Abdelhafid Boussouf University Center - Mila **Academic year 2024–2025**

Institute of Natural and Life Sciences

Department of Biotechnology

Module: Biophysics

CHAPTER3 : Surface phenomena

1. Surface Phenomena

1.1 Introduction

Surface phenomena, while they can be characterized by their purely mechanical effects, can also be compared to physicochemical reactions corresponding to changes in intermolecular bonds. Their effects can be viewed as variations in certain thermodynamic functions. The phenomenon of surface tension reveals an intensive property unique to liquids, which is of great importance in specific cases.

1.2 Observations

Certain insects, such as water striders, move at high speeds on the surface of the water as if they are gliding on a soft film (Fig. 1).

Fig. 1 A water strider floats on the surface of the water.

A drop of water on a leaf of a plant (Fig.2).

Fig. 2 A drop of water on a leaf

These phenomena give the impression that the surface of liquids behaves like a stretched elastic membrane.

2-Surface tension

2- 1Definition

Inside the liquid, each molecule is subjected to Van der Waals type attractive forces of electrostatic origin, which arise due to the polarity of certain molecules, resulting in a net force of zero.

On the other hand, molecules at the surface are primarily attracted towards the interior of the liquid, as air molecules are too few to achieve equilibrium; thus, the net attractive force on the surface molecules is directed inward, tending to compress the liquid and reduce its free surface.

Consequently, there exists a force, f, at the interface between a liquid and another medium. The surface tension σ is measured by the ratio of the force f to the length l over which it acts.

$$\sigma=\frac{f}{l}$$

where

$\sigma$is in $\mathrm{N \cdot m^{-1}}$, f is in N, and l is in m.

2-2 Adhesion Work of a Liquid on a Solid:

This is the work required to separate a liquid from a solid over a surface area of 1 m^2. Let

$\sigma_L$be the surface tension of the liquid, σ_S the surface tension of the solid, and $\sigma_{sL}$the interfacial tension between the liquid and solid. By separating the liquid from the solid over 1 m^2, we also create 1 m^2 of liquid-air interface and 1 m^2 of solid-air interface. Thus, the adhesion energy between solid and liquid is given by:

$$W_{SL}= (\sigma_S+ \sigma_L - \sigma_{sL})\ s$$

In this equation, only σ_L is known. The difference (σ_S–σ_{sL}) can be relatively easily measured, whereas the two terms cannot be measured separately.

2-3 Contact Angle θ:

Considering the equilibrium of a liquid droplet resting on a horizontal solid surface, Figure 3 illustrates the existence of three phases.

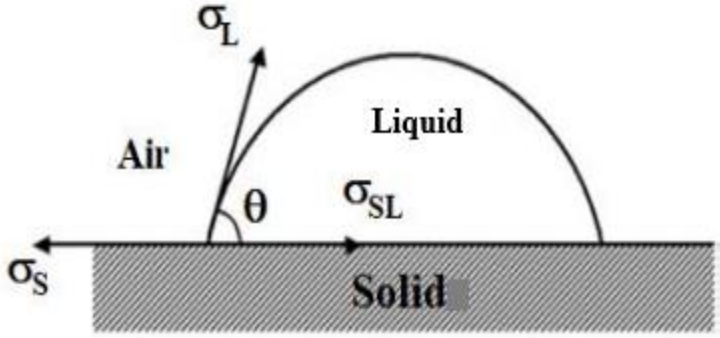

Figure 3

The equilibrium at point M can be expressed (horizontal components of the surface forces) as:

$$\sigma_S = \sigma_{sL} + \sigma_L \cos(\theta)$$

This means:

$$\sigma_S - \sigma_{sL} = \sigma_L \cos(\theta) \quad \Longrightarrow \quad \cos(\theta) = \frac{\sigma S - \sigma s L}{\sigma L}$$

The angle $\theta$is called the contact angle, which is measurable. The adhesion work can be expressed as:

$$W_{\mathrm{SL}} = \sigma_L\,(1+\cos(\theta))\ \mathbf{S}$$

It can be observed that the smaller the angle θ, the greater the adhesion work. We consider the following cases:

- **θ=0°: $W_{SL}=2\sigma_L=$** : The adhesion work is equal to the cohesion work of the liquid. This is the extreme case of equilibrium that corresponds to complete spreading of the liquid. The condition $W_{SL}=W_L$ represents the limit of perfect wetting. In principle, wetting is considered perfect if $W_{SL} \leq W_L$.
- **θ=180°: W_{SL}=0:** The adhesion work is zero. Wetting is null.
- **0<θ<90°** (acute): Good but not perfect wetting.
- **90°<θ<180°:** Poor but not null wetting.

2-4 Examples of Wetting Applications:

In phytopharmacy: Certain wetting agents are used in pharmacy to enhance the penetration of medications through the skin or mucous membranes. Conversely, one may seek anti-wetting agents to reduce the cutaneous penetration of toxic substances.

In the case of antiparasitic products, it is essential to achieve perfect adherence of the liquid to the surface to block the insect's pores, preventing it from breathing. Therefore, when the contact angle $\theta=0$, we have a wetting product.

In the case of herbicides, on the other hand, poor wetting is required since these products should not be harmful to insects, necessitating the choice of anti-wetting agents. Poor wetting can occur due to a layer formed on the surface of the solid, which must first be treated (it should be well polished).

To understand the adhesion of a liquid, or wetting, it is crucial to accurately determine the surface tension. There are several methods to measure surface tension, including the capillary rise method (Jurin's law), the immersed blade method, and the drop method (stalagmometry). We will detail the capillary rise method in the following sections.

3-Capillarity Phenomenon:

3-1 Definition:

It is the phenomenon that explains, among other things, the upward movement (vertical rise) of liquids against the force of gravity along a surface due to their surface tension.

3-2 Capillary Rise Method (Jurin's Law):

Consider a tube made from a solid with a wettability defined by an angle θ. When this tube is immersed in a liquid, we observe that for good wettability, the liquid level rises ($h > 0$) as shown in Figure 4 (a). Conversely, for poor wettability, the liquid level falls, as illustrated in Figure 4(b)

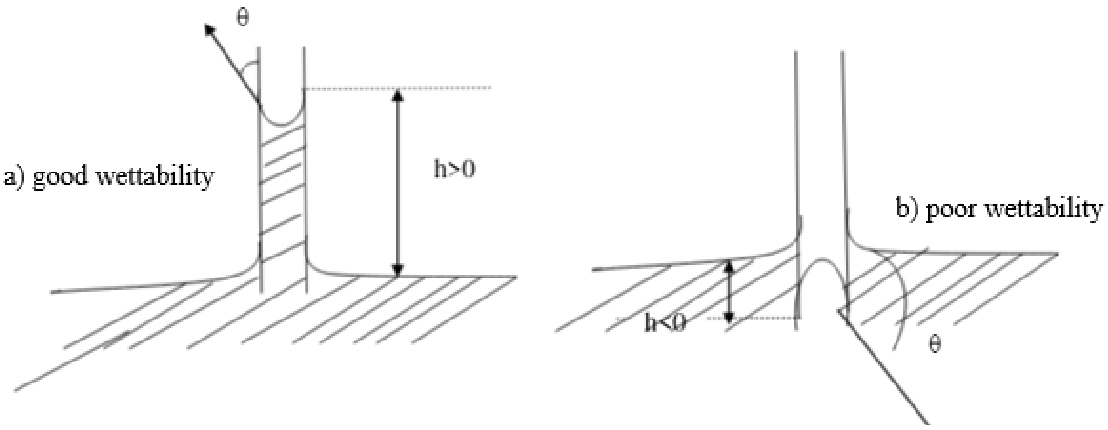

Figure 4

The height difference h is greater when the radius or meniscus is small. Let ΔF be the attraction exerted by the tube on the liquid inside:

$\Delta F = 2\pi r \sigma \cos\theta$

Equilibrium is established when the attraction and the weight of the liquid column balance each other. The weight of the liquid in the column is given by:

$P = h \cdot \pi r^2 \cdot g . \rho$

where:

g is the acceleration due to gravity,

h is the height (neglecting the menisci),

ρ is the density of the liquid,

$h \pi r^2$ is the volume of the liquid column.

By equating the two equations

$\Delta F = P$, we have:

$$\sigma \cos\theta = \frac{h \cdot r . \rho \cdot g}{2}$$

This is Jurin's Law.

3-3. Measurement of Surface Tension (Capillary Method)

By applying Jurin's law, we deduce a value for σ (surface tension) from the measurement of the height difference h and the knowledge of the other parameters.

4- Surface Tension Force (Liquid-Gas Interfaces):

Let there be a molecule (A) inside the liquid. It is surrounded on all sides by other molecules. If we neglect the influence of thermal agitation, the resultant of the attractive forces acting on molecule (A) is, on average, zero, since all directions are equivalent.

$\sum \vec{F}=\vec{0}$

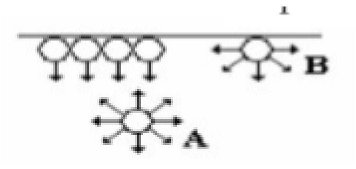

Figure 5

For another molecule (B) as shown in Figure 5, which is located at the surface of the liquid, if we neglect the attraction of gaseous molecules, this molecule is, on average, pulled inward perpendicular to the surface by the surrounding liquid molecules. The same applies to all surface molecules, which together form a kind of stretched film that compresses the interior of the liquid.To bring molecule (A) to the surface, i.e., to increase the surface area, energy must be supplied to move a molecule from the liquid phase to the vapor phase. This energy is called the surface energy, and it is directly related to intermolecular forces.

Any increase in surface area (ΔS) requires an external energy (ΔE), such that:

$\Delta W=\Delta E=\sigma\Delta S$

The proportionality coefficient σ, which is always positive, is called the surface tension. Its unit is either N/m (Newton per meter) or J/m² (Joules per square meter).

Another commonly used definition represents σ as a force F tangent to the surface.

Some measurements of surface tension.

Liquids (20°C)	σ (dynes/cm)
H_2O	72.8
Glycerin	60
Glycol	46
Benzene	28.5

Molten metals have surface tensions on the order of 500 dynes/cm.

The phenomenon of liquid-gas surface tension creates an overpressure inside a droplet or a column.

4-1 Overpressure inside a Droplet:

Consider a spherical droplet (Figure 6). The membrane surrounding it exerts an overpressure p inside the droplet:

P_0 : atmospheric pressure outside the droplet $=1.013\times10^5 N/m^2$ (pascals)

P: internal pressure.

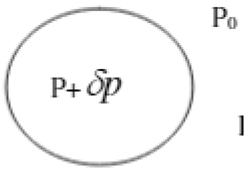

Figure 6

To calculate the overpressure p, we need to increase the volume of the droplet, which changes its radius from r to $r+\Delta r$. Thus, external energy ΔE must be supplied.

The work done on the system is:

$$\Delta W = \delta F \ \Delta x = \frac{\delta F}{S} S \ \Delta x = \delta p \ \Delta V$$

The force F is related to the surface tension and the change in radius:

$$\Delta W = \delta p \ \Delta V = \delta p \ \Delta\left(\frac{4}{3}\pi r^3\right) = \delta p \ 4\pi r^2 \Delta r \qquad \boxed{(1)}$$

This work increases the surface area of the droplet, so:

$$\Delta W = \sigma \ \Delta S = \sigma \ \Delta(4\pi r^2) = \sigma \ 8\pi r\Delta r \qquad \boxed{(2)}$$

By equating equations (1) and (2), we obtain:

$$p - p_0 = \delta p = \frac{2\sigma}{r}$$

This is Laplace's law, a relationship that links the pressure difference between the two sides of an elastic membrane or liquid film to the surface tension σ

4-2 Overpressure Inside a Soap Bubble:

Consider a soap bubble made up of two membranes: an inner membrane with radius

r and an outer membrane with radius r+Δr (Figure 7).

Let σ be the surface tension of the soap solution.

r: the radius of the inner membrane.

r+Δr: the radius of the outer membrane.

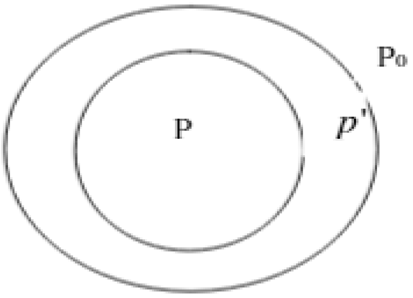

Figure 7

$$p - p' = \frac{2\sigma}{r}$$ (1) Overpressure created by the inner membrane,

$$p' - p_0 = \frac{2\sigma}{r + \delta r}$$ (2) overpressure created by the outer membrane

By adding these two equations, we obtain:

$$\delta p = p - p_0 = \frac{2\sigma}{r + \delta r} + \frac{2\sigma}{r} = \frac{4\sigma}{r}$$

δr<<<<<

δp: Overpressure inside the bubble relative to the outside. Therefore, the overpressure inside a soap bubble is twice as large as in the case of a droplet.

5- Some Applications of Surface Phenomena

- **Wettability** plays an important role in many fields such as: the chemical industry (paint, etc.), automotive, cosmetics, as well as in the healthcare sector more broadly (lung expansion at birth, eye hydration, etc.). It is worth noting that some wetting agents are used in pharmacy to facilitate the penetration of drugs through the skin. Conversely, anti-wetting agents can be sought to reduce the penetration of toxic substances.
- **The lung** is a gas exchange organ, where oxygen from the inspired air is captured. The surface area of the lungs is increased by the presence of alveoli. The expansion of the lungs requires considerable work because the surface tension that holds the alveolar membranes together is high. To facilitate ventilation, surfactants reduce the surface tension at the internal surface of the alveoli. The presence of these surfactants reduces the work needed to expand the lungs: when the alveolus expands, the surface tension increases. The resistance to expansion increases and protects the alveoli from rupturing.
- **Foam** is a dispersion of a gas in a liquid. By vigorously agitating a liquid in the presence of a gas, foam can be formed, meaning that new liquid-gas interfaces are created. This phenomenon is applied in the separation of dissolved surfactants. By multiplying the interfaces, concentration on these interfaces is enhanced, and it becomes sufficient to collect the foam to achieve an efficient separation. This method is used to separate certain steroid hormones from urine.
- **An emulsion** is a dispersion of one liquid in another immiscible liquid. It is obtained by violently shaking the two liquids together. One of the two liquids is the dispersing liquid, with its phase being continuous, while the other is dispersed, meaning it is separated into discrete droplets.