APPENDIX I - EXPERIMENT D

Extra resources for teachers on contact angle.

The concept can be illustrated with a small liquid droplet on a flat horizontal solid surface (**Figure 1**). The contact angle is the angle formed by the liquid and the three phase boundaries. The shape of the droplet is controlled by the three forces of interfacial tension, as shown in **Figure 1**. The contact angle provides information on the interaction energy between the surface and the liquid.

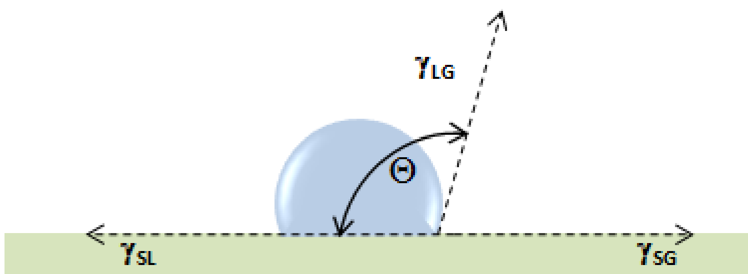

Figure 1. Static contact angle measurement of a droplet of water sitting on a flat solid surface.

In 1805 Thomas Young defined the contact angle θ by analysing the forces acting on a fluid droplet resting on a solid surface surrounded by a gas:

$\gamma_{SG}=\gamma_{SL}+ \cos\theta*\gamma_{LG}$

where:

γ_{SG} = Interfacial tension between the solid and gas
γ_{SL} = Interfacial tension between the solid and liquid
γ_{LG} = Interfacial tension between the liquid and gas

Young´s equation represents an idealistic situation where it is assumed that the surface is planar (without any roughness) and *chemically homogeneous*. “Real” surfaces are not like this, they will display a degree of surface heterogeneity and roughness.

Let’s first imagine a droplet of water sitting on a surface which is not chemically heterogeneous, but has “patches” of different chemistries:

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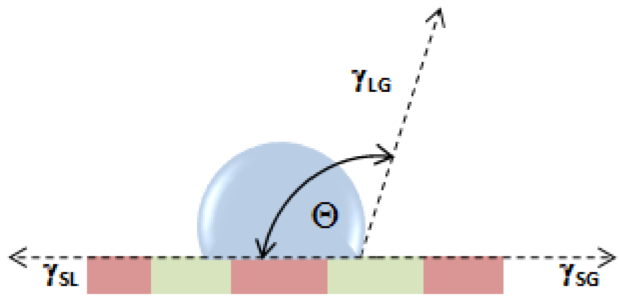

Figure 2. Contact angle measurement of a water droplet sitting on a flat heterogeneous surface having two different surface chemistries.

The Young´s equation can be re-written for the case of a heterogeneous surface composed of two fractions φ_1 and φ_2 each having its planar contact angle θ_1 and θ_2, producing a total effective contact angle θ^* equal to:

$$\cos\theta^* = \varphi_1 \cos\theta_1 + \varphi_2 \cos\theta_2 \qquad \text{(Eq 2.)}$$

Now let's consider a surface with a surface roughness. The water droplet resting on such a surface will be alternately in contact with air and with areas of solid surface (Cassie-Baxter model):

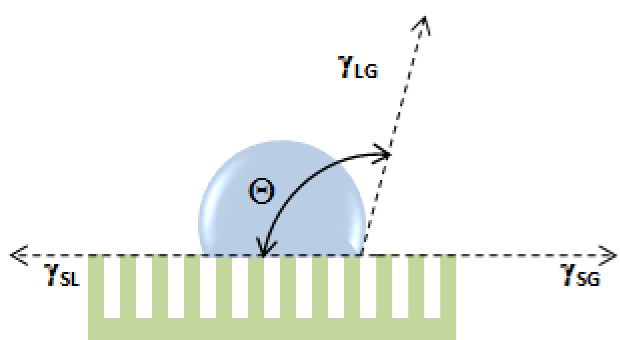

Figure 3. Cassie-Baxter model of contact angle measurement of a water droplet sitting on a surface with topographical features.

For an ideal surface that impedes total wetting, there is no contact with the surface, so there is no contact angle and θ_2= 180 ° C. In this case the Young´s equation can be re-written as in (Eq. 1) but the surface can be described as an alternating air and solid interface. This means that for the "air fraction" θ= 180 ° C and (Eq. 2) becomes:

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$\cos \theta^* = \varphi_1 \cos \theta_1 + \varphi_2 \cos 180$

since cos 180= 1 then:

$\cos \theta^* = \varphi_1 \cos \theta_1 + \varphi_2$ (Eq. 3)

In the extreme case where the droplet is in contact only with air, θ= 180 ° C. Therefore the bigger the air fraction of the surface roughness, the bigger is the contribution to the (Eq.3), and the higher the resulting contact angle. **For this reason, it is predicted that a surface with nanoscale surface roughness will give rise to surfaces with very high contact angle values (superhydrophobic).**

Figure 4 exemplifies this concept:

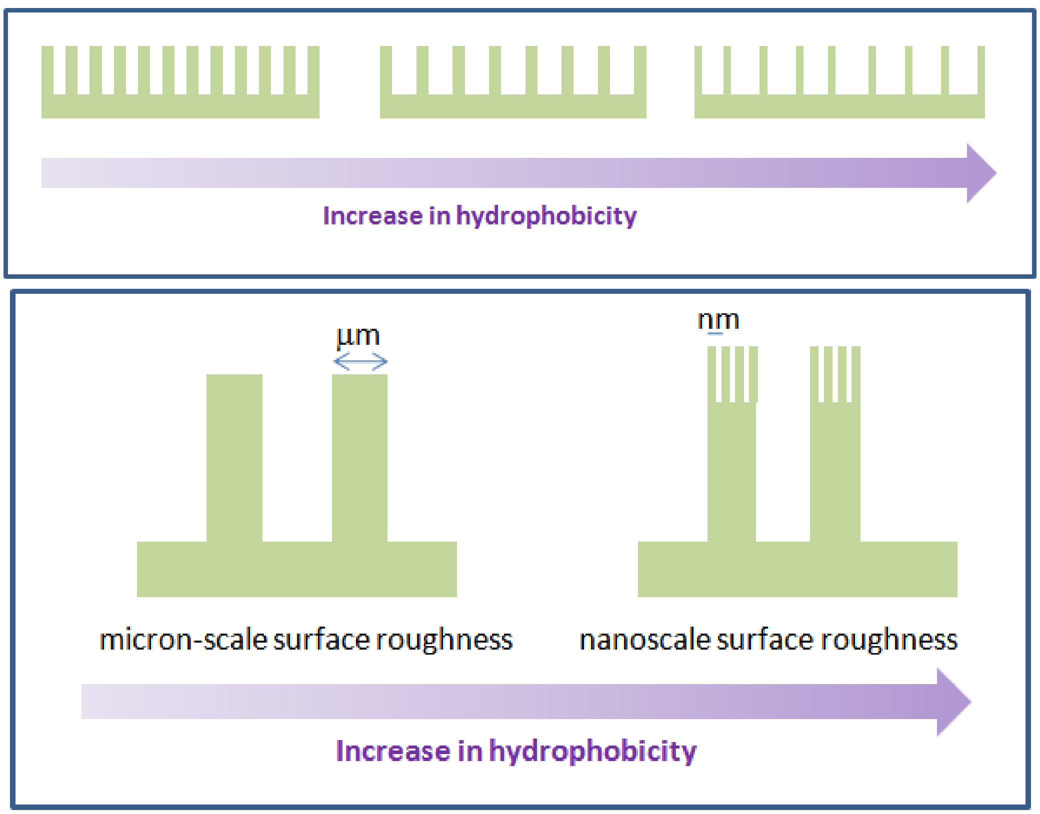

Figure 4. Schematic representations showing the effect of changing porosity (top) and size of the topography (bottom) on surface hydrophobicity.

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