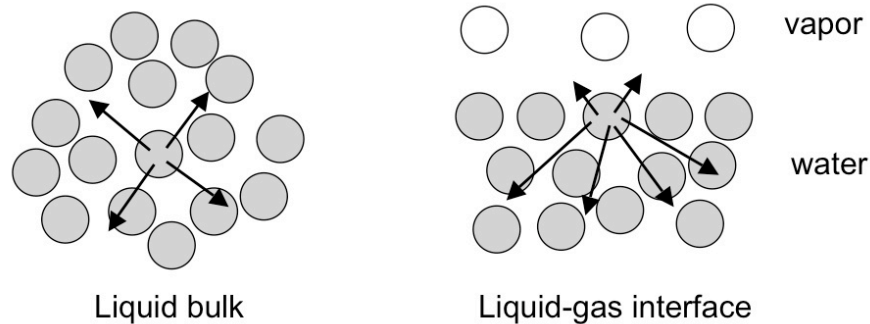


## Notes on surface tension phenomena.

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Let us take a closer look at what happens on the interface between two fluids. For instance, this could be the interface between water and its vapor.



Whereas in the bulk of either fluid there is an *isotropic* distribution of molecular forces (*i.e.*, the net force is the same regardless of direction), at the interface there is a definite force acting preferentially towards one of the two substances. If its water and its vapor, the net force on the water molecules points towards the water bulk.

The nature of this situation could be understood after realizing that molecular forces play a definite role in defining what we call an interface. In our example, water molecules experience an attractive force to other water molecules, which is stronger than vapor-water molecular interactions. Each “bond” type between molecules can be characterized by a form of energy; potential energy to be precise, similar to what you have studied before in mechanical systems, like a spring under tension or compression.

For molecules at the interface, there is an unequal distribution of energies when compared to the bulk. This difference is defined as the *interfacial energy*,  $E_i$ . It is clear that the interfacial energy will be proportional to the number of molecules at the surface. Therefore, it makes more sense to define the *surface energy*, or interfacial energy per unit area  $E_i/A$ , which is customarily known as the *surface tension*  $\gamma$ , of the interface.

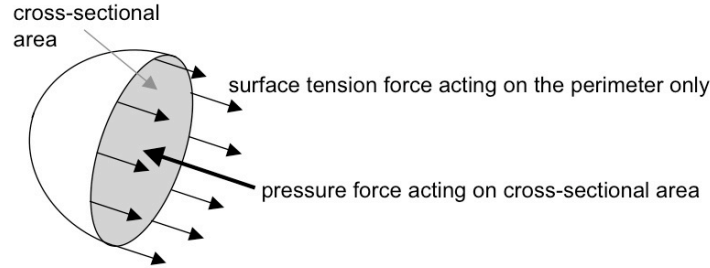
$$\text{Surface tension} \equiv \gamma \quad \text{in SI units [Joules/m}^2\text{]} \equiv [\text{N/m}]$$

Consider a liquid forming a spherical droplet of radius  $r$  floating in a gravity-free, vacuum environment (neglect vapor pressure!). What would the pressure be inside the droplet? We can answer this question using two approaches:

(1) The *thermodynamic* approach - The interfacial energy is given by  $E_i = 4\pi r^2\gamma$ . In a thermodynamic sense, work has been done to the liquid to give it a spherical shape and keep it that way. From the definition of work,  $dW = pdV$ . In absolute terms, the work done should be equal to the interfacial energy, therefore  $dW = dE_i$ . Taking the surface tension as constant, this means  $dE_i = 8\pi r\gamma dr$ . Also, a volume element in spherical coordinates is  $dV = 4\pi r^2 dr$ . This means that,

$$p = \frac{dW}{dV} = \frac{dE_i}{dV} = \frac{8\pi r\gamma dr}{4\pi r^2 dr} = \frac{2\gamma}{r}.$$

(2) The *mechanistic* approach - Consider the balance of forces occurring on any mid-cross section of the droplet:



Surface tension force acts inward exclusively on the interface and is distributed around the perimeter of the cross section. Therefore, this force is  $2\pi r\gamma$  and is exactly balanced by the droplet pressure force acting on the cross sectional area, or  $p\pi r^2$ . It immediately follows that, as before,  $p = 2\gamma/r$ . If the droplet is floating in a substance (*i.e.*, air) at some ambient pressure, say  $p_a$ , that pressure produces a force on the mid-cross section that effectively opposes the droplet internal pressure, therefore  $p - p_a = 2\gamma/r$ .

Approach (2) can be generalized for any shape, the result is  $p - p_a = \gamma\kappa$ , where  $\kappa$  is the curvature of the surface. In many instances the curvature needs to be found using differential geometry.

### What is the impact of surface tension phenomena on engineering problems?

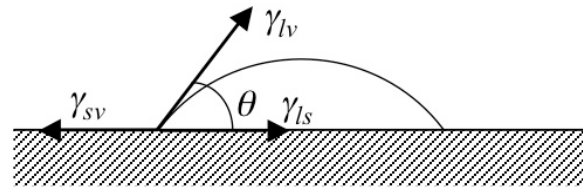
This is a matter of scales. In many applications, the effects are very small, in others is crucial. Consider once more a droplet of radius  $r$ . Under a gravitational field, the force acting on the droplet will be of the order of its weight  $F_g \approx mg = \rho \frac{4}{3}\pi r^3 g$ , whereas the surface tension force will be proportional to the droplet area  $F_\gamma \approx (p - p_a)4\pi r^2$ . It is easy to prove that both forces are of the same order when  $r \approx \sqrt{6\gamma/\rho g}$ . For water, with a surface tension of 0.07 N/m and a density of 1000 kg/m<sup>3</sup>, this *critical* radius is about 6.5 mm. In most engineering fluid-dynamics problems, gravity forces, or other pressure driven forces, dominate, thus making surface tension effects negligible. But for small dimensions, they could be quite significant. Even in some *macroscopic* situations, surface tension plays an important role. Take for instance the small ripple waves that propagate over a lake due to the wind blowing along the surface. These are for the most part surface tension waves, with a wavelength of about a few mm, as we found above.

In recent years, mostly due to the high interest in MEMS technologies applied to life sciences and precise liquid flow control in many different and diverse areas, the field of *microfluidics* has grown in a very significant way. This discipline deals with fluid flows at scales well below a few mm, and therefore surface tension effects are at the very core of its foundation. After all, surface tension forces give rise to capillarity action, which establishes the way in which water located in underground deposits find its way to the tops of trees, and the way blood distributes in the human body to reach every living cell.

### Surface interactions with solids

In most applications, liquids will be in contact with solids. At the *macro* scale, many of those interactions are inconsequential, but at the *micro* scale they are essential. Take for instance a small liquid droplet that has been deposited on a clean solid surface. If

gravitational forces are small compared to surface tension forces (i.e., for a droplet smaller than  $r \approx \sqrt{6\gamma/\rho g}$ ), then the shape will be semi-spherical.



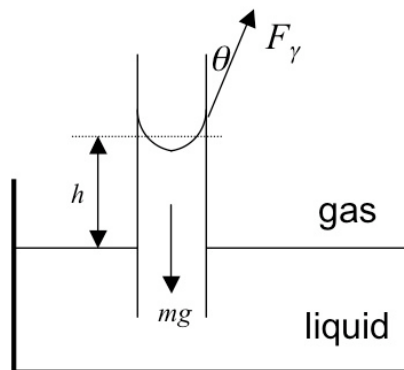
The equilibrium situation is completely specified by the contact angle  $\theta$  with the solid surface. Looking at this situation in detail, we notice that there are three interfaces acting along the contact line with the solid (the meniscus perimeter). We can therefore talk about an equilibrium between the surface tension forces on the liquid-solid, liquid-vapor and vapor-solid interfaces. Since all three act exclusively on the perimeter, this statement reduces to  $\gamma_{sv} = \gamma_{lv} \cos\theta + \gamma_{ls}$ . The contact angle is then,

$$\theta = \cos^{-1} \left[ \frac{\gamma_{sv} - \gamma_{ls}}{\gamma_{lv}} \right].$$

If we know the surface energies for the different interfaces, we then know the contact angle. There are both theoretical and empirical methods to obtain these values, which are beyond the scope of this lecture. Suffice to say, that interface properties establish the *wetting* behavior of liquids on solids. For example, pure water in water vapor has zero contact angle on clean glass. This is a case of perfect wetting. In contrast, the contact angle of water on Lotus leaves approaches  $180^\circ$ , which is a case of perfect *hydrophobicity*, i.e., no wetting at all. This, as you can imagine, has important consequences in many engineering applications, for instance, establishes the kind of surface treatment given to car, or aircraft, windshields. You want to select a hydrophobic surface in those cases, while good wetting is sought in applications as simple as painting.

### Capillarity rise

As an example to the role of wetting properties on solids, consider the situation in which a small straight tube with open ends and radius  $R$  is immersed in a fluid with surface tension  $\gamma$  and density  $\rho$ .



If the liquid wets the solid tube material, it will have a contact angle  $\theta$  smaller than  $90^\circ$ . Therefore, there will be a net surface tension force acting upwards  $F_\gamma = 2\pi R\gamma\cos\theta$ . The dynamic situation requires the introduction of viscous terms, which we have not studied yet. In turn, we focus on the static equilibrium case in which the liquid climbs to a height  $h$  such that the surface tension force balances the weight of the liquid column in the tube. This weight is given by  $F_g = mg = \rho Vg = \rho\pi R^2hg$ . The balance yields an equation for the column height,

$$h = \frac{2\gamma\cos\theta}{\rho g R}.$$

This equation holds the right dependences: as the tube radius becomes smaller, the height increases. This is the strength of capillarity:  $h$  can be very large for tubes with small radii.

To finalize, we look at how capillarity rise links to our previous discussion on manometers. The fact that we have a liquid column in a gravitational field means that there should be a difference in pressures between the top of the column and the bottom. The bottom coincides in height with the liquid surface level in the open container. If the gas pressure is  $p_a$ , that means that the liquid pressure in the container is also  $p_a$ , and this needs to be the pressure at the bottom of the column in the tube as well: they are all at the same level. Let us apply the hydrostatic equation to this case:

$$p - p_a = \rho g(y_0 - y)$$

Taking  $y_0 = 0$  as the reference level in the liquid container, we see that the pressure at the top of the column is:

$$p = p_a - \rho gh.$$

This pressure is lower than the atmospheric pressure (we of course neglect the gas pressure change with height: the gas density is very small). Where is the negative  $p - p_a$  pressure coming from? From our surface tension considerations  $p - p_a = \gamma\kappa$ , so the negative pressure is generated by the curved surface:  $\kappa = -\rho gh/\gamma$ . This means we could use directly the hydrostatic equation to find the column height, as long as we know the surface curvature:  $h = |\gamma\kappa/\rho g|$ . As an exercise, you could easily prove that this expression reduces to the one found above for the case of a semispherical meniscus.