Capillary action concerns the interplay of forces that are present at the boundary among surfaces of different phases; often referred to as interfaces. In this chapter we introduce some of the main concepts of capillarity on which the current study relies, giving special attention to the case when solids, liquids and air meet at a so-called contact (triple) line.

2.1 Surface Tension

It is generally recognized that surfaces exert forces. This hypothesis can successfully be demonstrated using a wire frame with a thin soap film bounded by it (Fig. 2.1a). If one side of the frame is free to move in a direction parallel to the plane of the frame, then one must do work in order to extend the interface between the film and the air by a distance $dx$, i.e.,

$$dW = Fdx$$ (2.1)

where $F$ is the force that one needs to apply for the film to stretch. As surface tension, $\gamma$, we define the force per unit length which is normal to the movable frame in the horizontal plane and directed toward the liquid

$$\gamma = \frac{F}{2l}$$ (2.2)

where $l$ is the length of the moving rod (de Gennes et al. [2004]). The factor 2 in the denominator indicates the existence of two interfaces, i.e., two sides of the soap film. As soon as the mobile part is once again released, this will move inward indicating that the soap film wants to minimize its surface area. Thus, surface tension can be considered as the resistance of an interface to the increasing of its area, described as the free energy per unit length. Alternatively, it could be said that one needs to perform work in order to bring molecules to the surface increasing the area of the latter.
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Figure 2.1: (a) A soap film will tend to resist any attempt of surface area increase owing to surface tension; (b) molecules at the surface of a liquid bath are subjected to a net force directed towards the bulk, whereas the attractive interactions that the molecules inside the liquid feel balance each other. This is why an excess energy is associated with the liquid-air interface; (c) the air pressure is always higher in the interior of an inflated balloon. When the balloon is untied the pressure difference drives the air out. One could say that the surface energy of the balloon is converted to the kinetic energy of the air jet, which makes the balloon hover around as a result of the produced thrust.

From a thermodynamic point of view, this concept falls under the classical principle based on which scientists treat most of the physical phenomena, that is to say the system tends to minimize its free energy in order to reach a state of equilibrium. The reason why a larger surface means a larger free energy can be seen in Fig. 2.1b. A molecule in the bulk of the liquid phase experiences almost the same attractive forces from all the neighboring molecules and therefore these forces balance each other. On the other hand, the uneven interactions that surface liquid molecules experience from neighboring liquid and vapor molecules make the available free energy higher there. Thus, a molecule would prefer to be in the bulk of the liquid where the energy state is more favorable. A consequence of this can be traced to the shape that liquid droplets or bubbles tend to adopt in the absence of gravity and other external forces. In particular, surface tension gives them a perfect spherical shape simply because for a given volume the geometry of a sphere exhibits the smallest surface area.

Surface tension can also be between two immiscible liquids, a solid and a liquid or a solid and a gas.

2.2 Laplace Pressure

When a surface is curved a pressure difference between the concave and the convex side of the interface is observed, with the pressure at the concave side being always higher. As an analogy, one could imagine an inflated balloon neglecting, for the sake of clarity, the tangential stresses along the elastic surface (Fig. 2.1c). In general, this overpressure is necessary for a mechanical equilibrium to be achieved as it balances the effect of surface tension that is directed towards the concave side of the balloon. The pressure difference across an interface of a certain curvature is often referred to as the Laplace pressure (Pellicer et al. [2000]), named after Pierre Simon de Laplace, and is given as

\[ \Delta P = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \]  

(2.3)

where \( R_1 \) and \( R_2 \) are the two radii of curvature necessary to specify the curvature of a surface.
2.3 Contact Between Three Phases

2.3.1 Equilibrium Contact Angle: Young’s Equation

As we mentioned in the introductory paragraph, our main interest concerns the interaction between three different interfaces and particularly the case where a liquid droplet is surrounded by air while sitting on a homogeneous solid substrate (Fig. 2.2a). Each interface is characterized by a respective interfacial tension and the line at which the three phases meet is the contact line. At a state of equilibrium, the three surface tensions are related through Young’s equation

\[ \gamma_{sv} = \gamma_{sl} + \gamma \cos \theta \]  

(2.4)

where \( \gamma_{sv} \), \( \gamma_{sl} \), and \( \gamma \) are the solid-vapor, solid-liquid and liquid-vapor interfacial tensions, respectively, and \( \theta \) is the equilibrium contact angle formed between the solid-liquid and liquid-vapor interface at the contact line and counted from the side of the liquid. Equation (2.4) can be derived by determining the work one would need to do in order to make the contact line slightly move by a distance, \( \delta x \), which has a negligible impact on the angle, i.e., \( \theta + \delta \theta \simeq \theta \), as shown in Fig. 2.2b. Such a distortion includes an increase of the liquid-solid interface accompanied by an equal decrease of the solid-vapor one, whereas the surface of the liquid is extended by \( \cos \theta \delta x \), therefore it is

\[ \delta W = \gamma_{sl} \delta x - \gamma_{sv} \delta x + \gamma \cos \theta \delta x \]  

(2.5)

Since at equilibrium there must be \( \delta W = 0 \), the above equation simplifies to Eq. (2.4). Some further comments on this general proof of Young’s equation can be found in the work of Roura and Fort [2004].

To elaborate a bit more on Young’s law, let us first consider the case of an initially dry solid substrate. The available surface energy of the system is then related only to the solid-vapor surface energy. If we now deposit some liquid on the substrate, two other interfaces are created instead, namely the solid-liquid and the liquid-vapor ones. If the surface energy of these two interfaces together exceeds the pre-existing surface energy then the liquid will form a droplet of a certain contact angle, in order to minimize the free energy of the system (Fig. 2.2a). In this case we say that the liquid partially wets the substrate. If, on the other hand, the surface energy of the dry substrate is equal to or larger than the sum of the other two surface tensions, there is no need for a drop to be formed and therefore the contact angle is zero. Then, equilibrium is described by a liquid layer expanding on top of the

![Figure 2.2:](a) Schematic representation of a sessile drop, which partially wets a substrate, and of the acting interfacial tensions at the contact line; (b) Derivation of Young’s equation based on free energy considerations; (c) schematic representation of a complete wetting situation where the equilibrium contact angle is zero.)
substrate, a case which is referred to as complete wetting (Fig. 2.2c). A water droplet, for example, will exhibit a different wetting behavior depending on whether it is deposited on cleaned glass or on a plastic surface; it will completely wet the former and partially wet the latter. Accordingly, one can also define a spreading parameter, $S$, which compares the surface free energy of a system consisted of a dry substrate to the available free energy assuming that the substrate is completely wet, so that

$$S = \gamma_{sv} - (\gamma_{sl} + \gamma)$$  \hspace{1cm} (2.6)$$

Following this, complete wetting is observed for $S \geq 0$, while $S < 0$ indicates that partially wetting occurs. In the latter case, when gravity, along with other external forces, is negligible the shape of the droplet is governed exclusively by surface tension, therefore it attains a spherical cap shape. Should the droplet becomes large, however, gravity tends to make it flatter (Fig. 2.3). The typical length up to which gravity can be neglected is found after balancing the Laplace and the hydrostatic pressures which yields

$$l_c = \sqrt{\frac{\gamma}{\rho_l g}}$$  \hspace{1cm} (2.7)$$

where $\rho_l$ and $g$ are the density of the liquid and the gravitational acceleration, respectively. Consequently, the more the droplet base radius exceeds the capillary length, the flatter the droplet will eventually become approaching the shape of a “pancake”. One should remark here that, at equilibrium, the drop will maintain the same contact angle even if gravity alters its shape (Fujii and Nakae [1995]).

### Contact Angle Hysteresis

As we have described so far, a liquid droplet that partially wets a perfectly smooth solid surface will lie on it retaining the equilibrium contact angle indicated by Young’s equation. Theoretically this means that each time liquid is removed from or added to the droplet, the contact line should immediately shift to let the drop preserve this angle (Fig. 2.4a). In reality, however, that is not the case. Most of the times, solids appear to have a rough surface characterized also by chemical heterogeneities on which the contact line will stay pinned until the equilibrium angle reaches a certain critical value. Specifically regarding the case in which the volume of the droplet is being increased, the apparent contact angle will exceed Young’s angle, while at the same time the contact line remains immobile (Fig. 2.4b). After a certain amount of liquid has been added to the drop, the angle becomes sufficiently large and finally the contact line moves.

The value of the apparent contact angle for which the contact line starts to advance, is called the advancing angle, $\theta_a$. Reversely, when the volume of the drop is reduced, we name as receding angle,
2.3. CONTACT BETWEEN THREE PHASES

\[ \theta = \theta_{eq} + \delta \theta \]

\[ \delta x \cos \theta \]

\[ \gamma \]

\[ \gamma_{SV} \]

\[ \gamma_{SL} \]

\[ \theta_{eq} \]

\[ \theta_{a} \]

\[ \theta_{r} \]

The apparent contact angle for which the contact line eventually starts to recede. The fact that these two angles are not equal is referred to as contact angle hysteresis (Quéré [2008]) with the value

\[ \Delta \theta = \theta_{a} - \theta_{r} \]  \hspace{1cm} (2.8)

In general, contact angle hysteresis should be sufficiently small, i.e., less than 5°, in order to characterize a surface as sufficiently clean and smooth (Bonn et al. [2009]). Repetition of hysteresis in time makes for a stick-slip cycle. At first, the contact line is pinned and the contact angle is changing, altering in this way the height of the drop but not the liquid-solid surface area (stick stage). Then, as soon as the contact angle has reached the advancing (or receding) value, the contact line shifts to a new point (slip stage) where it will once again stay pinned for some time (Shanahan [1995]).

In addition to this type of movement of the contact line, there exists also a more discontinuous mode, referred to as stick-jump, which can be observed when the ratio of the size of the pinning site to the size of the droplet increases (Zhang and Mi [2009]).

2.3.2 Non-Equilibrium Contact Angle

In the previous section we considered only immobile contact lines, where equilibrium is well-established. Even in case of hysteresis, the terms “advancing” and “receding” actually refer to static contact angles, despite the fact that at first sight they seem to imply a dynamic situation. But what happens while a contact line is moving before it eventually reaches a state of equilibrium and how the contact angle is defined in this case, are two questions whose answer is not so straightforward as before. Apparently, in a dynamic situation, such as the spreading of a droplet on a solid substrate, Young’s equation is not enough to describe the formation of the contact angle, at least until the drop comes to a rest once again. One can instead introduce the term apparent in order to signify the apparent angle that the liquid-vapor interface makes with the solid vapor each moment of the spreading (Fig. 2.5). For droplets that can be approximated by a spherical cap and small enough \( \theta_{ap} \) this angle is given as

\[ \theta_{ap} = \frac{4V}{\pi R^3} \]  \hspace{1cm} (2.9)

where \( V \) and \( R \) are the volume and the contact radius of the drop, respectively.

The spherical cap approximation requires now not only gravity to be negligible but also that viscous forces are small. The former is true for radii smaller than the capillary length while the latter holds
Figure 2.5: A drawing of a spreading droplet the macroscopic shape of which is described by an apparent contact angle. Nevertheless, near the contact line a dynamic angle which varies logarithmically with the distance from the contact line can be defined. The region surrounded by the dashed circle refers to a region in the vicinity of the contact line, shown in Fig. 2.6.

when the effect of surface tension dominates over viscous forces. In fact, the ratio between viscous and surface tension forces defines the capillary number

$$Ca = \frac{\mu_l U}{\gamma}$$

which is considered to be small when $Ca \approx 10^{-5}$. Here, $\mu_l$ is the dynamic viscosity of the liquid, $U$ is the contact line speed and $\gamma$ is the surface tension of the liquid-air interface.

Nevertheless, the apparent contact angle, as this is defined in Eq. (2.9), is based mainly on geometric considerations and it provides no information on what is really happening at the contact line. A more physical approach demands the hydrodynamics of this problem to come into play. Applying the classical theory of fluid dynamics, however, fails severely to predict the velocity field at the contact line due to the “no-slip” boundary condition which accompanies the Navier-Stokes equations. In particular, the “no-slip” condition yields a multivalued velocity at the contact line since it assumes that the velocity of the liquid is zero at the surface of a solid boundary and finite at the liquid-air interface. Due to this, it can be shown that the energy dissipation diverges at the contact line, something that would require an infinite force (Huh and Scriven [1971], Bertozzi [1998]).

Despite the emerged paradox, first Voinov [1976] and then Cox [1986] attempted to estimate the contact angle of a spreading droplet by applying the classical hydrodynamic theory in a region close to the contact line (magnified part of Fig. 2.5). To distinguish the angle calculated in this small region from the apparent contact angle that governs the shape of the full drop we will refer to it as dynamic contact angle. A detailed analysis following their work yields an expression for this angle that depends on the capillary number and a microscopic contact angle, $\theta_m$

$$\theta_d^3(x) = \theta_m^3 + 9Ca\ln(x/L)$$

where $x$ is the distance from the contact line and $L$ is a characteristic micro-length at which the so-called contact line singularity is relaxed.

The above equation is known as the Cox-Voinov law and is valid for small contact angles, after assuming an ideal substrate and a flow characterized by small capillary and Reynolds numbers. In essence,
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Figure 2.6: Microscopic parameters need to be included in the hydrodynamic analysis of a moving droplet to estimate the flow near the edge. In one of the models a precursor film is expected to be present ahead of the apparent contact line where the interactions between the liquid and solid molecules are not to be neglected.

This law predicts the slope of a profile of a spreading droplet but only for a small region close to the contact line. Moreover, this slope should vary logarithmically with distance $x$. As a result, one cannot define a unique angle, $\theta_d$, since this depends on the distance from the contact line at which the calculation is made (Bonn et al. [2009], Winkels et al. [2011]). However, if Eq. (2.11) is evaluated at a characteristic length that describes the full droplet, such as the base radius, we can approximate the dynamic contact angle by the apparent one (Bonn et al. [2009]) such that Cox-Voinov law yields

$$\theta_{ap}^3 = \theta^3 + 9Ca \ln \left( \frac{R}{(2e^2L)} \right)$$

(2.12)

where $e$ is Euler’s number and $\theta$ the equilibrium contact angle given by Young’s angle. The above relation indicates that the apparent contact angle is larger than the equilibrium one when the droplet spreads. Conversely, for receding drops, where the capillary number is defined as negative, the apparent contact angle is expected to be lower than Young’s angle. Apparently, the slower the drop moves, the less its apparent contact angle would deviate from its equilibrium one.

Nevertheless, one has yet to deal with the contact line singularity in order to properly define the parameter $L$ and in turn the apparent contact angle. To work in this direction, additional factors acting at a microscopic scale must be considered. For instance, taking into account the effect of long range Van der Waals interactions between solid and liquid molecules is one among the various theories suggested in order to alleviate this singularity. In such a physical model, explained below, a precursor film should generally (but not always) appear ahead of the spreading drop.

**Precursor Film Concept**

According to this approach, the existence of a thin film attached to a drop allows the latter to slip on a prewetted solid surface. The thickness of this film is so small that it is generally comparable to the range of molecular interactions, and therefore surface chemistry comes into play which can determine considerably the late stages of spreading, especially in a complete wetting situation. These interactions, in fact, indicate a repulsive force between the solid-liquid and liquid-gas interfaces that tends to thicken the film opposing to the capillary forces which tend to make it thinner through spreading. This pressure defines the disjoining pressure (Leger and Joanny [1992], Churaev [2003]), first formulated by Derjaguin in 1936 (Derjaguin [1992]). With respect to the long range Van der Waals interactions
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the disjoining pressure is given by

\[ P_D = \frac{A}{h^3} \]  \hspace{1cm} (2.13)

where \( A \) is the Hamaker constant (positive in this context) related to the strength of the interaction and \( h \) is the film thickness. Although other expressions exist as well, depending on the nature of the interaction (Bonn et al. [2009]), Eq. (2.13) with \( A > 0 \) is appropriate for the particular case of complete wetting, which is going to interest us in the following chapters.

As it can be seen in Fig. 2.6, the microfilm is linked to the drop through a transition zone where both the curvature and the disjoining pressure are important. One could then define the liquid pressure in that zone as follows

\[ P_l = P_o - P_L - P_D \]  \hspace{1cm} (2.14)

where \( P_o, P_L \) and \( P_D \) are the pressure in the gas phase, the Laplace pressure (positive if the liquid-air interface is convex towards the liquid) and the disjoining pressure, respectively. When the thickness is large (meniscus region) the disjoining pressure is weak \( (P_D \approx 0) \) and the pressure difference can be described exclusively by the Laplace pressure. On the contrary, as the thickness decreases (transition region) interactions between solid and liquid molecules begin to rise and become dominant in the microfilm \( (P_L \approx 0) \). In the latter case, one can consider the excess of pressure in the gas phase as a tendency to balance the repulsive forces present in the film, in a similar way that the overpressure inside a tied balloon balances the Laplace pressure as we described in section 2.2.

The arrows drawn in Fig. 2.6 point to a pressure gradient between the transition zone and the microfilm, due to the sudden decrease of the film thickness. This drop of pressure eventually drives liquid to the right promoting the spreading of the droplet. As the microscopic analysis excludes the presence of a contact line, one is now able to solve the hydrodynamics of spreading and calculate the local profile of the droplet. Then, for instance, the height of the precursor film can be used in Eq. (2.12) as the characteristic length \( L \) to estimate the apparent contact of moving droplets.

To summarize, two extra regions need to be distinguished before we are able to calculate the non-equilibrium contact angle that is apparent at a macroscopic scale. One concerns a small region close to the contact line where Cox-Voinov law is derived, while the other is a microregion in the vicinity of the presumable contact line where the molecular interactions come into play in the form of the disjoining pressure. Information extracted from the latter region, thanks to the elimination of the singularity at the contact line, can be applied to the former to give finally the value of the apparent contact angle.

Other theories, such as the molecular kinetic theory, also account for the variation of the contact angle with the velocity focusing mostly on microscopic quantities such as molecular displacements near the contact line (Blake et al. [1997]) rather than on classical hydrodynamic considerations as the Cox-Voinov theory does. Nevertheless, for small contact angles the hydrodynamic contribution tends to be predominant and thus we will stick to the Cox-Voinov law for the rest of the present study.

Non-equilibrium contact angles are also encountered in droplets that are subjected to evaporation, independently of whether they are moving or not. In Chapter 4 we will particularly focus on the case of freely receding evaporating drops.
Figure 2.7: (a) Thomas Young (1773-1829) and (b) Pierre Simon de Laplace (1749-1827) are both known for their contributions not only to the subject of capillarity but also to numerous other scientific fields, such as linguistics (Parkinson [1999]) and political sciences (Ball [2002]), respectively.