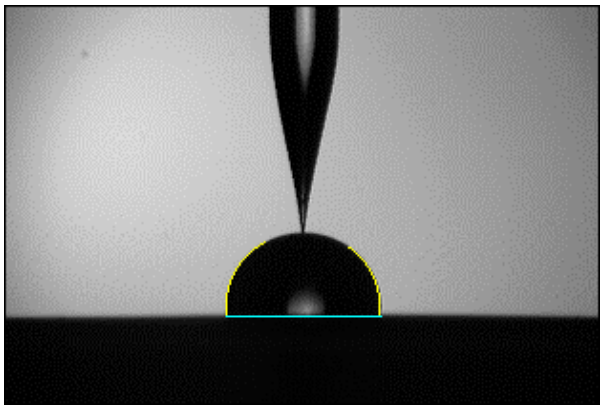

Figure 14. Just before detachment for Figure 11.

The drop in Figure 14 is clearly not distorted (it is quite spherical) and the drop in Figure 13 is, by the same measure, quite distorted by the tip. Even if at some microscopic level the true receding contact angle is present in Figure 13 at the LVS line, it can not be measured by drop shape analysis because of the overriding influence on shape of the fluid adhesion to the tip. The drop must clearly be ***much*** wider than the wetted tip for the tip to be ignored in receding angle work.

Finally, it was necessary to pump very slowly in order to achieve the results of Figures 11 and 12. The pump program was aspirating at a rate of 0.125µl/s in the final phase of the run. As the capillary tip was barely attached to the drop at the end, the effective rate decreased to 0.07µl/s, probably because some air was being picked up as the surface vibrated microscopically. Using the same spot, the following table shows the effect final pumping rate had on the asymptotic receding contact angle value. More importantly, when one views the movie of a run with very slow pumping, you can see the drop adjusting to a new, lower angle during the final phase. This adjustment appears in jumps, suggesting that small mechanical vibrations allow it to settle into the equilibrium value. This would be consistent with contact angle hysteresis being the consequence of metastable states on the surface, as discussed by Berg. Time must be allowed for the drop to stabilize; particularly for the receding angle drop.

Final Rate (µl/s)	Asymptotic Angle (°)
0.125	98
0.333	102
0.50	105
1.00	109

In summary, the procedure for making receding angle measurements with captive needle is to use a very small needle, aspirate very slowly, and use the last measured value if no plateau is found.

Advancing and Receding Angles on Tilted Plate. The classical way to make advancing and receding angle measurements is to tilt the sample until the drop just begins to roll downhill. FTA offers tilt tables for this purpose. An interesting alternative is to fix the tilt but increase the drop volume until movement begins. Larger drops will begin movement at smaller tilts than will small drops. The glass capillary tip offers a convenient way to have low contact area (minimizing adhesion) yet still inject fluid and thereby vary volume. Figure 15 shows a drop on PTFE just before detachment and movement.

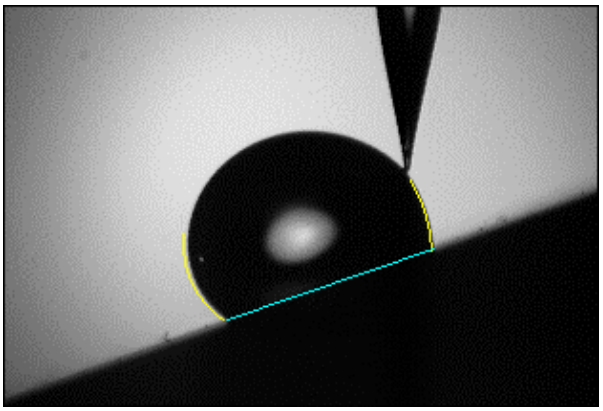

Figure 15. Tilted plate experiment.

Figure 16 shows the drop after it releases. Figures 17 and 18 plot the angles and movement after release. The captive tip data agrees well with this data. The small variations in Figures 17 and 18 are either from surface variations or motion effects. The classical equilibrium result is the t=0 data, i.e., after detachment and before motion: 129.0° advancing and 100.5° receding angles.

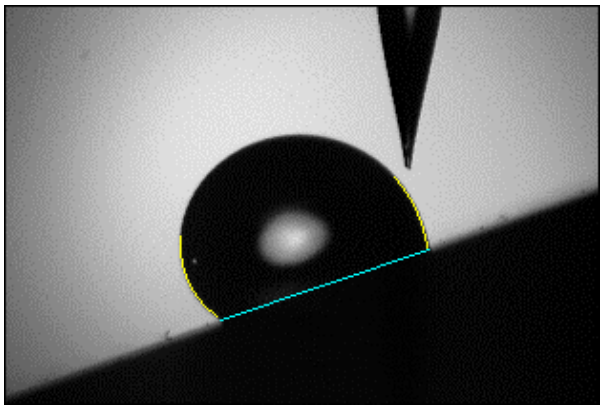

Figure 16. Tilted drop just after release.

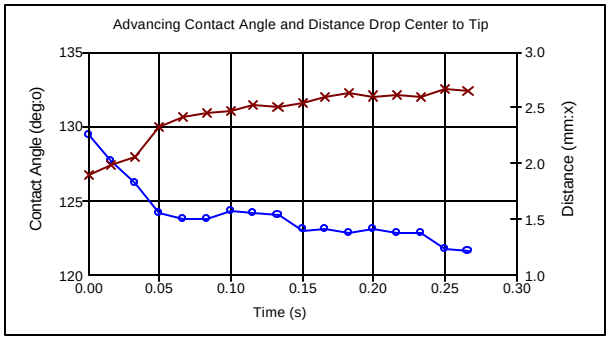

Figure 17. Advancing C.A. and drop position.

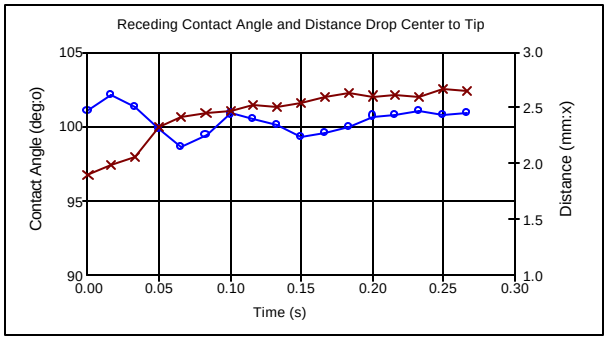

Figure 18. Receding C.A. and drop position.

References.

- *Fundamentals of Adhesion*, L. Lee, ISBN 0-306-43470-9
- *Physical Chemistry of Surfaces*, Arthur Adamson, ISBN 0-471-61019-4
- *Wettability*, Berg, ISBN 0-8247-9046-4