The study of capillarity and related phenomena requires both an acute faculty of observation and an intensity of imagination that truly allow one to see "all the world in a grain of sand." The process by which morning dew condenses into the unstable droplets that grace a spider's web, for example, has important implications for the industrial treatment of textile fibers. And an appreciation of underlying physical principles provides an answer to common questions about everyday phenomena—for example, why large drops of rain roll down a car windshield, while others descend leaving a trail of water behind them.

This latest book from renowned teacher and Nobel Laureate Pierre-Gilles de Gennes and two renowned experts in the field offers a compendium of principles designed to elucidate a wide range of phenomena. The rigor of numerical and other mathematical methods gives way to a *qualitative* rigor that aims to create a deep intuitive understanding of the mechanisms involved. Written in the spirit of Henri Bouasse's classic 1924 study, *Capillarity and Wetting Phenomena* takes a similarly subtle approach to complex problems and is destined to become a classic itself.

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Drops, Bubbles, Pearls, Waves

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1
Capillarity: Deformable Interfaces

Capillarity is the study of the interfaces between two immiscible liquids, or between a liquid and air. The interfaces are deformable: they are free to change their shape in order to minimize their surface energy. The field was created in the early part of the 19th century by Pierre Simon de Laplace (1749–1827) and Thomas Young (1773–1829). Henri Bouasse wrote a wonderful account of developments in capillarity in a book he published in 1924.[1] This discipline enables us to understand the games water can play to break the monotony of a rainy day or the tricks it performs while washing dishes. On a more serious note, capillarity plays a major role in numerous scientific endeavors (soil science, climate, plant biology, surface physics, and more), as well as in the chemical industry (product formulation in pharmacology and domestics, the glass industry, automobile manufacturing, textile production, etc.).

1.1 Surface Tension

A liquid flows readily; yet it can adopt extremely stable shapes. A drop of oil in water or a soap bubble forms a perfect sphere that is smooth on an atomic scale and is hardly deformable (Figure 1.1).[2] The fluctuations of the surface thickness are of the order of a mere Angström. A liquid surface can be thought of as a stretched membrane characterized by a surface tension that opposes its distortion.

We will focus our attention on the physical origin and consequences of the phenomenon of surface tension.

FIGURE 1.1. Drops and bubbles form perfect spheres.[2] (From *A Drop of Water: A Book of Science and Wonder*, by Walter Wick. Published by Scholastic Press, a division of Scholastic Inc. Photographs © 1997 by Walter Wick. Reproduced by permission.)

1.1.1 *Physical Origin*

A liquid is a condensed state in which molecules attract one another. When the attraction is stronger than thermal agitation, molecules switch from a gas phase to a phase that is dense, although still disordered—what we call a liquid. A molecule in the midst of a liquid benefits from interactions with all its neighbors and finds itself in a "happy" state. By contrast, a molecule that wanders to the surface loses half its cohesive interactions (Figure 1.2) and becomes "unhappy." That is the fundamental reason that liquids adjust their shape in order to expose the smallest possible surface area. When dry, your hair is likely to be full and thick, whereas the moment it gets wet, it sticks together in a drab, droopy mass. (Figure 1.3).

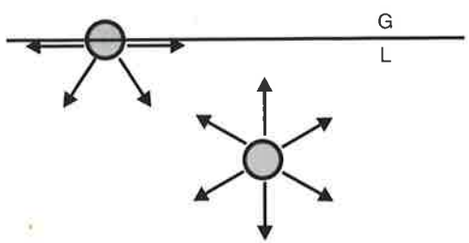


FIGURE 1.2. An "unhappy" molecule at the surface: It is missing half its attractive interactions.

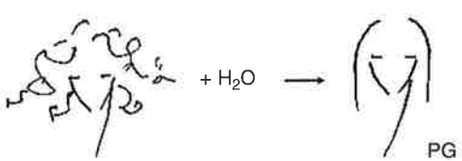


FIGURE 1.3. Full dry hair vs. sticky wet hair.

TABLE 1.1. Surface tension of a few common liquids (at 20°C unless otherwise noted) and interfacial tension of the water/oil system.

Liquid	Helium (4K)	Ethanol	Acetone	Cyclohexane	Glycerol
γ(mN/m)	0.1	23	24	25	63
Liquid	Water	Water (100°C)	Molten glass	Mercury	Water/oil
γ(mN/m)	73	58	~300	485	~ 50

When segregated to the surface, a liquid molecule is in an unfavorable energy state. If the cohesion energy per molecule is U inside the liquid, a molecule sitting at the surface finds itself short of roughly $U/2$. The surface tension is a direct measure of this energy shortfall per unit surface area. If a is the molecule's size and a^2 is its exposed area, the surface tension is of order $\gamma \cong U/(2a^2)$. For most oils, for which the interactions are of the van der Waals type, we have $U \cong kT$, which is the thermal energy. At a temperature of 25°C, kT is equal to 1/40 eV, which gives $\gamma = 20$ mJ/m^2.

Because water involves hydrogen bonds, its surface tension is larger ($\gamma \approx 72$ mJ/m^2). For mercury, which is a strongly cohesive liquid metal, $U \approx 1$ eV and $\gamma \approx 500$ mJ/m^2. Note that γ can equivalently be expressed in units of mN/m.

Likewise, the surface energy between two non-miscible liquids A and B is characterized by an interfacial tension γ_{AB}. Table 1.1 lists the surface tensions of some ordinary liquids (including those used in the experiments to be described in the course of these chapters), as well as the interface tension between water and oil.

Although its origin can be explained at the molecular level, the surface tension γ is a macroscopic parameter defined on a macroscopic scale, as we will see shortly.

1.1.2 *Mechanical Definition: Surface Energy and Capillary Force*

Surface Work

It is well known that supplying energy is necessary to create surfaces. That fact is plainly obvious when you beat egg whites into a meringue or when you make an emulsion of water in oil while preparing a mayonnaise.

Suppose one wants to distort a liquid to increase its surface area by an amount dA. The work required is proportional to the number of molecules that must be brought up to the surface, i.e., to dA; and one can write:

$$\delta W = \gamma \cdot dA \tag{1.1}$$

where γ is the surface (or interfacial) tension. Dimensionally, $[\gamma] = EL^{-2}$. The surface tension γ is thus expressed in units of $\mathrm{mJ/m^2}$. Stated in words,

> *γ is the energy that must be supplied to increase the surface area by one unit.*

Surface tension also contributes to thermodynamic work.[3] It can be defined as the increase in internal energy U or in free energy F that accompanies an increase in surface area:

$$\gamma = \left[\frac{\partial F}{\partial A}\right]_{T,V,n} \tag{1.2}$$

where n is the number of molecules and V is the total volume.

Surface thermodynamics is a rather subtle science, which we will refrain from reviewing here. The interested reader is urged to consult the text by Rowlinson and Widom.[3] We simply note that, if one works with a fixed chemical potential μ, it is convenient to use the grand potential $\Omega = F - n\mu = -pV + \gamma A$.

Capillary Forces

Surface tension can also be viewed as a force per unit length. Dimensionally, one can write $[\gamma] = \mathrm{FL^{-}1}$, and one can express γ in units of N/m. We proceed to describe a few experiments in which γ manifests itself as a force (Figure 1.4).

1. Imagine a rigid metal frame bent in the form of a wedge and its two extremities connected by a thin sewing thread. If one deposits a liquid film (such as a soap film) within the wedge, the film will want to shrink its surface area. As it does so, it pulls perpendicularly and uniformly on every element of the thread, which will ultimately lose its slack and take on the shape of a taut circular arc.
2. Consider a rigid frame supporting a liquid membrane. A flexible loop, secured by two threads to the frame, is embedded in the membrane (Figure 1.4). The loop is free to take on any shape until the membrane is punctured, at which time the loop stretches into a circle.
3. Visualize a glass rod bent to form three sides of a rectangle. A second rod, free to roll on the two parallel sides of the rectangle, constitutes the fourth side of length l (Figure 1.4). The apparatus is dipped into a glyceric liquid (containing water, bubble soap, and glycerine to make the mixture viscous). As soon as the apparatus is removed from the liquid, one observes that the mobile rod moves spontaneously in the direction of the arrow so as to decrease the surface area of the liquid. If the frame is tilted, it is even possible for the mobile rod to climb up the incline, only to fall back down suddenly the moment the liquid membrane is pierced.

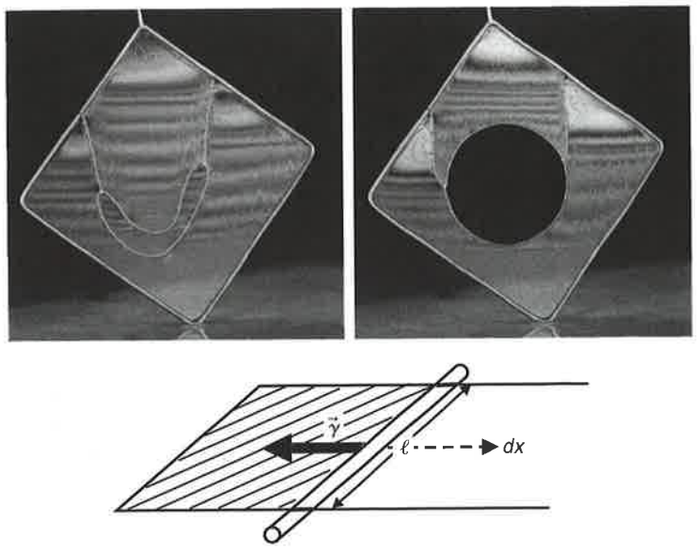


FIGURE 1.4. Manifestation of surface tension: force normal to the line (wire, rod). (From *A Drop of Water: A Book of Science and Wonder*, by Walter Wick. Published by Scholastic Press, a division of Scholastic Inc. Photographs © 1997 by Walter Wick. Reproduced by permission.)

If the mobile rod moves by a distance dx, the work done is

$$\delta W = F \cdot dx = 2\gamma \cdot l \cdot dx \tag{1.3}$$

where the factor of 2 reflects the presence of two interfaces. This demonstrates that γ is also the force exerted per unit length of the rod. In conclusion,

> *$\vec{\gamma}$ is a force (per unit length) normal to the rod in the plane of the surface and directed toward the liquid.*

Capillary forces are truly remarkable. They enable insects to walk on water. However, should the pond become polluted with detergents, which lower the surface tension, the unfortunate insects will drown! This phenomenon of flotation can be studied by depositing a sewing needle on a very thin piece of toilet paper brought up the surface. After gently removing the toilet paper, the needle keeps on floating. The moment one adds a drop of detergent, the needle sinks instantly.

As we will see later, these two aspects of surface tension—energy and force—will be a recurring theme.

1.1.3 *Measurements of Surface (or Interfacial) Tensions*

There exist numerous measurement techniques, all of which have been described in a book by A. W. Adamson.[4] It is worth mentioning a few standard methods, which will be discussed in detail in chapter 2. They include

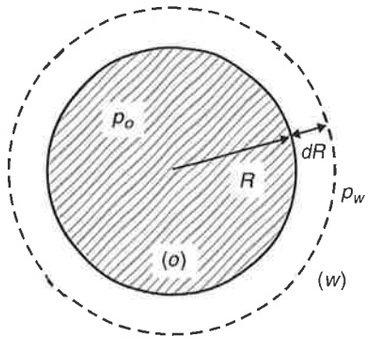
- Wilhelmy's method, in which one dips a thin plate or a ring and measures the capillary force acting on the plate (Figure 2.24),
- The rise of a liquid in a small capillary tube (Figure 2.17),
- The method of drops, in which one characterizes the shape of drops in various configurations (deposited, rotating, hanging), then matches the actual shape to theoretical simulations based on the parameter γ,
- Capillary waves: one excites capillary waves and one measures the relation between frequency and wavelength (described theoretically in chapter 5) by monitoring the distortion of the surface by means of a laser beam.

Every one of these methods requires considerable precautions. Liquid surfaces are ideal, smooth on an atomic scale, and chemically homogeneous. Unfortunately, they are easily contaminated. Early data on the surface tension of water were plagued with enormous variations until the day (about one hundred years ago) when Agnès Pockels, while experimenting in her kitchen, realized that it was necessary to "scrape" the surface of water. A surface of fresh water has a well-defined surface tension $\gamma = 72$ mN/m. But water, whose surface tension is particularly high, happens to easily get contaminated, which lowers its surface tension. To avoid this serious drawback and prepare liquid surfaces that do not change with time, one often uses silicone-based oils, which have a low surface tension ($\gamma \approx 20$ mN/m). For the same reason, these substances are also used as anti-graffiti and anti-stain agents to protect the facades of buildings: they make the surface non-adhesive.

1.1.4 *Laplace Pressure*

This section draws on the work of Laplace published in 1805.[5] Surface tension is at the origin of the overpressure existing in the interior of drops and bubbles. This pressure difference has multiple consequences. For instance, smaller drops will disappear in favor of larger ones in an emulsion, and they will be the first to evaporate during the cooling phase of an aerosol. The pressure difference also explains the phenomenon of capillary adhesion between two plates, between hairs or fibers, or in wet sand, all of which are induced by capillary bridges.

FIGURE 1.5. Overpressure inside a drop of oil "o" in water "w."



As one passes across a curved surface or interface, a jump in pressure occurs, which we proceed to evaluate, first for a sphere, and then for any curved surface.

Sphere

We take the example of a drop of oil (o) in water (w) (Figure 1.5). In order to lower its surface energy, the drop adopts a spherical shape of radius R. If the o/w interface is displaced by an amount dR, the work done by the pressure and capillary force can be written as

$$\delta W = -p_o\, dV_o - p_w\, dV_w + \gamma_{ow}\, dA \tag{1.4}$$

where $dV_o = 4\pi R^2\, dR = -dV_w$, and $dA = 8\pi R\, dR$ are the increase in volume and surface, respectively, of the drop, p_o and p_w are the pressures in the oil and water, and γ_{ow} is the interfacial tension between oil and water.

The condition for mechanical equilibrium is $\delta W = 0$, which amounts to

$$\Delta p = p_o - p_w = \frac{2\gamma_{ow}}{R}. \tag{1.5}$$

For an aerosol drop of radius 1 μm, Δp is typically comparable to the atmospheric pressure. Note that equation (1.5) can be obtained just as well by minimizing the grand potential $\Omega = -p_o V_o - p_w V_w + \gamma_{ow} A$.

The smaller the drop, therefore, the greater its inner pressure. This property can be verified with soap bubbles. By connecting two bubbles (Figure 1.6) of different sizes, one can readily observe that the smaller one empties itself into the larger one. In an emulsion of oil in water, small drops disappear in favor of large ones because of this overpressure, which makes them thermodynamically unstable (a phenomenon known as Ostwald's ripening).

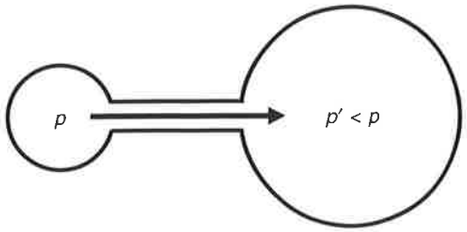


FIGURE 1.6. Small bubbles empty themselves into larger ones.

Generalization to Any Surface

Laplace's theorem:

The increase in hydrostatic pressure Δp that occurs upon traversing the boundary between two fluids is equal to the product of the surface tension γ and the curvature of the surface $C = \frac{1}{R} + \frac{1}{R'}$:

$$\Delta p = \gamma \left(\frac{1}{R} + \frac{1}{R'} \right) = \gamma C \tag{1.6}$$

where R and R' are the radii of curvature of the surface.

As was the case for the sphere, equation (1.6) can be demonstrated by calculating the work done by the forces of pressure and the capillary forces during an infinitesimally small displacement or, alternately, by minimizing the grand potential.[4]

A convenient way to illustrate how to measure the curvature of a surface is to use the example of a pear (Figure 1.7). The curvature at point M is determined by inserting a needle defining the direction $\vec{N}$ normal to the surface. Next, the pear is cut along two mutually orthogonal planes

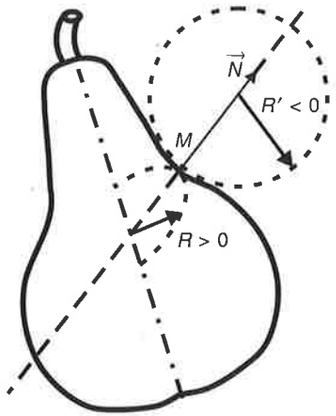


FIGURE 1.7. Measuring the curvature of a pear at a particular point.

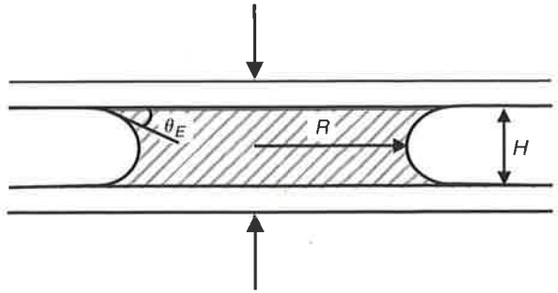


FIGURE 1.8. Capillary adhesion of two plates with a drop squeezed in-between.

intersecting each other along $\vec{N}$. The intersection of these planes with the surface of the pear defines two curves, the radii of curvature of which are R and R'. Note that R and R' are to be treated as *algebraic* quantities: R is defined as positive if the center of the corresponding circle lies *inside* the pear, and negative otherwise. A remarkable property of the curvature C is that it is independent of the orientation of the planes. If there exists a symmetry axis and one of the two planes contains that axis, the corresponding R and R' are then referred to as the *principal* radii of curvature.

Capillary Adhesion

Two wetted surfaces can stick together with great strength if the liquid wets them with an angle $\theta_E < \pi/2$. The angle θ_E is defined in Figure 1.8. (It will be discussed in more detail in Section 1.2.) Imagine that we mash a large drop between two plates separated by a distance H. The drop forms what is called a *capillary bridge* characterized by a radius R and a surface area $A = \pi R^2$. The Laplace pressure within the drop reads

$$\Delta p = \gamma \cdot \left(\frac{1}{R} - \frac{\cos\theta_E}{H/2} \right) \approx -\frac{2\gamma \cos\theta_E}{H}. \tag{1.7}$$

The force that glues the two plates together is attractive as long as $\theta_E < \pi/2$. If $H \ll R$, it is equal to

$$F = \pi R^2 \frac{2\gamma \cos\theta_E}{H}.$$

For water, using $R = 1$ cm, $H = 5$ µm, and $\theta_E = 0$ (best case), one calculates a pressure drop $\Delta p \sim 1/3$ atm and an adhesive force $F \sim 10$ N, which is enough to support the weight of one liter of water!

1.1.5 *Minimal Surfaces*

We have just seen that a liquid evolves spontaneously so as to minimize its surface area, and we illustrate this property in Figure 1.9. At equilibrium, minimum area surfaces satisfy Laplace's equation.

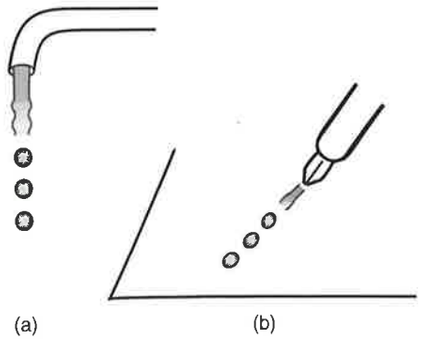


FIGURE 1.9. A stream of water and a trace of ink break up into droplets.

1.1.5.1 Jet

Upon opening a faucet, it is common to observe the water stream breaking up into droplets (Figure 1.9a) in order to lower its surface energy. To understand better the benefits of a lower surface area, we may mentally break up a cylinder of radius R and length L into n droplets of radius r. Conservation of volume dictates that

$$\pi R^2 L = \frac{4}{3}\pi r^3 n. \tag{1.8}$$

Let us examine the ratio of the final surface area S_n of the drops to the initial surface area S_0 of the cylinder. After eliminating n with the help of equation (1.8), we obtain

$$\frac{S_n}{S_0} = \frac{n \times 4\pi R^2}{2\pi RL} = \frac{3R}{2r}. \tag{1.9}$$

It is clear that the surface area of the drops is less than that of the original cylinder as soon as $r > \frac{3}{2}R$.

Plateau was the first to understand that the cylinder distorts itself spontaneously in order to lower its surface energy as soon as the wavelength λ_d of the distortion exceeds the perimeter of the cylinder.[6] The distortion then amplifies itself and the liquid cylinder fragments into drops. Some time later, Lord Rayleigh showed that the size of the drops was determined by the fastest distortion mode ($\lambda_d/2R \approx 4.5$ in the inertial regime).[7] This instability came to be named after Rayleigh. A liquid stream is one way to produce emulsions of uniform size. The technique is used in the manufacture of homogenized milk, as well as in many other industrial processes. We will return to the Plateau-Rayleigh instability in more detail when we describe the instability of liquid sheaths on fibers in chapter 5.

If one draws a line of ink on a piece of plastic, the line breaks up into droplets because, for exactly the same reason, a section of cylinder is less stable than a string of spherical caps. In a subsequent chapter devoted to the dynamics of wetting, we will see how this phenomenon controls numerous hydrodynamic instabilities that show up when a liquid flows and

collects in a ridge in the vicinity of the line marking the boundary between liquid, air, and substrate. A very simple experiment consists in depositing oil on half a Teflon pan and tilting it. The boundary line becomes wavy as fingers (or run-offs) begin to grow and expand.

1.1.5.2 Drop on a Fiber

Consider a drop of radius R deposited on a fiber of radius b (b is typically 10 to 100 μm). Assume that the liquid is able to wet the fiber, which means that the two media will connect smoothly at an angle equal to zero. The fiber may be a strand of hair, a textile thread, or a thin glass fiber. The shape taken on by the drop is sketched in Figure 1.10. Since its radius R is very much greater than b, the overpressure within the drop remains low ($\Delta p \approx 2\gamma/R$). At the outer point of contact between the drop and the fiber, one of the radii of curvature becomes very small (equal to b). Therefore, the other radius of curvature must become negative (of the order of $-b$) in order for the total radius of curvature to remain small.

We may calculate the details of the drop's profile $z(x)$. The surface has a constant curvature throughout given by

$$\frac{1}{R_1} + \frac{1}{R_2} = C = \frac{\Delta p}{\gamma} \tag{1.10}$$

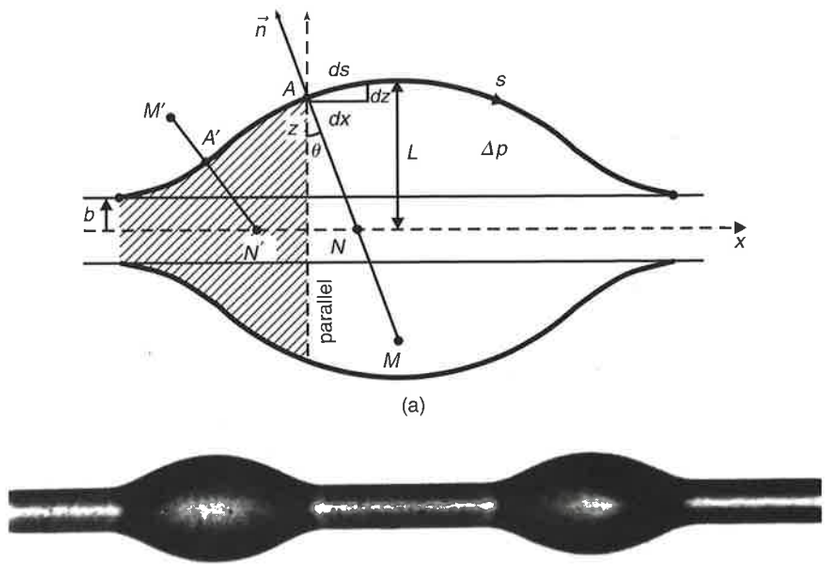


FIGURE 1.10. Drop deposited on a fiber. Schematic cross section (a); photograph of silicone oil drops deposited on a carbon fiber (b).

where Δp is the overpressure within the drop. The radii R_1 and R_2 at point A are $R_1 = AM$ (M is the center of curvature of the meridian curve in the plane of the figure) and $R_2 = AN$ (in the perpendicular plane). Point N lies at the intersection of the normal to the surface at point A and the symmetry axis. R_2 is always positive, while R_1 is positive if points M and N are on the same side of A, and negative if M switches to the other side. As an example, at point A', $R_1' = A'M'$ is negative, and $R_2' = A'N'$ is positive.

If s is the curvilinear coordinate along the meridian curve oriented from left to right and θ is the angle between the normal to the drop's surface and the vertical direction, R_1 and R_2 are given by

$$z = R_2 \cos\theta \tag{1.11}$$

$$ds = -R_1 d\theta. \tag{1.12}$$

Equation (1.10) leads to

$$-\frac{d\theta}{ds} + \frac{\cos\theta}{z} = \frac{\Delta p}{\gamma}. \tag{1.13}$$

Along the meridian curve $z(x)$, we have $dz = ds \sin\theta$ and $dx = ds\cos\theta$. With the notation $\dot{z} = \frac{dz}{dx}$ and $\ddot{z} = \frac{d^2z}{dx^2}$, we get $ds = dx\sqrt{1+\dot{z}^2}$ (ds and dx always have the same sign), from which it follows that

$$\frac{d\theta}{ds} = \frac{d\theta}{dx}\cdot\frac{dx}{ds} = \frac{d\theta}{dx}\cdot\left(\frac{1}{\sqrt{1+\dot{z}^2}}\right)$$

and

$$\ddot{z} = \frac{d(\tan\theta)}{dx} = (1+\tan^2(\theta))\frac{d\theta}{dx}$$

or

$$\frac{d\theta}{dx} = \frac{\ddot{z}}{1+\dot{z}^2}.$$

When $\cos\theta = (1+\dot{z}^2)^{-1/2} > 0$, equation (1.13) can then be recast in the form

$$-\frac{\ddot{z}}{(1+\dot{z}^2)^{3/2}} + \frac{1}{z(1+\dot{z}^2)^{1/2}} = \frac{\Delta p}{\gamma}. \tag{1.14}$$

This equation can be integrated mathematically. Alternatively, the result can be worked from physical arguments, by expressing the fact that the sum of the forces (projected onto the x-axis) acting on a portion of the drop (shown as a shaded section in Figure 1.10) must add up to zero. The forces in question are

1. the capillary force integrated over the contour, equal to $f_1 = 2\pi z\gamma\cos\theta$,
2. the force of pressure $f_2 = -\Delta p\pi(z^2 - b^2)$,
3. the force exerted by the fiber on the drop, equal to $f_3 = -2\pi b\gamma$ (capillary force on the inner contour).

The condition $f_1 + f_2 + f_3 = 0$ leads to

$$\frac{z}{\sqrt{1+\dot{z}^2}} - \frac{\Delta p}{2\gamma}(z^2 - b^2) = b. \tag{1.15}$$

The maximum radius of the drop is obtained when $\dot{z} = 0$ and $z = L$. Equation (1.15) then gives

$$\frac{\Delta p}{2\gamma}(L^2 - b^2) = L - b. \tag{1.16}$$

For a large drop, the overpressure $\Delta p = \frac{2\gamma}{L+b}$ is roughly equal to the Laplace pressure for a drop of radius L since the correction term b then is negligible.

1.1.6 Minimal Surfaces With Zero Curvature

Henri Poincaré made some key contributions in this area.[8]

Meniscus on a Fiber

Consider an experiment in which one dips a fiber into a liquid bath. Our goal is to study the rise of the liquid while neglecting the influence of gravity (Figure 1.11). The liquid is assumed to wet the fiber.

There is a difference between the present situation and the previous experiment where a drop was deposited on a fiber. Here the liquid in the meniscus is in equilibrium with the liquid bath. As a result, we have $\Delta p = 0$, which defines a surface with zero curvature. The profile is given by equation (1.15), which reduces to

$$\frac{z}{\sqrt{1+\dot{z}^2}} = b. \tag{1.17}$$

This last equation could be obtained directly by noting that the vertical projection of the tension forces must be conserved. At a height x, the tension force is $2\pi z\gamma\cos\theta = 2\pi\gamma b$. Since $\tan\theta = \dot{z}$, equation (1.17) is readily

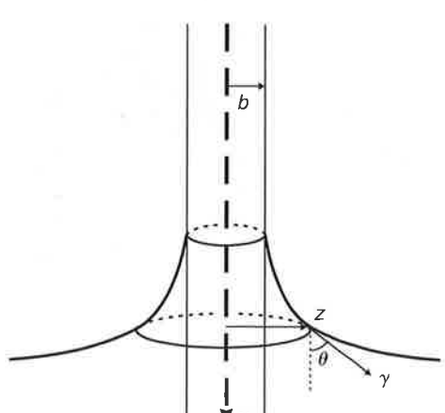


FIGURE 1.11. Water climbing up a glass fiber of radius $b \approx 10$ μm.

recovered. The profile of the drop is that of a hanging chain, known as a *catenary curve:*

$$z = b \cdot \cosh\left(\frac{x}{b}\right). \tag{1.18}$$

Soap Film

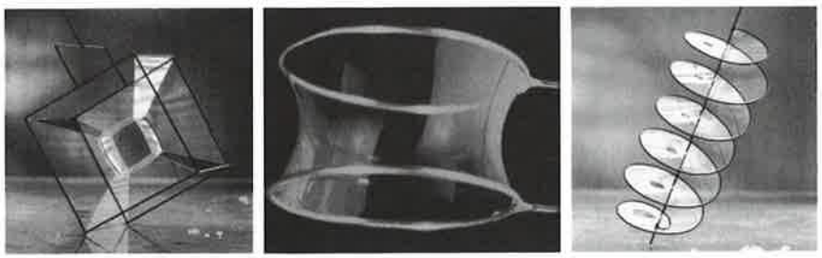
Let us reenact Plateau's experiment, which consists in stretching a soap film (glyceric liquid) between two circular rings of radius R. The rings can be fashioned out of heavy-duty copper wire hammered flat. One subsequently dips them into the soap mixture and then gently pulls them apart (Figure 1.12b). The distance between the two rings is $2D$. Since the pressure is the same inside and outside, the surface of the film has zero curvature ($R_1^{-1} + R_2^{-1} = 0$). As the rings are pulled ever farther apart, the surface area of the film between the rings stretches until the film bursts when $R/D \approx 1.5$. Plateau was the first to study the surface created between the two rings. The profile $r(x)$ is that of a surface of revolution with zero curvature, which satisfies equation (1.13) where Δp is set equal to 0. In accordance with equation (1.18), the profile of the liquid must adopt the shape of a catenary curve that connects smoothly with the rings, at which point $r(x = \pm D) = R$. If R_m is the radius of the circle at the waist (where $x = 0$), then the profile is

$$r(x) = R_m \cdot \cosh\left(\frac{x}{R_m}\right). \tag{1.19}$$

When $x = D$, we have

$$\frac{R}{R_m} = \cosh\left(\frac{D}{R_m}\right). \tag{1.20}$$

This equation has two solutions for R_m, corresponding to two surfaces, both with zero curvature. The surface area is minimum for the first and maximum for the second.



(a) (b) (c)

FIGURE 1.12. Soap films: cubic structure (a); catenary (b); spiral (c); (a) and (c): From *A Drop of Water: A Book of Science and Wonder*, by Walter Wick. Published by Scholastic Press, a division of Scholastic Inc. Photographs © 1997 by Walter Wick. (b): Palais de la Découverte. Reproduced by permission.

For a critical value of the ratio R/D ($R/D = 1.509$), the two solutions become identical. For $R/D \leq 1.509$, solutions no longer exist and the film bursts.

With more complex frames, one can generate a variety of minimal surfaces with zero curvature. Figure 1.12 shows a cubic structure, a hanging chain, and a spiral.

1.2 Contact Between Three Phases: Wetting

Wetting refers to the study of how a liquid deposited on a solid (or liquid) substrate spreads out. The phenomenon is pertinent to numerous industrial areas, a few of which are listed below:

- chemical industry (paints, ink, coloring ingredients, insecticides),
- automobile manufacturing (surface preparation prior to painting, treatment of glass to prevent water from dewetting, treatment of tires to promote adhesion even on wet or icy roadways),
- glass (anti-stain or anti-frost treatment),
- food (dissolving powders such as milk or cocoa),
- soil science (penetration of liquids into porous rocks),
- construction (waterproofing of concrete, protection of monuments, treatment of greenhouse plastic),
- domestics (spreading of creams, application of mascara to eyelashes, self-drying shampoos).

It also plays a role in the life sciences. A few notable examples follow:

- inflation of lungs at birth initiated by surfactant molecules that lower the surface energy of the lungs. In some premature babies, these molecules are missing and the lungs are not ready to function on their own. This respiratory stress syndrome, known as hyaline membrane disease, is alleviated by the swift delivery of suitable surfactants),
- rise of sap in plants,
- locomotion of insects on the surface of water,
- adhesion of parasites on wet surface (e.g., pyriculariosis of rice, or rice blast),
- wetting of the eye. The cornea is by nature very hydrophobic, yet a normal eye is wet! Proteins (called mucins), present in tears, turn the surface of the eye hydrophilic, stabilizing the lachrymal film. If one accidentally smears a fatty cream on the eye, it dries up, causing considerable discomfort. Some individuals happen to suffer from "dry eyes" and must apply artificial tears to compensate for their natural deficiency in mucins.

"Understanding" wetting enables us to explain why water spreads readily on clean glass but not on a plastic sheet. "Controlling" it means being able to modify a surface to turn a non-wettable solid into one that is wettable

(plastic covered with a layer of gold, cornea coated with mucin), or, vice versa. For instance, it is possible to turn glass just as non-wetting as Teflon by depositing a thin coating of fluorinated molecules on it.

In the following section, we begin by characterizing two types of wetting:

- total wetting, when the liquid has a strong affinity for the solid; and
- partial wetting, in the opposite case.

Next we will describe criteria useful for predicting whether or not a liquid will wet a particular substrate. We will show how a simple monolayer deposited on the substrate can reverse the behavior of the interface, i.e., change it from wetting to non-wetting and vice versa. We will pay particular attention to those liquids and solids that have been used to implement well-controlled systems and we will describe the most common surface treatments used in the physical chemistry of wetting. The modifications involved will be discussed in chapter 2.

1.2.1 *Two Types of Wetting: The Spreading Parameter S*

When a water drop is placed down on very clean glass, it spreads completely. By contrast, the same drop deposited on a sheet of plastic remains stuck in place. The conclusion is that there exist two regimes of wetting depicted in Figure 1.13. The parameter that distinguishes them is the so-called *spreading parameter* S, which measures the difference between the surface energy (per unit area) of the substrate when dry and wet:

$$S = [E_{substrate}]_{dry} - [E_{substrate}]_{wet} \tag{1.21}$$

or

$$S = \gamma_{SO} - (\gamma_{SL} + \gamma), \tag{1.22}$$

where the three coefficients γ are the surface tensions at the solid/air, solid/liquid, and liquid/air interfaces, respectively.

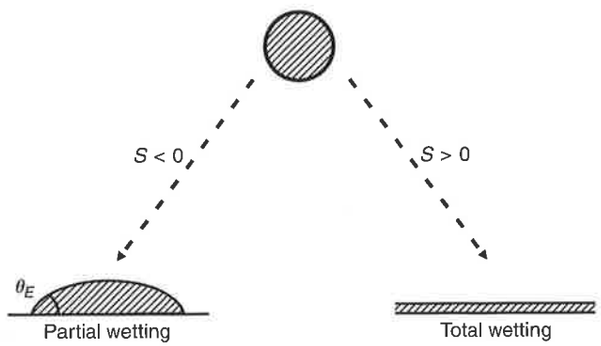


FIGURE 1.13. The two wetting regimes for sessile drops.

$S > 0$: Total Wetting

If the parameter S is positive, the liquid spreads completely in order to lower its surface energy ($\theta_E = 0$). The final outcome is a film of nanoscopic thickness resulting from competition between molecular and capillary force (see chapter 4).

$S < 0$: Partial Wetting

The drop does not spread but, instead, forms at equilibrium a spherical cap resting on the substrate with a contact angle θ_E. A liquid is said to be "mostly wetting" when $\theta_E \leq \pi/2$, and "mostly non-wetting" when $\theta_E > \pi/2$. Note, however, that $\theta_E = \pi/2$ plays no particularly significant role from a thermodynamical standpoint, in contrast to $\theta_E = 0$, which corresponds to a condition of wetting transition. We will see in chapter 2 that a "mostly wetting" liquid spontaneously invades a capillary, a porous medium, or a sponge.

Law of Young-Dupré

The contact angle can be obtained via one of two methods (Figure 1.14):

1. The first method consists in tallying up the capillary forces acting on the line of contact (also called triple line) and equating the sum to zero. When normalized to a unit length, these forces are the interface tensions between the three phases (S/L/G). By projecting the equilibrium forces onto the solid plane, one obtains Young's relation (which he derived in 1805):[9]

$$\gamma \cos\theta_E = \gamma_{SO} - \gamma_{SL} \tag{1.23}$$

Substituting (1.22) into (1.23) yields:

$$S = \gamma(\cos\theta_E - 1)$$

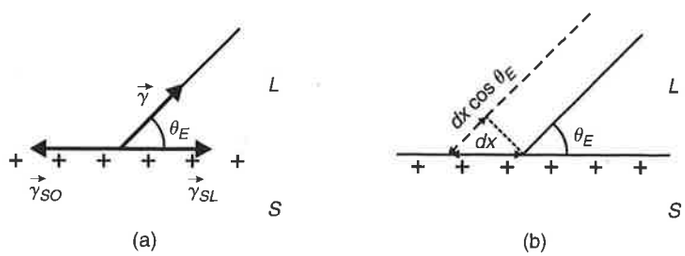


FIGURE 1.14. Determination of θ_E: (a) via forces or (b) via works.

It is evident that θ_E can be defined only if the spreading parameter is negative. θ_E increases when the liquid is non-wetting.

The projection of the capillary forces onto the vertical axis is balanced out by a force of reaction exerted by the solid. If the solid is hard, no distortion is observable. If, on the other hand, it is soft (e.g., rubber or a coat of paint), it does distort. That is the reason why a water drop left on a fresh coat of paint leaves behind a circular mark.

2. The second method relies on calculating the work done by moving the line of contact by a distance dx:

$$\delta W = (\gamma_{SO} - \gamma_{SL})\, dx - \gamma \cos\theta_E\, dx \tag{1.24}$$

This work is equal to zero at equilibrium, which indeed leads to equation (1.23).

Measuring Contact Angles

There are several methods for measuring θ_E, which will be discussed in chapter 2. For relatively large angles, it is possible to take a side-view photograph of the profile and use the snapshot to determine the angle. For better precision and for angles less than $\pi/4$, an optical reflection technique is often used. The drop is illuminated by a collimated laser beam which, upon reflection, becomes divergent. The divergence angle is related to the contact angle. For small angles and a higher precision still, an interference method is preferred; it relies on monitoring the constant-thickness fringes generated by a liquid wedge. Finally, a less accurate method, but one that is useful when studying the dynamics of wetting (when the dynamical contact angle θ_D is different from the static angle θ_E), consists in recording the distortion of the image of a grid seen through the liquid wedge.

1.2.2 *Wetting Criteria: Zisman's Rule*

Is it possible to predict whether a solid surface is wettable? Fortunately, the answer is yes.[10,11] Surfaces belong in one of two categories:

1. "High-energy" (HE) surfaces are those for which the chemical binding energy is of the order of 1 eV, on which nearly any liquid spreads. High-energy surfaces are made of materials that are ionic, covalent, or metallic. In this category, the interface tension is given by

$$\gamma_{SO} \approx \frac{E_{binding}}{a^2} \sim 500 - 5{,}000 \text{ mN/m}. \tag{1.25}$$

2. Low-energy (LE) surfaces, for which the chemical binding energy is of the order of kT, which are generally hardly wettable. They include molecular crystals and plastics. In this case, we have

$$\gamma_{SO} \approx \frac{kT}{a^2} \sim 10 - 50 \text{ mN/m}. \tag{1.26}$$

Actually, the surface energy γ_{SO} in contact with air is not altogether sufficient to predict wettability. What is in fact needed is the sign of the spreading parameter S given by

$$S = \gamma_{SO} - (\gamma_{SL} + \gamma). \tag{1.27}$$

We shall now restrict our attention to an idealized (but important) case—the interactions (liquid–liquid and liquid–solid) are purely of the van der Waals type. It is then possible to relate S to the **electric polarisabilites** (α_S, α_L) of S and L.[12,13]

The approach is schematically illustrated in Figure 1.15. To estimate γ_{SO}, one brings together two semi-infinite solid media. At first, the energy is $2\gamma_{SO}$. Upon merging them, one gains the van der Waals energy V_{SS} (per unit area). The latter energy is related to the polarizability α_S of the solid via the relation $V_{SS} = k \cdot \alpha_S^2$, where k is a constant. The surface energy of the resultant solid is zero. Hence,

$$2\gamma_{SO} - V_{SS} = 0. \tag{1.28}$$

To estimate γ_{SL}, one brings the solid and the liquid together. One starts with an energy $\gamma + \gamma_{SO}$, and one picks up the van der Waals interactions V_{SL} between the solid and the liquid (as before, we have $V_{SL} = k\alpha_S\alpha_L$). This leads to

$$\gamma_{SL} = \gamma + \gamma_{SO} - V_{SL}, \tag{1.29}$$

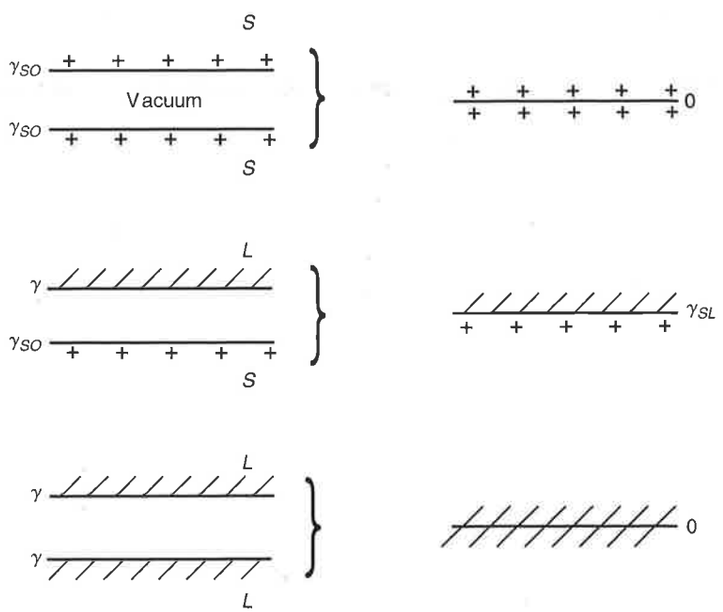


FIGURE 1.15. Determining the interface energies γ_{ij} by bonding i and j together.

To estimate γ, one brings two semi-infinite liquid media together. One starts with 2γ and then gains the van der Waals interaction V_{LL}, which yields

$$2\gamma - V_{LL} = 0. \tag{1.30}$$

Equations (1.28)–(1.30) can now be combined to produce an estimate of the spreading parameter S:

$$S = \gamma_{SO} - (\gamma_{SL} + \gamma) = V_{SL} - V_{LL} = k(\alpha_S - \alpha_L)\alpha_L. \tag{1.31}$$

It becomes clear that the wettability criterion is not γ_{SO}, since that quantity drops out. What does matter is the sign of S. If $\alpha_S > \alpha_L$, S is positive and wettability is total. Hence the rule

A liquid spreads completely if it is less polarizable than the solid.

This explains why liquid helium, with its extremely low polarizability, spreads on most solids.

All liquids spread on glass, metals, and ionic crystals. By contrast, wetting may be total or partial on plastics and molecular crystals, depending on which specific liquid is used. The empirical criterion worked out by Zisman allows us to classify solids. Each solid substrate has a critical surface tension γ_C such that

$\gamma > \gamma_C \Rightarrow$ partial wetting; $\gamma < \gamma_C \Rightarrow$ total wetting

where γ is the surface tension of the liquid.

The critical surface tension γ_C can be determined by studying the wetting properties of a series of chemical compounds (n-alkanes, with n variable) and plotting $\cos\theta_E$ as a function of γ, as shown in Figure 1.16.

For non-polar liquids, γ_C turns out to be independent of the liquid! Rather, it is a property of the solid. This can be understood in terms

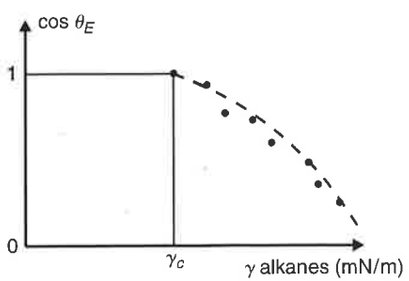


FIGURE 1.16. Determination of the critical tension γ_C of a sheet of plastic by means of a series of alkanes.

TABLE 1.2. Critical surface tension of a few solid polymers.

Solid	Nylon	PVC	PE	PVF_2	PVF_4
γ_C (mN/m)	46	39	31	28	18

of equation (1.31), which shows that $S(\gamma_C) = 0$ (by definition of γ_C) is satisfied when $\alpha_L = \alpha_S$, α_S being a characteristic of the solid. Indeed, we have $S(\gamma_C) = k(\alpha_S - \alpha_L)\alpha_S = 0$ when $\alpha_S = \alpha_L$. When $\gamma < \gamma_C$, we have $S > 0$ and wetting is total. When $\gamma > \gamma_C$, we have $S < 0$ and wetting is partial.

The method just described makes it possible to characterize not only the surface of non-wettable solids (see Table 1.2), but also the surfaces of HE solids made non-wettable by a suitable surface treatment. For example, glass covered with a fluorinated molecular coating can have a critical surface tension γ_C as low as 10 mN/m, rather than the 150 mN/m characteristic of clean glass

1.2.3 Choice of Solid/Liquid Pairs

We now discuss a few of the characteristics of selected liquids and solids that are often used in wetting experiments. The primary emphasis is on those materials that are suitable for well-controlled experiments ("ideal" liquids and solids).

1.2.3.1 Ideal Liquids

Careful experiments often rely on the following categories of fluids:

- *Pure and non-volatile liquids*, to avoid the Marangoni effects related to evaporation (see chapter 10): Hydrogenated and fluorinated silicone-based oils, long alkanes.
- *Liquids of the "van der Waals" type*, in which the analysis of long-range forces simplifies itself (see chapter 4),
- *Liquids with low surface tension*, which are relatively immune to self contamination;
- *Liquids with an adjustable viscosity coefficient* η (*usually polymer melts with different chain lengths*). They are useful for studying time-dependent phenomena. A characteristic velocity $V^* = \gamma/\eta$ controls the dynamics of wetting. That velocity can range from about 1 μm/s to 70 m/s (for water).

PDMS

Polydimethylsiloxanes (or PDMSs) are silicone oils that readily comply with the criteria listed above (Table 1.3). They are routinely used in numerous industrial applications such as lubricating agents and waterproofing

TABLE 1.3. Main characteristics of selected PDMSs at ambient temperature. η is the viscosity, ρ the density, κ^{-1} the capillary length, and $V^* = \gamma/\eta$ the characteristic liquid velocity.

Molecular Mass (g)	η (mPa-s)	ρ (kg/m^3)	γ (mN/m)	κ^{-1} (mm)	V* (mm/s)
3780	48	960	20.8	1.49	433
9430	193	968	21.0	1.49	109
28,000	971	971	21.2	1.49	22
62,700	11,780	974	21.5	1.5	1.8
204,000	293,100	977	21.5	1.5	0.07

compounds (paper, textiles, and anti-foam agents). Their general formula is $(CH_3)_3$–Si–O–$[(CH_3)_2SiO]_n$–$Si(CH_3)_3$.

PDMSs consist of a siloxane skeleton (Si–O group) linked to two methyl groups. These groups are responsible for the non-polar and hydrophobic characters of PDMSs and their great thermal stability, as well as their optical transparency. The number n of monomer units is called the degree of polymerization.

PDMSs have a number of noteworthy characteristics:

- The chains are highly flexible and the corresponding oils are fluid at ambient temperature. The glass transition temperature T_g is $-128°C$.[14]
- Even for relatively small values of the number n of monomers, the vapor pressure is quite low. These substances are therefore non-volatile liquids.
- Their surface tension γ is low and practically independent of the molecular weight (see Table 1.3). γ decreases with temperature, typically at a rate 0.1 mN/m per degree.
- The viscosity η depends very strongly on the molecular weight, increasing by a factor of 6,000 as the molecular weight goes from 3,780 g to 204,000 g. It decreases slowly with increasing temperature. The linear temperature coefficient is of the order of 10^{-2} K^{-1}, giving a dependence of the type $\eta(T) = \eta(T_0) \cdot [1 - 10^{-2}(T - T_0)]$.

Alkanes

Alkanes are made of a carbon chain terminated by a methyl group at either end. The basic formula of a linear alkane containing n carbon atoms is C_nH_{2n+2}.

The alkanes listed in Table 1.4 range from nonane ($n = 9$) to hexadecane ($n = 16$). They are liquids at 25°C and non-volatile (the saturation vapor pressure of nonane at 20°C is 5 mbar). These liquids are stable and non-polar. Therefore, they do not react with the surface of a substrate.

Alkanes have a low viscosity, of the order of 1 mPa-s (comparable to that of water). The viscosity increases with the length of the chain, as does the surface tension. Consequently, the contact angle between a drop

TABLE 1.4. Primary characteristics of a few alkanes (same notation as in Table 1.3).

Number n of carbon atoms	η (mPa-s)	γ (mN/m)	κ^{-1} (mm)	V^* (m/s)
9	0.71	22.9	1.8	32
10	0.92	23.9	1.8	26
12	1.35	25.4	1.9	19
16	3.34	27.6	1.9	8

of alkane and a given solid is an increasing function of the number n of carbon atoms (in a partial wetting regime) as observed in Figure 1.16. The characteristic velocity $V^* = \gamma/\eta$ is of the order of 1 m/s. Therefore, the observable dynamical processes are quite rapid.

1.2.3.2 Solid Substrates

Smooth Substrates or Substrates with a Controlled Roughness

To avoid hysteresis effects, it is advisable to use surfaces that are smooth on an atomic scale. Excellent candidates are

- silicon wafers of the type used in the microelectronics industry,
- floated glass, produced by flowing molten glass on liquid tin, which generates surfaces with a liquid-like smoothness (the technique is known as the Pilkington process),
- elastomers obtained by cross-linking a liquid film or a drop.

At the other extreme are fractal surfaces (exhibiting a roughness with scale-invariant self-similarity) that have recently been developed, in particular in Japan.[15] They can be either hydrophobic or hydrophilic. As we will describe in chapter 9, the surface roughness can control the degree of wettability (for a given surface chemistry) by enhancing the material's natural tendency. As the roughness increases, a hydrophilic substance becomes even more hydrophilic, while one that starts hydrophobic can become literally "super-hydrophobic" (see Figure 1.17).

Surface Treatments

Hydrophilic Surfaces Made Hydrophobic. We have seen that glass and silicon are high-energy solids that are wetted by all liquids (with the exception of mercury) because their critical surface tension γ_C is quite high (of the order of 150 mN/m). It is possible to lower γ_C by coating such solids with a hydrophobic molecular layer of the type –(CH_2)– or –(CF_2)–. This trick can create surfaces with extremely low energies, mimicking Teflon (a fluorinated polymer). The parameter γ_C drops down to values of the order of 20 mN/m for hydrogenated coatings and 10 mN/m for fluorinated ones. Practically no

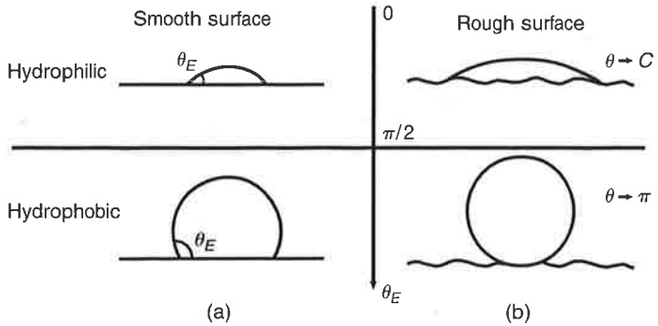


FIGURE 1.17. Controlling the wettability of a substrate through its roughness. Smooth surface (a); rough surface (b). Hydrophilic substrate becoming even more hydrophilic with a rough surface (top); hydrophobic substrate becoming "super-hydrophobic" (bottom).

liquid spreads on a fluorinated surface. On a hydrogenated surface, PDMS spreads totally if $\gamma_C > 21$ mN/m, and partially otherwise. Such surfaces turn out to be extremely interesting because they can be wetted totally by oils, while at the same time their low energy protects them against contamination effects and promotes stability over long periods of time. Two substances capable of altering the wetting properties of surfaces are octadecyltrichlorosilane (OTS), whose chemical formula is Cl_3–Si–$(CH_2)_{17}$–CF_3, and heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane, whose formula is Cl_3–Si–$(CH_2)_2$–$(CF_2)_7$–CF_3.

Hydrophobic Surfaces Made Hydrophilic. Greenhouses are often covered with transparent plastic sheets. Morning dew condensing into fine droplets on the plastic scatters the light and robs flowers and plants of much needed sunlight. It is desirable to find a way to force water to spread into a continuous film, in other words, to "wet" the material. There are "plasma" treatments that can create hydrophilic groups on the surface of the plastic, thereby lowering γ_C.

The human cornea is extremely hydrophobic. Our tears "treat" the surface of the cornea by depositing hydrophilic proteins that stabilize the lachrymal film. Another interesting example is that of mushroom spores that can play havoc in rice plantations. Their destructive effect can be traced to their ability to alter the surface of the rice plant—normally very hydrophobic—by turning it hydrophilic, enabling the spores to readily attach themselves to it.

Plastics and molecular crystals generally have a low γ_C and, therefore, are poorly wettable by water. One technique to increase their wettability is to coat them with gold. However, it would be a mistake to believe that gold-coated plastic behaves like bulk gold. The liquid does interact with gold, but that does not mean that interactions with the plastic substrate are entirely

masked. While a very thin liquid film "thinks" it sits on pure gold, a thick one will still "sense" the underlying substrate. This paradoxical situation leads to "pseudopartial" wetting, where the liquid covers the solid with an extremely thin film without truly spreading (the contact angle θ_E remains finite). This will be discussed in more detail in Section 4.2.3.

An Ideal Substrate: The Silicon Wafer

As stated earlier, silicon wafers of the type developed for the microelectronics industry are a popular choice of solid surface. In their natural state (that is to say, when stored in ordinary atmosphere), such wafers are coated with a thin layer of native oxide (SiO_2) about 14 Å thick. These surfaces bear a close resemblance to those of molten silica, particularly with regard to silanol groups (Si–OH). One of the primary advantages of these substrates is their planarity, flatness, and smoothness. X-ray studies reveal a residual roughness of no more than 5 Å. More detailed measurements suggest that the underlying silicon surface has a few atomic steps spaced by about a centimeter.

Cleaning. Before use, the surface must be carefully cleaned according to a process involving two steps.

The wafers are immersed for at least 30 minutes into an acid bath mixture of sulfuric acid and hydrogen peroxide (in the ratio of 70:30%) maintained at a temperature of 70°C. Next, they are rinsed in distilled water and dried in an oven at 100°C. At this point, they are exposed to UV radiation in an oxygen atmosphere. The ozone produced during this step breaks up any residual organic impurities that might remain on the surface.

A standard test for cleanliness consists in watching what happens to a water drop deposited on the surface of the silicon. Water wets "bare" silicon, whereas it does not spread in the presence of impurities. One can also exhale onto the surface and watch the result. If the surface is clean, water vapor coats the silicon in the form of a homogeneous film that evaporates uniformly; if not, a haze forms that disappears more slowly. This phenomenon has been studied in France; it is called "figure de souffle" (breath pattern).

Surface Treatments (Glass and Silicon).[16,17] Silicon surfaces belong in the high-energy (HE) category. Their critical tension γ_C for wetting exceeds 150 mN/m. As mentioned earlier, it is possible to modify this value by depositing a LE layer onto the solid. The parameter γ_C can be lowered to make the surface non-wetting relative to impurities and contaminants present in the ambient atmosphere or for the specific liquids chosen (i.e., PDMS's, alkanes, etc.).

Since γ_C depends essentially on the specific chemical groups on the surface, one can choose the type of coating to achieve a desired value of γ_C. A compact layer of methyl groups has a γ_C of 22 mN/m; a similarly compact

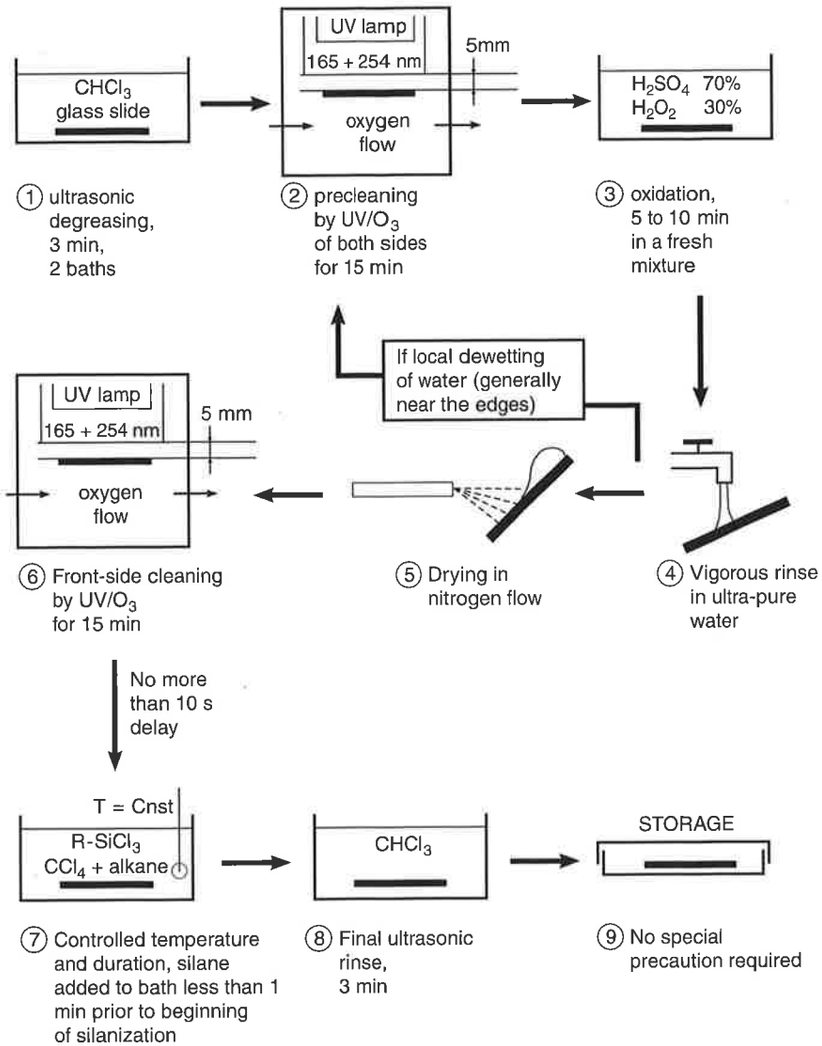


FIGURE 1.18. Flow diagram of the silanization process (courtesy J. B. Brzoska).

layer of fluorinated groups has a γ_C of only 6 mN/m. The reaction involved is known as *silanization*. A trichlorosilane group reacts chemically with the silanols on the surface, grafting one hydrophobic chain onto the substrate. The silanization process is illustrated in Figure 1.18.

One can obtain two different types of chemical surfaces.

1. *Silanized substrates* (OTS). This type itself splits into two subtypes depending on the compactness of the coating:

- "Fluffy" layer. When the coating is partial (meaning that the deposited layer does not form dense, continuous coating), γ_C comes out to be between 24 and 28 mN/m. In this case, wetting is total for silicone oils, although the surface is less sensitive to external conditions than the bare surface (which has a much higher γ_C).
- "Dense" layer. γ_C is equal to 21 ± 2 mN/m. The resultant substrates are then non-wetting as far as alkanes are concerned.

2. *"Teflon-like" surfaces.* Here γ_C is equal to 15 ± 2 mN/m. Neither silicone oils nor alkanes are then able to spread.

Glass

One routinely uses floated glass, which is somewhat less smooth than a silicon wafer and less pure as well because of the incorporation of inorganic substances during the floating process. Its advantage is to be much cheaper. Additionally, it is optically transparent. Its surface composition (silanols) is compatible with the various surface treatments described earlier, including cleaning and silanization.

Usual (Non-Ideal) Substrates

In practice, one deals with less smooth substrates displaying a wide variety of chemical properties: glass, plastics, ceramics, metals, and others. It is a challenge to make simple predictions concerning the interfacial energies of such materials. Nonetheless, a body of empirical knowledge is gradually building up, involving three main types of liquid/solid interactions:

- London–van der Waals forces, which have already been discussed;
- interactions between permanent dipoles;
- "acid/base"-type interactions.

These concepts have been developed by Good, Fowkes, Van Oss, and Chaudhury. The reader may want to consult a good text on the topic.[18] The effects of surface roughness will be discussed in detail in chapters 3 and 9.

1.2.4 Liquid Substrates: Neumann's Construction[19]

Consider a liquid A (oil) wetting a second liquid B (water). A and B are assumed to be immiscible. The surface of liquid B is no longer planar. Rather, it adjusts itself so as to minimize its surface energy. The contact angle is no longer given by Young's relation, derived earlier, but can be worked out by means of Neumann's construction (Figure 1.19). Both the horizontal and vertical components of the capillary forces must add up to zero. The construction is possible only if $S = \gamma_B - (\gamma_A + \gamma_{AB}) < 0$. If $S > 0$, liquid A wets liquid B and spreads totally on the free surface of B, as exemplified by PDMS on water.

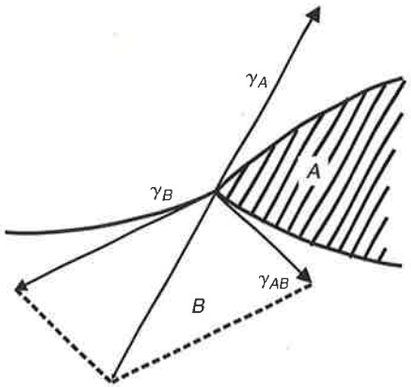


FIGURE 1.19. Neumann's construction.

The advantage of liquid substrates is that they are smooth on an atomic scale and chemically homogeneous. Furthermore, one can readily measure the three interfacial tensions γ_A, γ_B, and, γ_{AB}, a luxury not available with a solid substrate. The wettability can easily be adjusted by selecting liquids that are more or less polar.

The price to pay is that the substrate is not rigid and that it flows. When studying the dynamics of wetting, it becomes necessary to take into account the flows induced in the substrate as liquid A spreads or dewets (chapter 7).[20]

To avoid contamination effects, it is a good idea to select liquids with a low surface tension. A possible choice is the PDMS/fluoroalkylsiloxane pair (the latter is a fluorinated derivative of PDMS). These two liquids are immiscible. PDMS, which happens to be lighter, does not wet the fluorinated siloxane.

If the goal is to work with systems with very low viscosity, we recommend either water, which does not spread on CCl_4 or $CHCl_3$, or alkanes on water.

In chapter 2, we will describe a simple technique for determining the interfacial tension γ_{AB} by measuring the thickness of a floating lens.

Appendix: Minimal Surfaces – Euler-Lagrange Equations

Minimal surfaces can be calculated with the help of Laplace's formula [equation (1.6)]. Alternatively, one can minimize the surface, keeping the volume constant, by means of Euler-Lagrange's equations.

We proceed to demonstrate the method by rederiving the profile of a drop of initial radius R deposited on a fiber of radius b (see Figure 1.10).

The drop has a volume $\Omega = \frac{4}{3}\pi R^3$. We assume that the drop merges with the fiber with a contact angle equal to zero. At equilibrium, the surface energy of the drop is minimum, while the volume is constrained to a fixed value. Thus, we are faced with minimizing the function $G = \gamma A - \lambda\Omega$, where A is the surface area of the drop and the coefficient λ is a Lagrange multiplier, which has the dimension of a pressure. Indeed, we will show that λ is in fact the pressure difference between the inside of the drop and the outside medium.

The profile of the drop is described in terms of the distance $z(x)$ of its outer edge to the axis of the fiber. We have

$$G = 2\pi\gamma \int z\sqrt{1+\dot{z}^2}\,dx - \lambda\pi \int (z^2 - b^2)\,dx \tag{1.32}$$

where $\dot{z} = \frac{dz}{dx}$ and $2\pi z\sqrt{1+\dot{z}^2}\,dx$ is a differential element of surface, taking into account the axial symmetry of the drop. We minimize the energy by using Euler-Lagrange's equations. If $G = \int f(z,\dot{z})\,dx$, the extremum of G satisfies the condition

$$-\frac{d}{dx}\left[\frac{\partial f}{d\dot{z}}\right] + \frac{\partial f}{\partial z} = 0. \tag{1.33}$$

This can be integrated to

$$\dot{z}\frac{\partial f}{\partial \dot{z}} - f = cnst. \tag{1.34}$$

The first equation (1.33) corresponds to Newton's fundamental dynamics equation. It can be recast in the form

$$\gamma\left[\frac{-\ddot{z}}{(1+\dot{z}^2)^{3/2}} + \frac{1}{z(1+\dot{z}^2)^{1/2}}\right] = \lambda. \tag{1.35}$$

We have just rediscovered Laplace's formula $\gamma(\frac{1}{R} + \frac{1}{R'}) = \lambda$, which proves that $\lambda = \Delta p$.

The second equation (1.34) is equivalent to the principle of energy conservation. Its physical meaning here is the conservation of the force acting on a section of drop:

$$-\lambda\frac{z^2}{2} + \gamma\frac{z}{\sqrt{1+\dot{z}^2}} = C. \tag{1.36}$$

The constant C is determined from the boundary conditions, namely, $\dot{z} = 0$ at $z = b$, which yields

$$-\lambda\frac{z^2 - b^2}{2} + \gamma\left(\frac{z}{\sqrt{1+\dot{z}^2}} - b\right) = 0. \tag{1.37}$$

This last equation is identical with equation (1.15), which was written directly based on a force conservation argument.

The maximum radius L of the drop is obtained when $\dot{z} = 0$, which leads to $\frac{\lambda}{2} \cdot (L^2 - b^2) = \gamma \cdot (L - b)$. This last result simplifies to

$$L = \frac{2\gamma}{\lambda} - b. \tag{1.38}$$

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