Influence of Drop's Volume on Contact Angle

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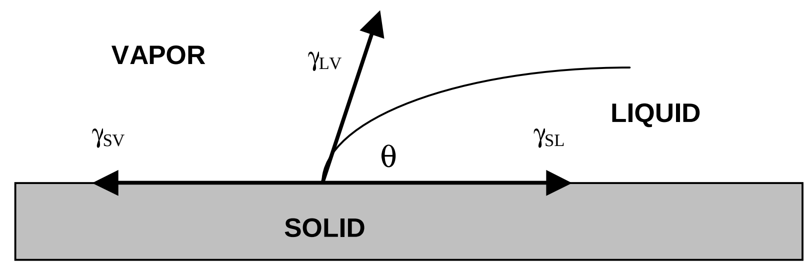
It is sometimes said that the volume of the test drop influences the contact angle. In order to understand what this means, *and what it does not mean*, we must carefully define a few terms:

- θ, the angle referred to in Young's equation:



$$\gamma_{LV} \cos(\theta) = \gamma_{SV} - \gamma_{SL}$$

  is a geometric quantity describing the shape of the drop at the liquid-solid-vapor three-phase line while in thermodynamic equilibrium. This assumes an absolutely smooth surface. If gravity is not present, the drop shape is spherical.

- for chemistry purposes, we are normally interested in the *advancing contact angle*, which is Young's contact angle when, if any more liquid were added to the drop, the interfacial area would expand and the three-phase line would move out. There is also a *receding contact angle*, which is Young's contact angle when, if any more liquid were removed from the drop, the interfacial area would contract and the three-phase line would move in. The advancing contact angle is the largest Young's contact angle can be and the receding is the smallest it can be.

- the *measured contact angle*, observed and reported by an instrument, may or may not be Young's angle. In addition to the normal measurement errors (noise, inadequate calibration, etc.), the macroscopic shape of the drop may be distorted. Gravity and dispense needles inserted into the drop are two very real and common causes of drop distortion. By distortion, we mean that whatever shape the drop has near the three-phase line is not carried forth over the whole of the drop. Therefore, the instrument can not make assumptions about the drop shape at the three-phase line from the shape of the drop as a whole, as would be desirable since the whole of the drop is much easier to observe.

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Laplace's Equation and the Young-Laplace Equation

Laplace's equation describes the pressure inside a drop because its surface is curved, and the Young-Laplace equation describes how a drop's curvature will change from gravity. These two equations are not repeated here (they are in every physical chemistry book), but they have two important consequences:

- At the scale of a few microns or less, the shape of the drop curves smoothly to meet the solid surface. Arthur Adamson's book, *Physical Chemistry of Surfaces*, ISBN 0-471-61019-4, has a scanning electron micrograph of a drop at high magnification showing this. The shape of the drop is strongly influenced by surface roughness at this scale. However, this is *not* Young's angle and this drop curvature can *not* be seen in ordinary instrumentation where the field of view is a millimeter or more. We do not need to be concerned with these localized effects while performing ordinary, classical contact angle measurements.

- At scales of several millimeters or more, gravity distorts the drop noticeably. Here the Young-Laplace equation applies. Good instrumentation will correct for gravity's effect. In particular, for small drops of water, say 1 to 5 microliters in volume, gravity's effect is so small that it can be ignored (causing less than, say, a degree of error) and the shape of the drop can then be approximated by a circle. This is convenient because a circle is easy to approximate and the math is simple. Therefore most instruments will have a *spherical* mode where the shape of the drop is approximated by a circle in the image. This is the <u>only</u> mode for some instruments. The alternative is to have a more complex equation to better approximate the drop shape when it is no longer spherical.

What Does the FTÅ Instrument Do?

1. Drop volume is controllable by the dispense mechanism and can vary from a microliter or two to over 20 microliters.

2. The software offers the choice of *spherical* or *non-spherical* modes.

3. In non-spherical mode, the software uses the Young-Laplace equation to govern the curve fit to the drop. This removes any effect of gravity or drop size on the measured angle.

4. The FTÅ non-spherical mode will avoid dispense needles in contact with the drop (some experiments require the needle to stay in contact so as to expand or contract drop volume).

5. FTÅ dispense modes offer specific facilities to ensure true advancing and receding angles.