MicroDrop Measurements on Paper

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The FTÅ4000 can place very small drops on a sample and measure the contact angle. To produce small drops, the instrument uses glass capillary needles and a piezo electric pump to control the small volumes required. Two cameras are provided so the user can place the drops at a precise location on the sample. Figure 1 shows a small drop ready to be placed on the sample, which in this case is a printed business card. The width of the printing is measured to illustrate the size of the drop (in the bottom of the "2"). The instrument can produce drops which are considerable smaller than the one illustrated, but then the "weave" or roughness of the paper becomes an issue in making contact angle measurements.

Figure 1. Drop on end of glass needle, ready for deposition.

The drop deposition process begins by forming a pendant drop on the tip of the dispense needle while the needle is high enough above the sample surface that the drop can not touch the surface. Often the initial drop formed will be too large, but once formed it can be made smaller by pulling

some fluid back into the needle. All of this is necessary because the pressure to form the initial drop is quite large according to Laplace's equation:

$\Delta P = 2 \gamma / R$

where

ΔP = interfacial pressure across liquid-vapor interface
γ = surface tension of liquid, 72.8 mN/m for water
R = radius of drop

Because the radius of the initially formed drop is quite small, say 10 microns, the pressure at this point in time (when the emerging drop just fills the end of the dispense tip) can be quite high, e.g., 15KPa. The slight compliance ("stretching") of the system under pressure causes the initial drop to increase rapidly as the interfacial pressure drops with increasing radius and volume. To summarize, the initial spherical drop formed below the tip may be of, say, 25 nanoliters volume whereas the desired volume might be 10 or even 1 or less nanoliters. That's where the ability of the piezo pump to back up some liquid becomes important. An ordinary mechanical pump or syringe pump will have too much backlash to do this.

After the desired drop size has been formed, the dispense tip is lowered by a stepper motor to "touch off" the drop on the surface. This ensures that the droplet will not fall free or otherwise gain momentum and spread out on contact with the surface. Figures 2, 3, and 4 show the drop being touched off. All of this takes place within a second or so, once the tip is set in motion. The time into the run is shown in the center of the status panel below the image. In Figure 1 it is 29.783 seconds, in Figure 2 it is 30.116 seconds, etc.

One might ask if all this effort to form a pendant drop is necessary. What is necessary, without question, is that the dispense needle not distort the drop, else an *advancing* contact angle will not be measured. Drop distortion is the most common form of error in making contact angle measurements and results in one measurement being entirely different from another. The advancing angle is the highest contact angle possible, and is the one in Young's equation and the one used in surface energy calculations. Other angles are smaller because the drop has been spread out too much by the action of placing it on the surface. Spreading can come from dropping it too far or by action of the dispense tip when touching off a drop. An advancing angle is assured when the adhesion of the drop to the dispense needle is small compared to its adhesion to the surface. One way of telling this is when the hanging drop is spherical until it touches off. Figures 5, 6, and 7, later in this paper will illustrate this process. It is not possible to touch off a drop from a needle the same diameter as the intended drop.

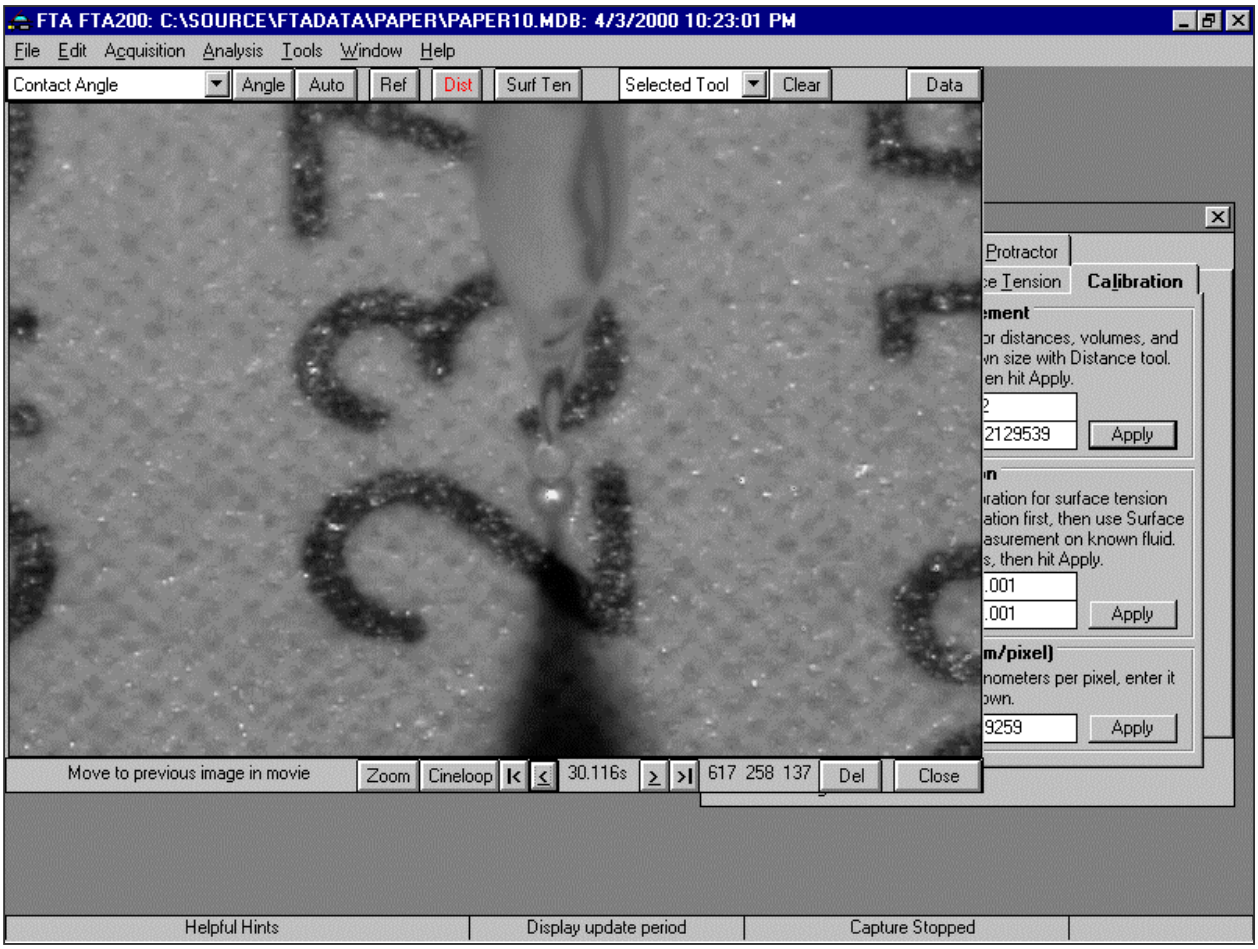

Figure 2. Drop just above surface.

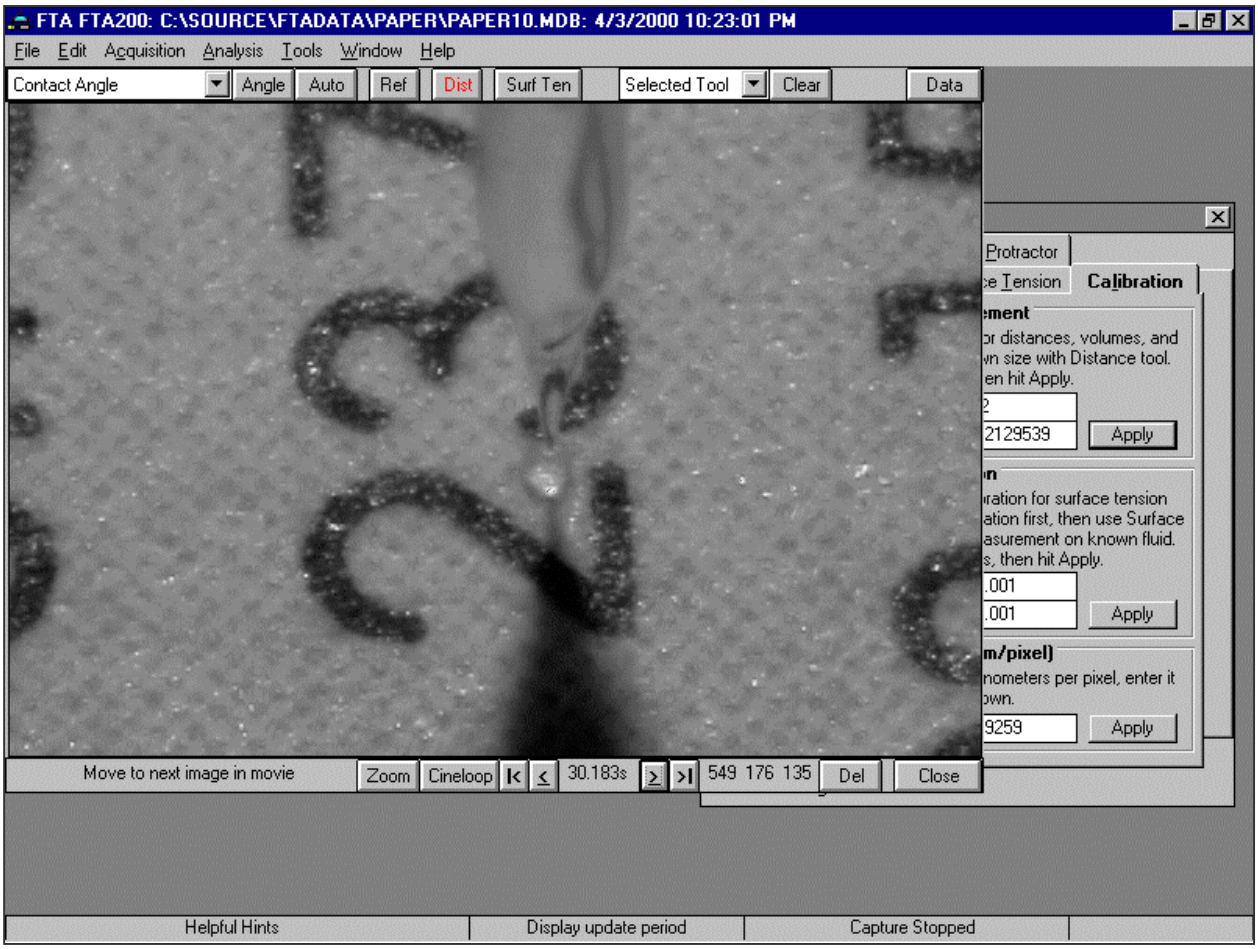

Figure 3. Drop deposited on surface, but needle still in top of drop.

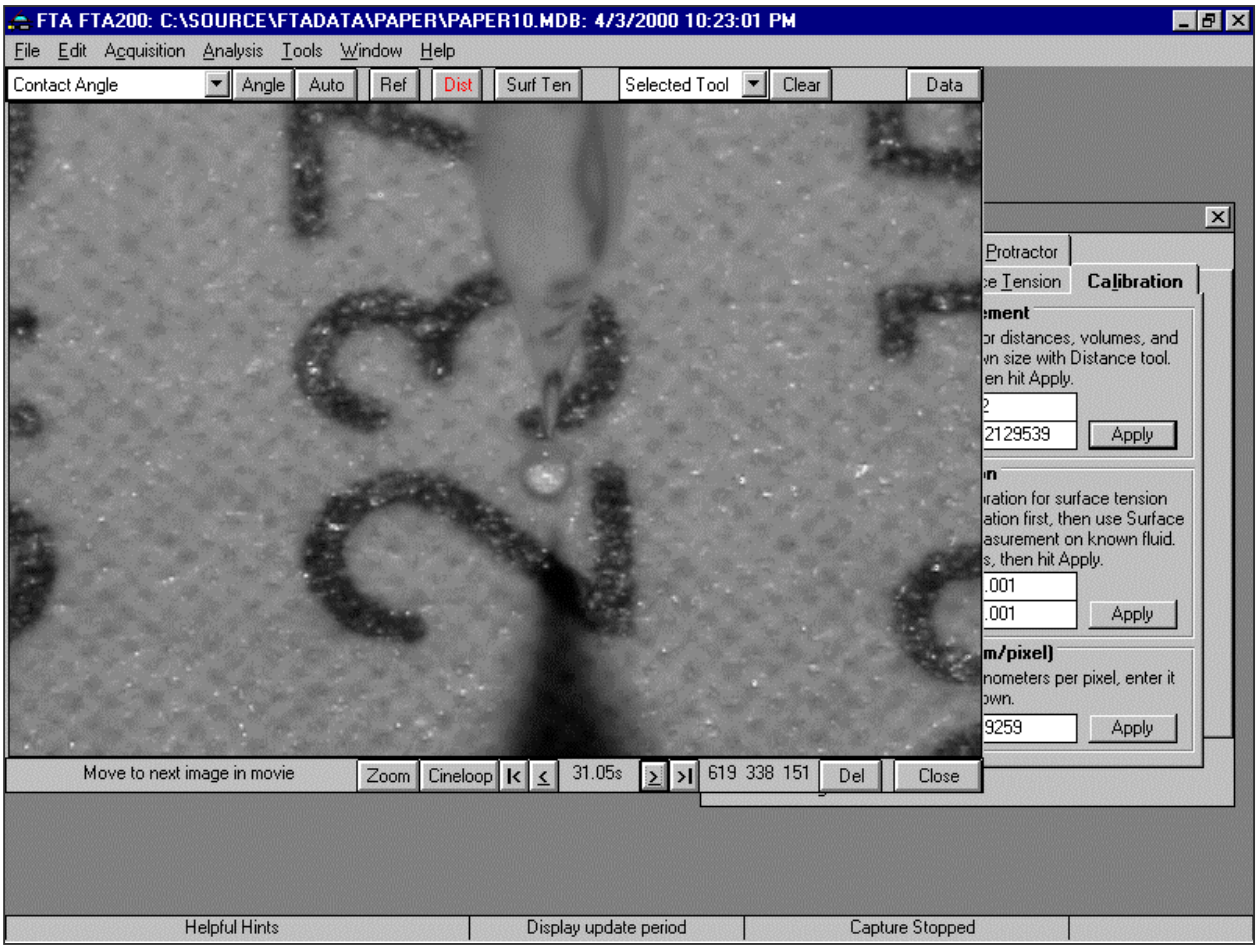

Figure 4. Needle tip lifting clear of deposited drop.

The next sequence shows a different, but similar, drop being deposited on the business card surface. It has a slightly larger volume, about 40nl. Again, smaller drops are feasible and higher magnifications are feasible than are shown in this sequence of images. Figures 5 and 6 show the drop touching off and Figure 7 shows the first stable contact angle.

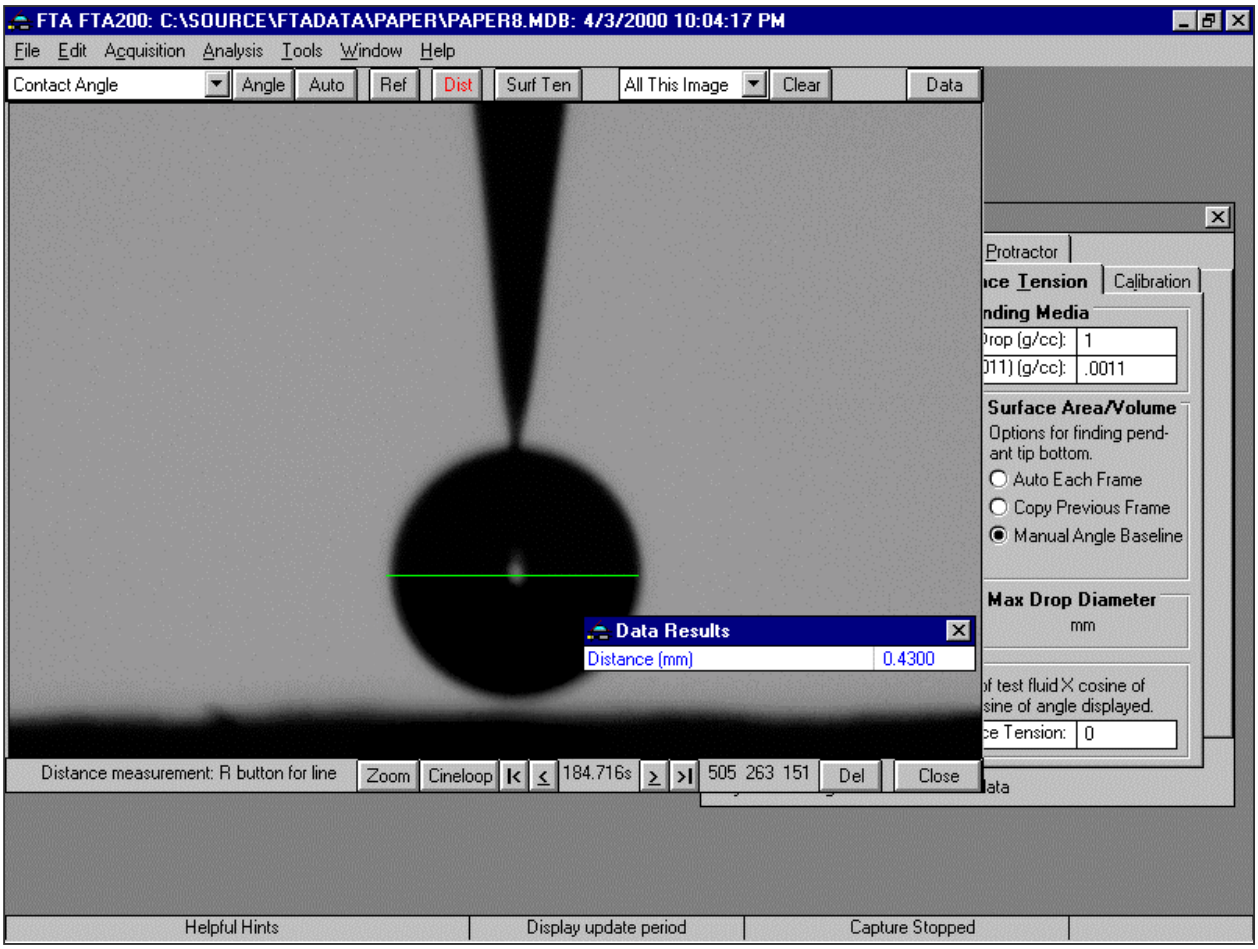

Figure 5. Drop just before touching off.

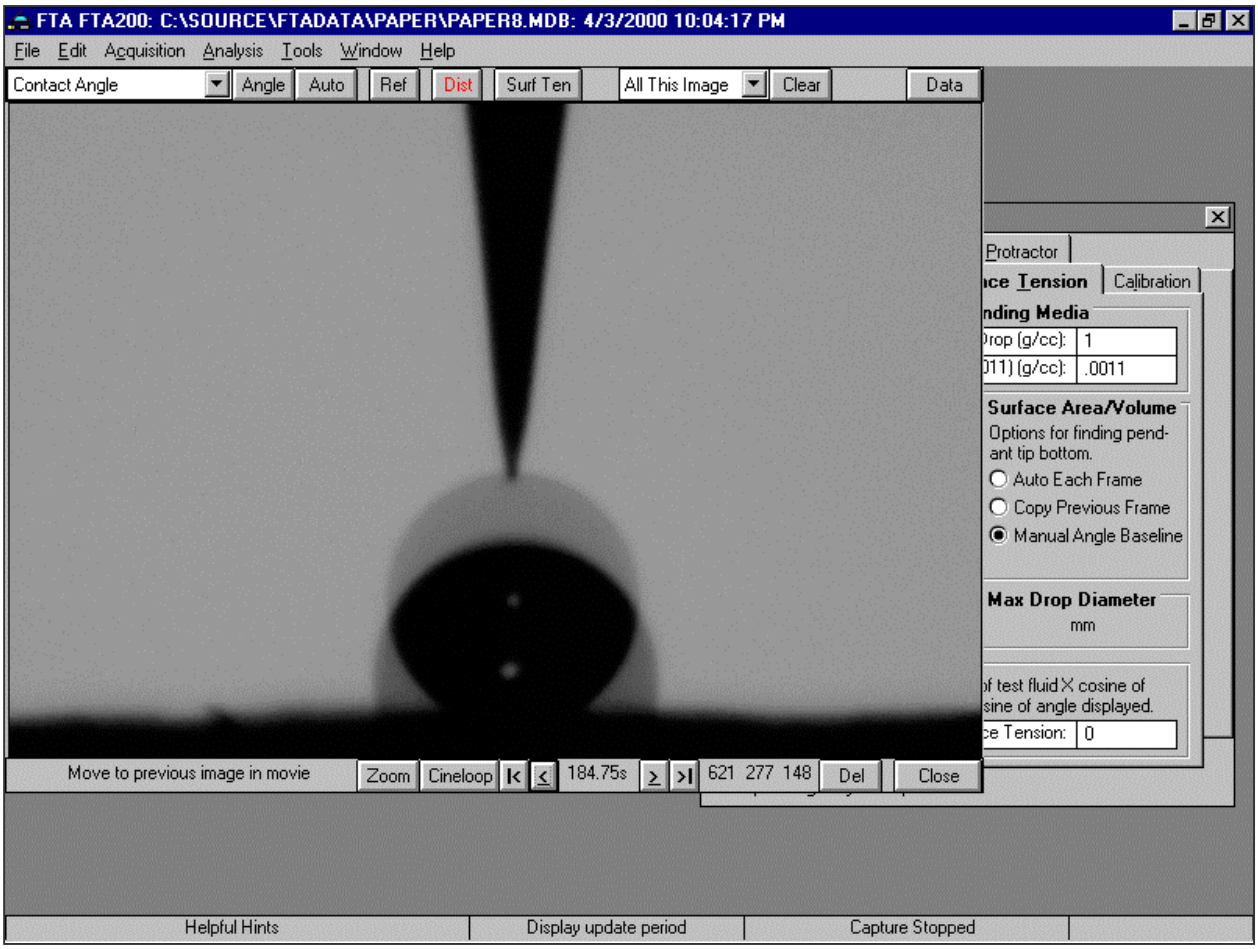

Figure 6. Drop in act of touching surface and detaching from needle.

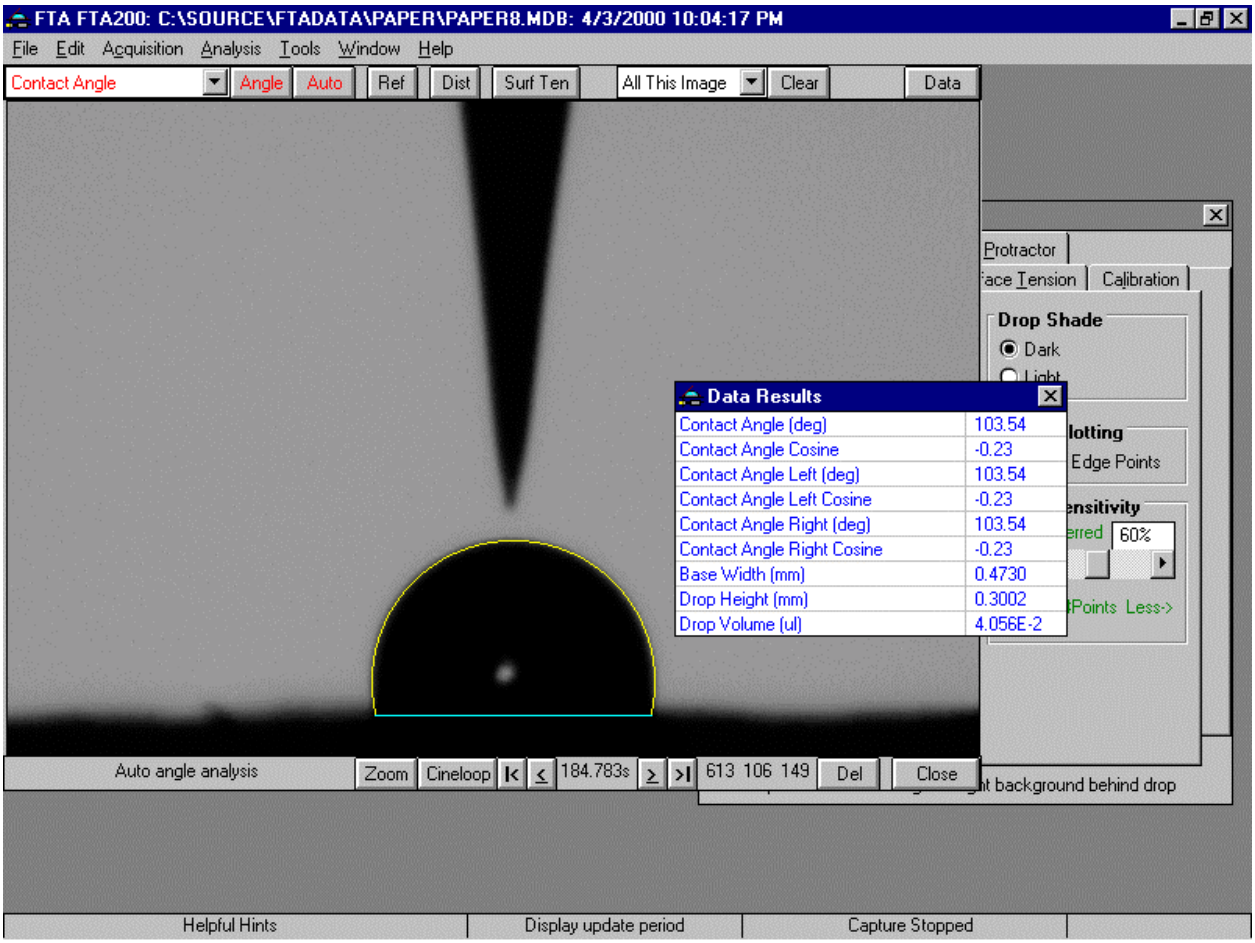

Figure 7. Contact angle measurement.