

Lecture 1: Capillarity – Surface effects

Introduction

Capillarity is the study of interfaces i) between gas/liquid or ii) between 2 immiscible liquids. Such interfaces are deformable, in contrary to solid interfaces; they are free to change their shape to minimize their energy. Forces/energies at stake are negligible for large scales but become preponderant at milli- and micro-meter scales.

Capillarity plays a major role in numerous scientific fields such as soil science, climate, biology,... It is found in chemical, food, cosmetic and pharmaceutical industries, especially for product formulation: production of foams, gels, emulsions, particle formation and in many other processes: printing, coating, spraying...

1) Surface tension

Liquids flow but adopt very stable shapes with surface fluctuations limited to the molecular scale. The liquid interface is thus stretched by a surface tension which opposes its distortion.

This can be observed with soap bubbles and films, oil lenses on top of water, water droplets on plants leaves or floating insects to name a few examples, see Figure 1 (<http://www.freeimages.com>, JFM 2010 Hu and Busch).

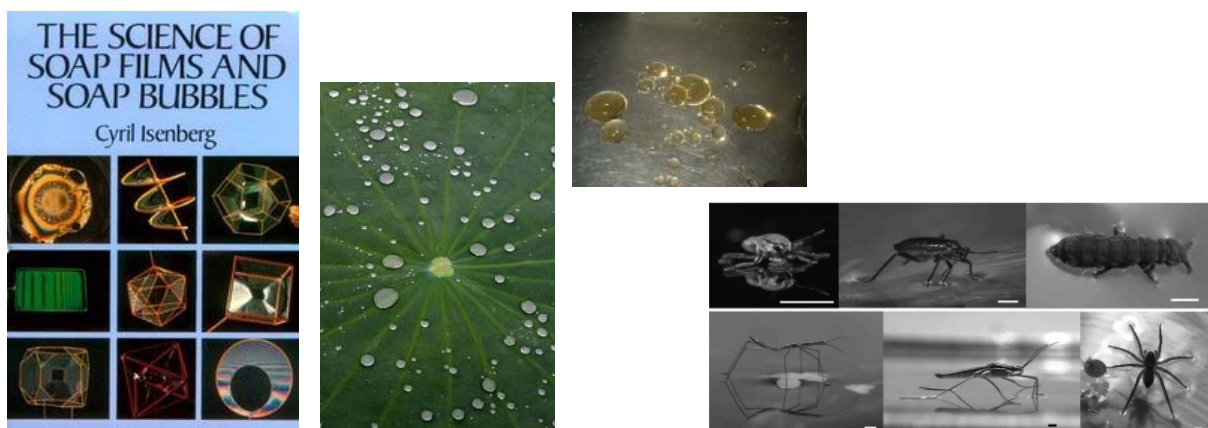


Figure 1: some illustration of surface tension (<http://www.freeimages.com>, JFM 2010 Hu and Busch).

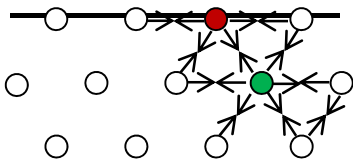
What is thus the physical origin of this surface tension? how can we model it in physics? what consequences can we expect?

1)1) Physical origin or microscopic point of view

Solid State

The atoms/molecules are tightly bound to each other either in a regular geometric lattice (crystals) or irregularly (amorphous)

Attractive interactions \gg thermal agitation



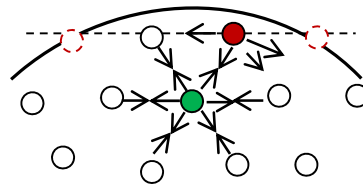
Solid interface: a molecule at the interface misses “half” its attractive interactions. Existence of surface energy but no surface tension

→ no possibility to minimize the energy cost of an interface

Liquid State

Attraction between atoms/molecules is stronger than thermal agitation leading to a dense and cohesive phase. Since the molecules are still able to vibrate and move, a liquid can flow

Attractive interactions $>$ thermal agitation



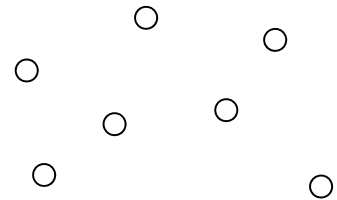
Liquid interface: a molecule at the interface misses “half” its attractive interactions. As liquids can flow they adjust their shape to expose the smallest possible number of molecules and thus the smallest possible surface area

→ that is surface tension

Gas State

The atoms/molecules have a strong thermal agitation and interact only weakly between each other. In a gas, atoms/molecules spread to occupy all space.

Attractive interactions \ll thermal agitation



Gas interface does not exist as gas is not cohesive enough; it spreads to occupy all space, no surface energy

→ no surface tension

Order of magnitude:

Liquid	Ethanol	Water	Mercury	Oil	Water/oil
$s \text{ (mJ.m}^{-2}\text{)}$	23	73	485	20	35

Estimation can be obtained considering U , the cohesion energy per molecule in the liquid → a molecule at the surface sees $U/2$ and if the molecule's size is a → surface tension $\sim U/2a^2$

Examples:

- oils $U \sim kT \sim 4 \cdot 10^{-21} \text{ J}$, $a \sim 3 \cdot 10^{-9} \text{ m}$ → 20 mJ/m^2 ie 20 mN/m ,
- water hydrogen bonds $U \sim 7 \cdot 22 \cdot 10^{-21} \text{ J}$ → 70 mN/m
- mercury, strong cohesive metal $U \sim 1 \text{ eV} \sim 10^{-19} \text{ J}$, $a \sim 3 \cdot 10^{-9} \text{ m}$ → 500 mN/m

1)2) Macroscopic point of view

“Energy” point of view: energy is needed to distort a liquid in order to increase its surface area by an amount dA . More precisely, the work required is proportional to the number of molecules that must be brought up to the interface i.e. to dA . The work writes:

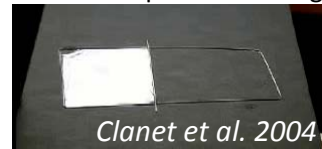
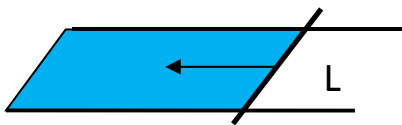
$$dW = \sigma dA$$

where σ is the surface (or interfacial) tension. $[\sigma] = \text{E} \cdot \text{L}^{-2} \quad \text{J} \cdot \text{m}^{-2}$ or in practice $\text{mJ} \cdot \text{m}^{-2}$

To remember $\rightarrow \sigma$ is the energy that must be supplied to increase the surface area by one unit

“Mechanics” point of view: surface tension can also be seen as a force per unit of length. Dimensionally, one can write $[\sigma] = \text{F} \cdot \text{L}^{-1} \quad \text{N} \cdot \text{m}^{-1}$ or $\text{mN} \cdot \text{m}^{-1}$.

Typical experiment showing that surface tension can be seen as a force per unit of length:



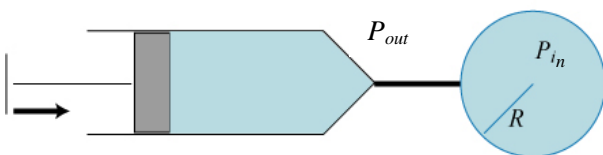
the mobile rod moves by a distance. The work done is: $dW = F \cdot dx = 2 \cdot \sigma \cdot L \cdot dx$

To remember $\rightarrow \vec{\sigma}$ is a force (per unit of length) normal to the rod in the plane of the interface and directed toward the liquid.

1)3) Surface tension and curved interfaces: Laplace pressure

Surface tension is at the origin of overpressure existing in drops and bubbles and has been evidenced by Laplace in 1805.

Energy approach: case of a sphere



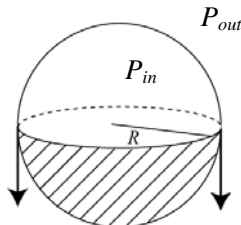
$$(P_{in} - P_{out}) \cdot \Delta V = \sigma \Delta S$$

$$\Delta V = 4 \pi R^2 dR$$

$$\Delta S = d(4 \pi R^2)$$

$$\rightarrow (P_{in} - P_{out}) = 2 \sigma / R$$

Mechanics approach: case of a sphere



$$(P_{in} - P_{out}) \cdot S = \sigma L$$

$$S = \pi R^2$$

$$L = 2 \pi R$$

$$\rightarrow (P_{in} - P_{out}) = 2 \sigma / R$$

General case: $P_{in} - P_{out} = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \sigma C$

To remember → The increase in pressure ΔP (Laplace) that occurs upon traversing the interface between two fluids is equal to the product of the surface tension σ and the curvature of the surface $C=1/R_1+1/R_2$ with R_1 and R_2 the radii of curvature of the interface.

Specific cases:

- sphere: $R_1=R_2=R \rightarrow \Delta P=2\sigma/R$
- cylinder: $R_1=R, R_2=\infty \rightarrow \Delta P=\sigma/R$
- catenoid: $R_1=-R_2 \rightarrow \Delta P=0$
- bubble (2 interfaces): $R_1=R_2=R \rightarrow \Delta P=4\sigma/R$

Consequences: smaller drops/bubbles disappear in favor of larger ones (emulsion, foam - Ostwald ripening), capillary adhesion between particles (particle manufacturability), fibers (wet hair), plates,...

2) Contact between three phases: wetting

It refers to the study of how a liquid deposited on a solid (or a liquid) spreads out. Here, we limit ourselves to quasi-static wetting (thermodynamical equilibrium).

Relevant in many industrial applications such as paints and coating, inks and printing, treatment of surface to prevent dewetting, anti-stain treatment, waterproofing of concrete, spreading of creams, application of make-up, inflation of lungs from new borns, locomotion of insects at the water surface,....

2)1) Spreading parameter

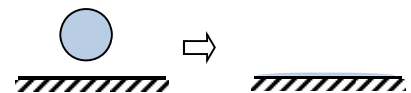
Surface energy (σ , surface tension – vapor/liquid) can be extended to others interfaces: solid/liquid σ_{sl} , solid/vapor σ_{sv} . This allows the calculation of the difference between surface energy (per unit of area) of a dry and a wet substrate. This difference of energy is called the spreading parameter S .

$$S = E_{sub-dry} - E_{sub-wet} = \sigma_{sv} - (\sigma_{sl} + \sigma)$$

Two kinds of wetting have to be distinguished:

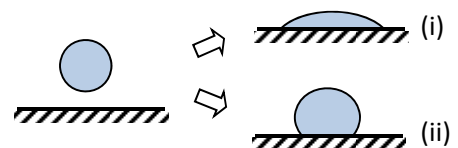
i) total wetting: $S > 0$

In this case the liquid spreads totally to lower the surface energy. The final outcome is a nanoscopic film.

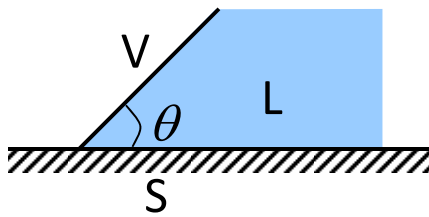


ii) partial wetting: $S < 0$

In this case, the drop does not fully spread but adopts a stable shape (spherical cap) at equilibrium. This spherical cap makes an angle of θ with the substrate. A liquid is said to be mostly wetting on a substrate when $\theta < \pi/2$ (i) and mostly non wetting on a substrate when $\theta > \pi/2$ (ii) - convention



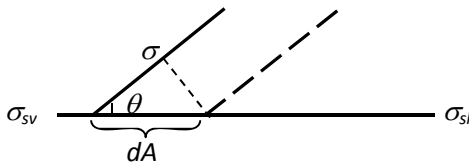
2)2) Law of Young-Dupré – Solid substrate:



$$\sigma \cos \theta = \sigma_{sv} - \sigma_{sl}$$

$$\cos \theta = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma} = 1 + \frac{S}{\sigma}$$

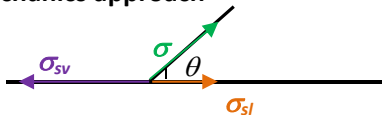
Energy approach



$$dW = \sigma dA \cos \theta - \sigma_{sv} dA + \sigma_{sl} dA = 0$$

$$\rightarrow \sigma \cos \theta = \sigma_{sv} - \sigma_{sl}$$

Mechanics approach

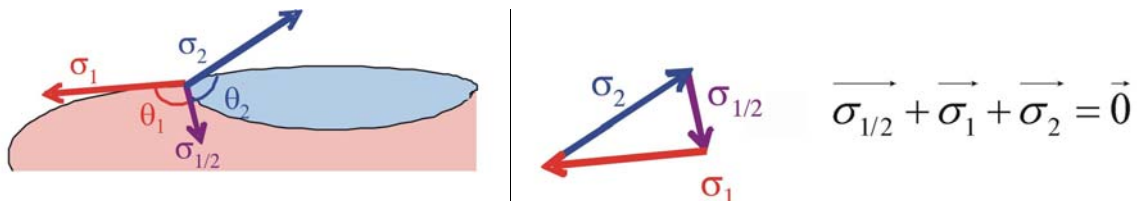


Balancing forces (horizontally): $\sigma \cos \theta + \sigma_{sl} = \sigma_{sv}$

$$\rightarrow \sigma \cos \theta = \sigma_{sv} - \sigma_{sl}$$

2)3) Neumann's construction – Liquid substrate:

The contact angle is no longer given by Young-Dupré's relation. As the "substrate" is liquid it does not remain planar but minimizes its energy by adjusting its shape. Now, both the vertical contribution of the capillary forces and the horizontal one should be balanced. This can be done using Neumann's construction.



Remark: the construction is only possible if $S < 0$, indeed if $S > 0$ one liquid totally wets the other one.

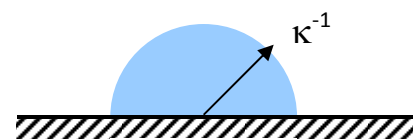
3) Capillary length or when should capillarity be accounted for?

There exists a critical length - the so-called capillary length κ^{-1} - under which capillarity dominates. Above it, gravity dominates.

The determination of κ^{-1} can be done by balancing:

- Hydrostatic over-pressure at the depth of κ^{-1} , $P_{\text{hydro}} \sim \rho g \kappa^{-1}$
- Laplace pressure for a radius of κ^{-1} , $P_{\text{Laplace}} \sim \sigma / \kappa^{-1}$

At equilibrium, we obtain $\kappa^{-1} = (\sigma / \rho g)^{1/2}$



To remember: the capillary length κ^{-1} is the critical length for which the transition between capillarity and gravity dominated regimes is observed

Order of magnitudes:

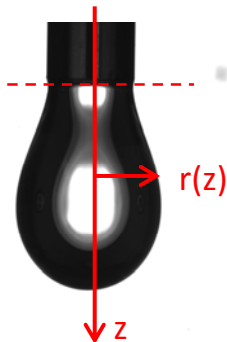
Liquid	Ethanol	Water	Mercury	Oil	Water/oil
κ^{-1}, mm	1.7	2.7	2	1.5	6

To work in the regime where capillarity dominates: $r < \kappa^{-1}$ or $g \rightarrow 0$ (microgravity) or non-miscible liquids with similar densities

4) Measuring surface (interfacial) tension

4)1) Shape of drops

- the pendant drop method:



$$\Delta P = \rho g z \quad \text{and} \quad \Delta P = \sigma C \rightarrow \rho g z = \sigma C$$

$$C = -\frac{r_{zz}}{(1+r_z^2)^{3/2}} + \frac{1}{r(1+r_z^2)^{1/2}}$$

$$r_z = \frac{dr}{dz} \quad r_{zz} = \frac{d^2r}{dz^2}$$

- the spinning drop

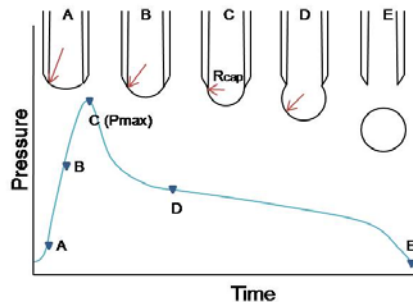
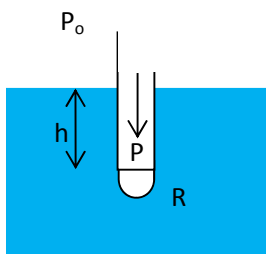


$$E = \frac{1}{2} J \omega^2 + 2 \pi r L \sigma$$

$$J = \frac{\Delta \rho \pi r^4 L}{2} \quad V = \pi r^2 L$$

$$\frac{\partial E}{\partial r} = 0 \rightarrow \sigma = \frac{1}{4\pi^{3/2}} \Delta \rho \omega^2 \left(\frac{V}{L}\right)^{3/2}$$

4)2) Pressure measurements

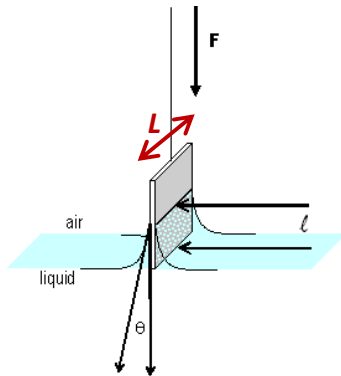


$$P(R) = P_o + \rho g h + \frac{2\sigma}{R}$$

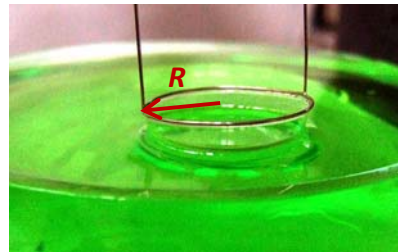
[Bubble Pressure Method](http://www.krussusa.com) at KrussUSA.com

4)3) Force measurements

- Wilhelmy plate



- Noüy ring



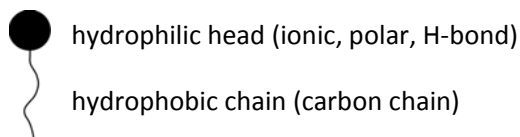
Wikipedia

$$F = \sigma L \cos\theta$$

With L, the plate width and $L=2\pi R$ and R is the ring radius

5) Modifying surface tension

Surfactant



These molecules naturally place themselves at the interface between gas (air) and polar liquids or between non polar and polar liquids minimizing the interfacial tension. When the interface is saturated, the surface tension reaches a plateau (lowest value): this corresponds to the Critical Micellar Concentration (CMC).

Remark: capillary forces enable the insects to walk on water. If surface tension is lowered (pollution) insects are drowning!

Temperature

Surface tension decreases with increasing temperature

$$\sigma_{\text{water/vap}} = 72 \text{ mN/m @ } 20 \text{ }^\circ\text{C}$$

$$\sigma_{\text{water/vap}} = 58 \text{ mN/m @ } 100 \text{ }^\circ\text{C}$$

→ Consequences: Marangoni effect: flow from high surface tension areas to low surface tension areas