

## PHYSICS FUNDAMENTALS-Effects at liquid surfaces

### Free surface energy

Figure 1 shows a liquid in contact with its vapour. There is a gradual change of properties in the interface region between the phases, which is about 1nm thick. Molecules are attracted to each other: those at the surface of a liquid have no molecules above them, resulting in a net attractive force inwards.

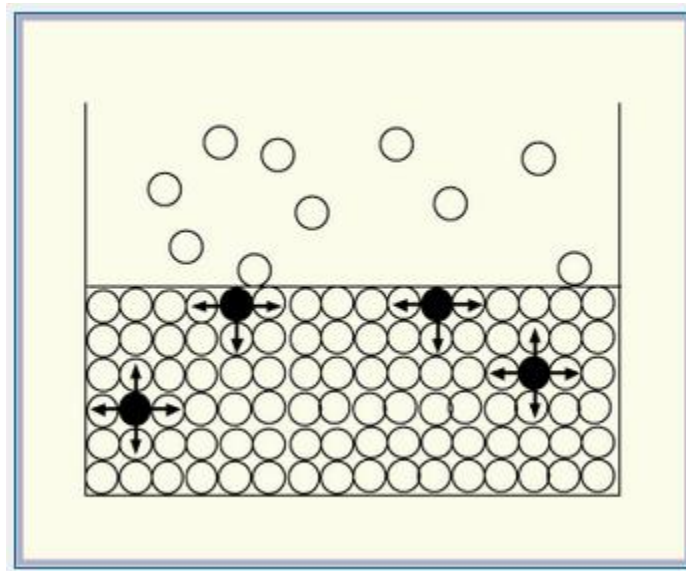


Figure 1: The origin of surface tension

If the surface area of a liquid is to be increased, more molecules have to be moved into the interface region against the cohesive forces of the liquid, and energy is thus required. This is referred to as the 'free surface energy', defined as the energy required to produce unit area of surface: it has the symbol  $\gamma$  (Greek letter gamma) and units of  $\text{J}\cdot\text{m}^{-2}$ .

Water, at room temperature, has a free surface energy of  $0.073\text{J}\cdot\text{m}^{-2}$ . The free surface energies of liquid metals are much higher, for example molten aluminium  $0.50\text{J}\cdot\text{m}^{-2}$  and molten iron  $1.50\text{J}\cdot\text{m}^{-2}$ .

From thermodynamics it is known that a system will always move in such a way as to minimise its free surface energy, which equates to having the smallest surface area possible. Small droplets of liquid are therefore spherical (until flattened by gravity) because this shape has the minimum surface area for a given volume. Think of the shape of water droplets on the roof of your newly cleaned and polished

car – the small droplets are spheres, while large ones are flattened, with convex edges<sup>1</sup>.

Solids also have free surface energies, because atoms in the bulk of a solid are subject to attractive forces in all directions, while those in the surface experience only inward-directed forces. As with liquids, increasing the surface area requires energy, as when a crack propagates and new surfaces are produced.

### Surface tension

The net inward force on the surface of a liquid makes the surface act as if it was an elastic skin that constantly tries to decrease its area, and an alternative way of looking at surface free energy in a liquid was first used by Young in 1805. In describing what he referred to as 'surface tension', Young showed that the mechanical properties of an interface can be modelled as an imaginary membrane stretched over the surface.

The tension in this membrane is expressed as force per unit length and in units of N.m<sup>-1</sup>.

Note that, when dealing with liquids, it is more usual to use the term surface tension than surface energy, even though both terms refer to the same dimensional quantity (as shown in the equation below) and share the same symbol  $\gamma$ :

$$\text{surface energy} = \frac{\text{energy}}{\text{area}} = \frac{\text{joule}}{\text{m}^2} = \frac{\text{newton} \times \text{m}}{\text{m}^2} = \frac{\text{newton}}{\text{m}} = \frac{\text{force}}{\text{length}} = \text{surface tension}$$

### Contact angle

When a liquid meets a vertical solid surface, the liquid surface will curve, usually upwards, to form a 'meniscus' (the Greek word for crescent), as shown in Figure 2. For some materials, such as mercury in a thermometer, the meniscus is negative, as shown in Figure 3. The angle enclosed between the tangent to the liquid surface and the interface between substrate and liquid at their line of intersection is called the 'contact angle', denoted by the symbol  $\theta$  (Greek letter theta). [Note that the contact angle is always measured through the liquid]

Figure 2: A positive meniscus 2, Figure 3: A negative meniscus 3

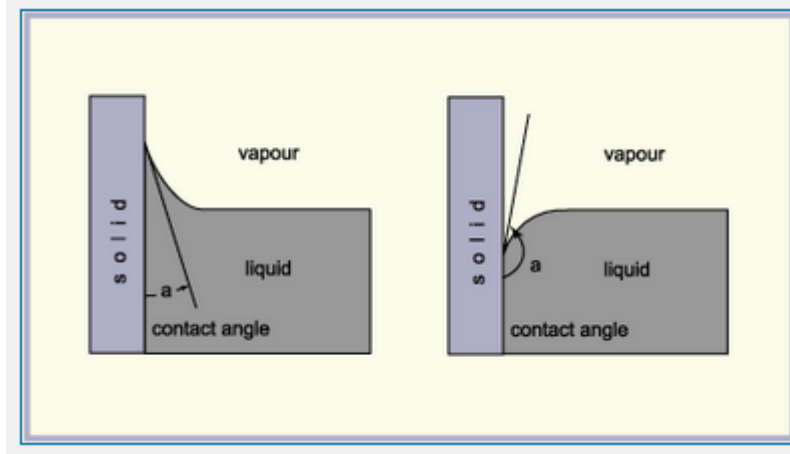


Figure 2: A positive meniscus 2, Figure 3: A negative meniscus 3

Surface tensions create forces acting along the interfaces, as shown in Figure 4. The contact angle is determined by the relative surface tensions of the three pairs of materials:

$\gamma_{SV}$ , the surface tension between the solid (for example, a laminate surface) and the surrounding vapour (for example, gas or flux)

$\gamma_{SL}$ , the surface tension between the solid and the liquid (for example, solder or adhesive)

$\gamma_{LV}$ , the surface tension between the liquid and the surrounding vapour

Figure 4: Contact angle forces

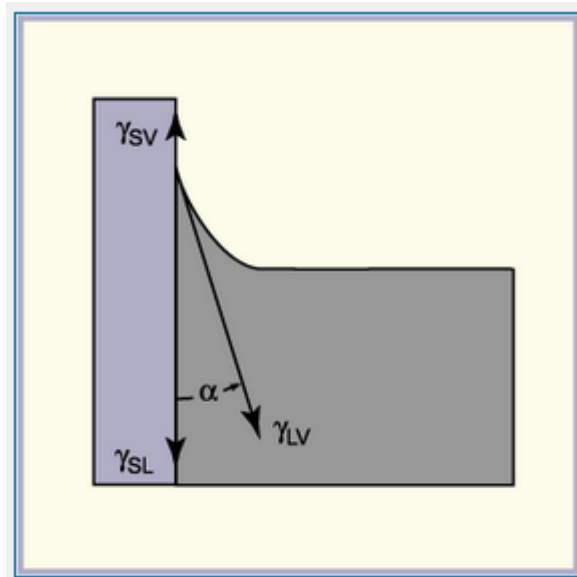


Figure 4: Contact angle forces

In equilibrium, the vertical forces must be in balance, so that:

$$\gamma_{SV} = \gamma_{LV} \cos \alpha + \gamma_{SL} \text{ from which } \cos \alpha = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

These are forms of what is known as the Young-Dupré equation.

The contact angle will depend on the relative values of  $\gamma_{SV}$ ,  $\gamma_{SL}$  and  $\gamma_{LV}$ , and the consequent values of  $\cos \alpha$ :

When  $\alpha$  is less than  $90^\circ$  ( $0 < \cos \alpha < 1$ ), the meniscus is positive, and the liquid is said to 'wet' the surface. Typical values of contact angles for materials which wet glass are  $< 10^\circ$  for most solvents and up to  $20^\circ$  for water, though getting close to  $0^\circ$  ( $\cos \alpha = 1$ ) for very pure water.

When  $\alpha$  is greater than  $90^\circ$  ( $-1 < \cos \alpha < 0$ ), the meniscus is negative, and the liquid does not wet the surface. Typical values of contact angles for materials which do not wet are  $106^\circ$  for water to paraffin wax and  $148^\circ$  for mercury to glass.

## Wetting

Wetting is what happens when water comes in contact with the roof of a typical dirty car! There is no polish left, and the water is attracted by the dirty surface, and spreads over it. As you will know, you get different results, depending on whether you use plain water or add some kind of detergent.

The extent to which a liquid will spread across a surface, or flow into a gap between surfaces depends, among other things, on the surface tensions acting between the interfaces. Depending on the values of the surface tensions, it is possible to find values for  $\alpha$  between  $0^\circ$  and  $180^\circ$ , where  $\alpha = 180^\circ$  represents liquid which has not wet the surface at all, and  $\alpha = 0^\circ$  is complete wetting (Figure 5). The term 'wetting' is often used loosely, but for practical purposes  $\alpha > 90^\circ$  is taken as non-wetting.

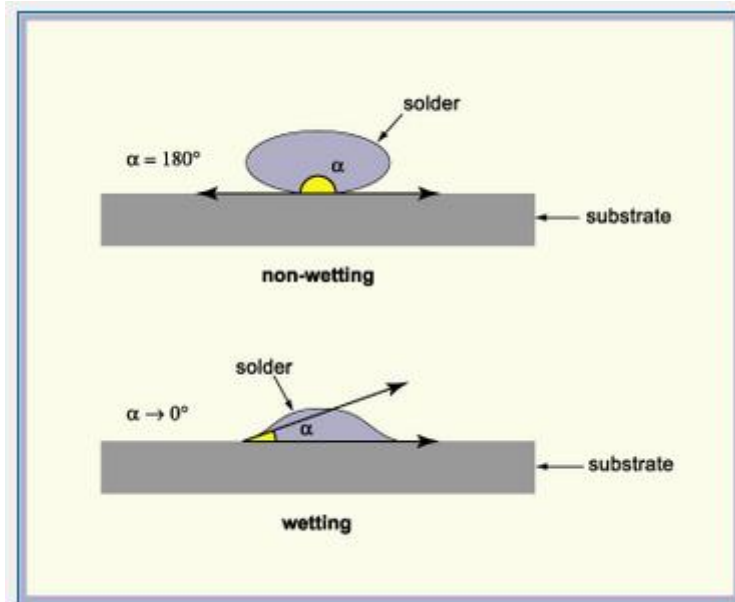


Figure 5: Wetting and the contact angle

Figure 6 shows the relationship between surface tension forces during wetting, which again are governed by the Young-Dupré equation:

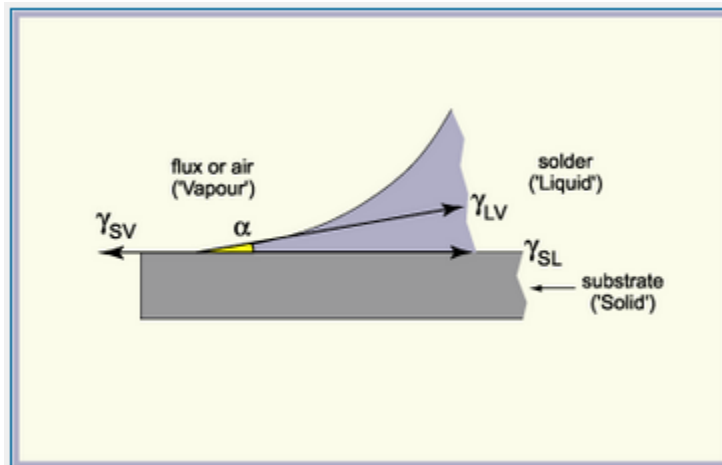


Figure 6: Wetting forces equilibrium diagram

Clearly how far and how fast the droplet spreads depends on the relationship between the value of  $\gamma_{SV}$  and the combined values of  $\gamma_{SL}$  and  $\gamma_{LV}$ .

Another way of looking at wetting is from the perspective of surface free energy. Figure 7 shows a droplet of liquid moving outwards, and increasing the area of its top surface ( $AL$ ) by an amount  $\Delta AL$ . As a result of the spread, the surface area of

the substrate (AS) is reduced by  $\Delta A_S$ , which of course is the same as the increase in the contact area between droplet and substrate.

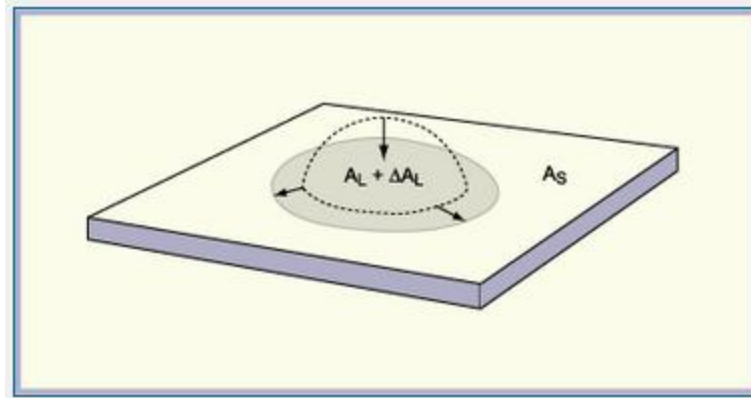


Figure 7: Spreading of a droplet

In consequence, there is a change in surface free energy  $\Delta E$ , given by:

$$\Delta E = \gamma_{LV}\Delta A_L + \gamma_{SL}\Delta A_S - \gamma_{SV}\Delta A_S$$

For flat droplets,  $A_L$  will be almost equal to  $A_S$ , so the equation can be simplified to:

$$\frac{\Delta E}{\Delta A_S} = \gamma_{LV} + \gamma_{SL} - \gamma_{SV}$$

If the droplet is to wet the surface spontaneously, there must be a reduction in free energy, that is  $\Delta E$  must be negative for a positive value of  $\Delta A_S$ . In other words, if

$$\gamma_{LV} + \gamma_{SL} - \gamma_{SV} < 0$$

wetting will take place spontaneously, driven only by surface tension. In practice, other small forces such as the weight of the droplet will aid wetting.

The discussion above relates to the wetting of solid surfaces by all kinds of liquids. As such, we experience wetting in the electronics manufacturing context in cleaning (both during board fabrication and after solder assembly), in laminate manufacture, where the resin has to wet the reinforcement, and in multilayer lamination, where it is important the adhesive wets to the copper surface in order to create a good bond.

Note that liquids in contact with contaminated surfaces will not wet, unless the liquid can either dissolve the contaminant completely or a surfactant is present, which enables the fluid to bond to the surface.

### **Solder wetting**

Whilst solder wetting at first seems very similar, and is indeed driven by the same equations and uses the same concept of contact angle, it has the complication that an interaction takes place between the liquid solder and the solid surface of the part to be soldered. Mere contact does not automatically imply wetting, as a barrier may be present: for example, any firmly adherent contamination such as oxides on the surface to be soldered will inhibit wetting (just like polish on the car).

If the surface is clean, then wetting takes place and the solder flows across it. The solder will form an alloy at the interface with the base metal, ensuring good electrical contact and adhesion. The formation of this alloy makes it impossible to revert to the pre-wetting situation.

Wetting is promoted by small values of  $\gamma_{LV}$  and  $\gamma_{SL}$  in combination with a relatively large value of  $\gamma_{SV}$ . This usually means that solder will not wet and spread on an oxide-covered substrate since the surface tensions of oxides ( $\gamma_{SV}$ ) are distinctly lower than the values of their corresponding unoxidised metals. By removing the oxide, flux increases the surface energy of the board surface, making it thermodynamically advantageous for the liquid solder to wet and spread.

### **Capillary action**

A capillary is a small bore tube. If you dip such a tube into a fluid, the liquid inside will either rise or fall, depending on whether or not the fluid wets the inner surface. This 'capillary action', shown in Figure 8, is the result of surface tension.

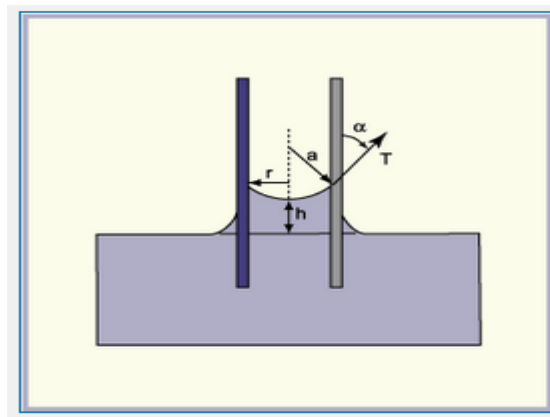


Figure 8: Capillary action

Stability is reached when the upward component of the surface tension force balances the weight of the liquid column, represented approximately<sup>2</sup> by the equation:

<sup>2</sup> This is the usual approximation, but does not take into account the weight of the meniscus itself.

$$T \times 2\pi r \times \cos \alpha = mg = (\pi r^2 h \rho) \times g$$

Where:

T is the surface tension

r is the radius of the tube (so that 2πr is the total length of the meniscus)

m is the mass of the liquid

ρ is the specific gravity of the liquid

g is the acceleration due to gravity

h is the height to which the liquid rises

Rearranging the equation gives

$$h = \frac{T \times 2\pi r \times \cos \alpha}{\pi r^2 \rho \times g} = \frac{2T \cos \alpha}{\rho g r}$$

The same equation applies if α is greater than 90°, but then the column is depressed below the level of the bulk of the fluid.

Capillary action is important both during laminate manufacture, aiding the wetting of reinforcement by resin, and in relation to the behaviour of the many small holes drilled in the board, during cleaning, plating and soldering. The clearest example is that of the solder rise within the barrel which is a necessary requirement in wave soldering. In this case, capillary action is assisted by upward pressure from the wave, but the limitation on solder height (and therefore on the thickness of board which can be soldered successfully) comes from the wetting of the internal wall, and the rise of the solder inside the hole.



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