Water Physics: Capillarity and Wetting

Vincent Démery

March 12, 2026

Figure 1: Water drops on a lotus leaf (Aathavan Jaffna / CC-BY-SA-3.0).

Contents

1 Introduction

Contrary to gases, liquids condensate and fill "all" the available volume in a small region of space. They do so because of an attractive component in the interparticle interactions. Because of this attractive component, liquid molecules feel better when they are surrounded by neighbours: they have a lower energy. As a consequence, the global energy is lower if more molecules are surrounded by neighbours, corresponding to a system with less interface area. The energy penalty associated with interfaces is the *surface tension*. In this lecture, we define surface tension and explore its consequences, which have major implications in soft matter, chemistry and biology, for instance.

A nice introduction to this topic, going beyond what is covered in these notes, can be found in Ref. [1].

2 Surface tension

2.1 Definition from interparticle forces

We introduce surface tension from a very schematic model. We assume that two liquid molecules in contact have gain an energy ϵ. Imagining that the molecules lie on a cubic lattice, each molecule has 6 neighbours; when placed at a flat interface a molecule loses one neighbour, which costs $\epsilon/2$. The number of molecules at the interface is $N_{\text{int}} = A/a^2$, where A is the total area of the interface and a^2 is the area occupied by one molecule. The total energy cost is thus:

$$E_{\text{int}} = \frac{A\epsilon}{2a^2} = \gamma A, \tag{1}$$

where γ is the *surface tension*, which is an energy per unit area. All that matters for the following is that interfaces have an energetic cost proportional to their area.

The schematic model above allows to evaluate the order of magnitude of the surface energy. Taking

$$\epsilon \simeq k_{\text{B}}T \simeq 3 \times 10^{21}\,\text{J}, \tag{2}$$

$$a \simeq 3 \times 10^{-10}\,\text{m}, \tag{3}$$

we arrive at

$$\gamma \simeq 0.02\,\text{J/m}^2. \tag{4}$$

This is the right order of magnitude. Because of the hydrogen bonds, which have an energy of $\epsilon \simeq 3 \times 10^{-20}\,\text{J}$, the water has a higher surface tension: $\gamma_{\text{water-air}} \simeq 72 \times 10^{-3}\,\text{J/m}^2$.

2.2 Laplace law

We consider a liquid droplet in air in the absence of gravity. In order to minimize the area of its interface, it adopts a spherical shape.

We have introduced surface tension as an energy per unit area, but this is equivalent to a force per unit length, that is, a force pulling on lines; this is the origin of the term "tension". With this in mind, we apply force balance to a half of the droplet; let's say that we cut it horizontally and focus on the upper half.

Denoting R the radius of the droplet, the surface tension on the "equator" exerts a force on the upper half, oriented towards the bottom, with a magnitude $F_{\text{tens}} = 2\pi R \times \gamma$. This force should be compensated by a larger pressure in the drop; we denote Δp the difference between the pressure in the drop and the outer pressure. The extra pressure exerts a force on the upper half, oriented towards the top, with a magnitude $F_{\text{pressure}} = \pi R^2 \times \Delta p$. Equating the two forces gives the extra pressure

$$\Delta p = \frac{2\gamma}{R}. \tag{5}$$

water	air	72
water	oil	50
metal	air	500 to 3000

Table 1: Some surface tensions, in mJ/m^2.

This is the *Laplace law*.

The Laplace law can be made local: the pressure drop accross an interface with surface tension γ and mean curvature H is given by

$$\Delta p = -2\gamma H; \tag{6}$$

for a sphere with radius R, $H = -1/R$. The minus sign comes from the fact that interface is curved towards the bottom.

An intuitive way to think about surface tension is to compare the droplet with a rubber balloon: the tension in the rubber equilibrates with the extra pressure in the balloon.

The Laplace law (5) can also be recovered by minimizing the grand potential $\Omega = \gamma A - pV$, with $A = 4\pi R^2$ and $V = 4\pi R^3/3$, with respect to the radius R.

2.3 Rayleigh-Plateau instability

We have assumed that a liquid wants to form droplets to reduce the energy of its interface. What about the thin "water tube" running from a tap? Does it want to form droplets too?

To answer this question we compare the energy of the straight liquid tube with the energy of a perturbed liquid tube. We consider a tube with radius R_0 and length L. Its volume is $V_0 = \pi L R_0^2$ and its interface area is $A_0 = 2\pi R_0 L$ (we neglect the area of the tube "ends").

We now consider a varying radius, $R(x) = a + b\cos(kx)$, where k is a wavenumber and a and b are constants. We assume a small perturbation, that is, $b \ll a$. First, we impose the conservation of the volume of liquid; the volume of the perturbed tube is

$$V_1 = \int_0^L \pi R(x)^2 \mathrm{d}x = \pi \int_0^L \left[a^2 + 2ab\cos(kx) + b^2\cos(kx)^2\right] = \pi L\left(a^2 + \frac{b^2}{2}\right). \tag{7}$$

Equating V_0 and V_1, we get $a^2 + b^2/2 = R_0^2$, from which we deduce

$$a = \sqrt{R_0^2 - \frac{b^2}{2}} \simeq R_0\left(1 - \frac{b^2}{4}\right). \tag{8}$$

The interface area of the perturbed tube is

$$\begin{aligned}
A_1 &= \int_0^L 2\pi R(x)\sqrt{1 + R'(x)^2}\mathrm{d}x && (9)\\
&= 2\pi\int_0^L \left[a + b\cos(kx)\right]\sqrt{1 + b^2k^2\sin(kx)^2}\mathrm{d}x && (10)\\
&\simeq 2\pi\int_0^L \left[a + b\cos(kx)\right]\left[1 + \frac{b^2k^2}{2}\sin(kx)^2\right]\mathrm{d}x && (11)\\
&= 2\pi a\int_0^L \left[1 + \frac{b^2k^2}{2}\sin(kx)^2\right]\mathrm{d}x && (12)\\
&= 2\pi a L\left(1 + \frac{b^2k^2}{4}\right). && (13)
\end{aligned}$$

Comparing with the area of the straight tube and using the volume conservation (8), we have

$$\begin{aligned}
\Delta A = A_1 - A_0 &= 2\pi L R_0\left[\left(1 - \frac{b^2}{4}\right)\left(1 + \frac{b^2k^2}{4}\right) - 1\right] && (14)\\
&\simeq \frac{\pi L R_0 b^2}{2}\left(k^2 - R_0^{-2}\right). && (15)
\end{aligned}$$

If $k < R_0^{-1}$, $\Delta A < 0$, meaning that the perturbed tube has less interface area than the straight one, so that the straight tube is unstable and forms droplets. Since k is free, the straight is thus always unstable against droplet formation, this is the *Rayleigh-Plateau instability*.

2.4 Emulsions, Ostwald ripening

In an emulsion such as a vinaigrette, small drops of one phase are dispersed in a different phase. In the vinaigrette, droplets of an aqueous solution are dispersed in oil. If a total volume V of water is

dispersed in oil in form of droplets of radius R, the volume of each droplet is $v = \frac{4}{3}\pi R^3$ and there are $N = V/v = 3V/(4\pi R^3)$ droplets. The total area of water-oil interfaces is $A = N \times 4\pi R^2 = 3V/R$: the smaller the droplets, the larger the interface. The total surface energy of the interface, $U = \gamma_{\text{w-o}} A$, should be injected into the system to form the emulsion: it is usually injected mechanically through mixing.

As the emulsion as a lot of interfacial energy, in particular much more than the state where the two phases are separated, it is unstable and eventually return to macroscopic phase separation after some time. An aging mechanism is the *Ostwald ripening*. The droplets are always polydisperse: there are smaller and bigger ones. Due to the Laplace law (5), the pressure in the smaller droplets is larger than the pressure in the larger droplets, which causes water to leak from the small droplets to the large one through oil. As a consequence, the smaller droplets disappear and the larger ones get bigger; the average droplet size increases and the energy of the emulsion decreases.

We can estimate the temporal evolution of the typical droplet radius, $R(t)$, due to Ostwald ripening, using scaling arguments. The current of water J between two drops of radius R_1 and $R_2 > R_1$ is proportional to $R^2 \Delta p/d$, where $\Delta p = \gamma(R_1^{-1} - R_2^{-1}) \approx \gamma/R_1$ and d is the distance between the droplets. If the droplets have a total volume V, there are $N \approx V/R^3$ droplets; when they are dispersed in a "box" of side length L, the typical distance between droplets is $d = L/N^{1/3} \approx LR/V^{1/3}$. Finally, the current J does not depend on R. The volume change of a droplet is proportional to J, so that

$$\frac{\mathrm{d}v}{\mathrm{d}t} \approx \frac{\mathrm{d}[R(t)^3]}{\mathrm{d}t} \approx J. \tag{16}$$

Integrating this equation, we find $R(t)^3 - R(0)^3 \sim t$, so that, at large times

$$R(t) \sim t^{1/3}. \tag{17}$$

3 Liquid on a substrate: wetting

3.1 Young-Dupré law

If a liquid droplet is not floating in air but in contact with a substrate, there are three different interfaces instead of just one: liquid-air, liquid-substrate and substrate-air. Each of these interfaces has a surface tension. We evaluate the forces exerted by these surface tensions on the contact line where the three phases meet. We denote θ the *contact angle*, the angle at which the liquid-air interface meets the substrate. Projecting the forces on the plane tangent to the substrate, we obtain

$$\gamma_{\text{s-a}} = \gamma_{\text{s-l}} + \gamma_{\text{l-a}} \cos(\theta_{\text{YD}}). \tag{18}$$

This is the *Young-Dupré law* and θ_{YD} is the Young-Dupré angle.

We start with the cases where the Young-Dupré equation has a solution for the contact angle, which corresponds to *partial wetting*. If $\gamma_{\text{s-a}} > \gamma_{\text{s-l}}$, the substrate "prefers" to be in contact with the liquid than with air; if the liquid is water, the substrate is said to be *hydrophilic*. In this case, the contact angle is acute, $0 \leq \theta \leq \pi/2$. On the contrary, if $\gamma_{\text{s-a}} < \gamma_{\text{s-l}}$, the substrate is said to be *hydrophobic* and the contact angle is obtuse, $\pi/2 \leq \theta \leq \pi$.

If there is no solution, there is *complete wetting* if $\gamma_{\text{s-a}} > \gamma_{\text{s-l}} + \gamma_{\text{l-a}}$ and *zero wetting* if $\gamma_{\text{s-a}} < \gamma_{\text{s-l}} - \gamma_{\text{l-a}}$.

Spherical particle at a liquid interface. The Young-Dupré law can also be used to obtain the position of a spherical solid particle at a water-air interface, for instance. The height z of the particle with respect to the flat interface is given by

$$z = -R\cos(\theta_{\text{YD}}). \tag{19}$$

We recover that if θ_{YD} is acute, $z < 0$, meaning that the particle prefers the liquid phase, while $z > 0$ if θ_{YD} is obtuse.

3.2 Substrate deformation

Projecting the surface tensions in the direction perpendicular to the substrate, it appears that the contribution of the liquid-air tension, $\gamma_{\text{l-a}} \sin(\theta)$, is unbalanced. This force is actually balanced by the elasticity of the substrate, meaning that surface tension can, in principle, deform the substrate. The amplitude of the deformation is obtained by comparing the surface tension $\gamma_{\text{l-a}}$ with the Young's modulus of the solid

E, which is an energy per unit volume. The ratio of these quantities, $\gamma_{\text{l-a}}/E$, is the *elasto-capillary length* ℓ_{ec}, which turns out to give the amplitude of the deformation. For typical solids, $E \simeq 1\,\text{MPa}$ to $1\,\text{GPa}$, so that with $\gamma_{\text{l-a}} \simeq 0.1\,\text{N m}^{-1}$, the elasto-capillary length is

$$\ell_{\text{ec}} = \frac{\gamma_{\text{l-a}}}{E} \simeq 0.1\,\text{nm to } 100\,\text{nm}. \tag{20}$$

The substrate deformation may be observable for very soft gels, $E \simeq 1\,\text{kPa}$.

3.3 Liquid substrate

We consider here the situation where a drop is deposited on a liquid interface, for instance a droplet of oil on an water-air interface. In this problem also there are three interfaces: water-air, water-oil and oil-air; we use water and oil for convenience, but this works for any liquid. The difference is that now the "water substrate" can deform freely. As a consequence, the oil-water and oil-air interfaces take the form of spherical caps.

At the contact line, the angles of the oil-air and oil-water interfaces with the flat water-air interface, $\phi_{\text{o-a}}$ and $\phi_{\text{o-w}}$, are given by the horizontal and vertical force balance:

$$\gamma_{\text{w-a}} = \gamma_{\text{o-a}} \cos(\phi_{\text{o-a}}) + \gamma_{\text{o-w}} \cos(\phi_{\text{o-w}}), \tag{21}$$

$$0 = \gamma_{\text{o-a}} \sin(\phi_{\text{o-a}}) + \gamma_{\text{o-w}} \sin(\phi_{\text{o-w}}). \tag{22}$$

We thus have a system of two equations with two unknowns, $\phi_{\text{o-a}}$ and $\phi_{\text{o-w}}$, which we can solve. The second equation can be squared to give $\gamma_{\text{o-a}}^2 \sin(\phi_{\text{o-a}})^2 = \gamma_{\text{o-w}}^2 \sin(\phi_{\text{o-w}})^2$, so that $\gamma_{\text{o-a}}^2[1 - \cos(\phi_{\text{o-a}})^2] = \gamma_{\text{o-w}}^2[1 - \cos(\phi_{\text{o-w}})^2]$. Introducing $x_i = \gamma_i \cos(\phi_i)$ for $i = \text{o-a}$ or $i = \text{o-w}$, the two equations can be written as

$$x_{\text{o-a}} + x_{\text{o-w}} = \gamma_{\text{w-a}}, \tag{23}$$

$$\gamma_{\text{o-a}}^2 - x_{\text{o-a}}^2 = \gamma_{\text{o-w}}^2 - x_{\text{o-w}}^2. \tag{24}$$

Using the first equation to write $x_{\text{o-w}} = \gamma_{\text{w-a}} - x_{\text{o-a}}$ and using it in the second equation, we finally get

$$x_{\text{o-a}} = \frac{\gamma_{\text{o-a}}^2 + \gamma_{\text{w-a}}^2 - \gamma_{\text{w-o}}^2}{2\gamma_{\text{w-a}}} = \gamma_{\text{o-a}} \cos(\phi_{\text{o-a}}). \tag{25}$$

3.4 Other contact laws

The contact laws below aim to take into account the effect of the roughness of the substrate (Wenzel) and the effect of a porous substrate, in which air pockets remain between the substrate and the liquid. In both cases, the substrate can be replaced by an effective substrate with effective substrate-air and substrate-liquid surface energies, $\gamma_{\text{s-a}}^{\text{eff}}$ and $\gamma_{\text{s-l}}^{\text{eff}}$.

Wenzel law. Rough substrates have a true area A_0 than their apparent area A. The ratio of these two areas is the roughness $r = A_0/A \geq 1$. The ideal case is recovered for $r = 1$. As a consequence, the energy of a substrate-liquid interface with apparent area is

$$U_{\text{s-l}} = \gamma_{\text{s-l}} A_0 = \gamma_{\text{s-l}} r A = \gamma_{\text{s-l}}^{\text{eff}} A, \tag{26}$$

with

$$\gamma_{\text{s-l}}^{\text{eff}} = r \gamma_{\text{s-l}}. \tag{27}$$

The same is true for the substrate-air interface, so that $\gamma_{\text{s-a}}^{\text{eff}} = r\gamma_{\text{s-a}}$. Using the effective surface energies in the Young-Dupré law (18), we find

$$\cos(\theta_{\text{W}}) = \frac{\gamma_{\text{s-a}}^{\text{eff}} - \gamma_{\text{s-l}}^{\text{eff}}}{\gamma_{\text{l-a}}} = r \frac{\gamma_{\text{s-a}} - \gamma_{\text{s-l}}}{\gamma_{\text{l-a}}} = r \cos(\theta_{\text{YD}}). \tag{28}$$

The effect of the roughness thus amplifies the hydrophilic or hydrophobic character of the substrate.

Cassie-Baxter law. Porous substrates are not perfectly wet and pockets of air remain trapped between the substrate and the liquid. Where these pockets are present, there are a substrate-air and a liquid-air interface instead of a substrate-liquid interface. We denote by $f \leq 1$ the fraction of the area that is actually wet. The energy of an apparently wet surface with area A is

$$U_{\text{s-l}} = fA\gamma_{\text{s-l}} + (1-f)A(\gamma_{\text{s-a}} + \gamma_{\text{l-a}}) = \gamma_{\text{s-l}}^{\text{eff}} A, \tag{29}$$

where

$$\gamma_{\text{s-l}}^{\text{eff}} = f\gamma_{\text{s-l}} + (1-f)(\gamma_{\text{s-a}} + \gamma_{\text{l-a}}). \tag{30}$$

The other interfaces are not affected.

Applying the Young-Dupré law (18) with this effective surface energy, we get

$$\gamma_{\text{s-a}} = f\gamma_{\text{s-l}} + (1-f)(\gamma_{\text{s-a}} + \gamma_{\text{l-a}}) + \gamma_{\text{l-a}}\cos(\theta_{\text{CB}}). \tag{31}$$

It can be simplified into

$$\gamma_{\text{l-a}}\cos(\theta_{\text{CB}}) = f(\gamma_{\text{s-a}} - \gamma_{\text{s-l}}) - (1-f)\gamma_{\text{l-a}}. \tag{32}$$

We recover the Young-Dupré case when $f = 1$. The derivative with respect to f gives

$$\frac{\mathrm{d}}{\mathrm{d}f}\left[\cos(\theta_{\text{CB}})\right] = \frac{\gamma_{\text{s-a}} - \gamma_{\text{s-l}} + \gamma_{\text{l-a}}}{\gamma_{\text{l-a}}} = 1 + \cos(\theta_{\text{YD}}) \geq 0. \tag{33}$$

The last equality and the inequality hold if the Young-Dupré angle is defined. In this case, $\cos(\theta_{\text{CB}})$ decreases as f decreases, so that θ_{CB} increases. When f approaches 0, θ_{CB} approaches π. The physical mechanism of this hydrophobic behavior is that the apparent substrate-liquid interface is very expensive as it involves substrate-air and liquid-air interfaces.

Adding roughness to this model, it is possible to unify the Cassie-Baxter and Wenzel models. These models may actually refer to the same system. Depending on the conditions (the pressure, or the wetting "history") the system can be in the *Wenzel state*, where the substrate cavities are wet, or in the *Cassie-Baxter state*, where the substrate cavities are dry.

The porous substrate giving rise to hydrophobic Cassie-Baxter states are often *patterned* substrates, which can be natural, as lotus leaves or gecko feet, or artificial.

In the following, we often denote the contact angle as θ_{YD}, but it may refer to the Young-Dupré contact angle with effective parameters.

3.5 Capillary adhesion

We consider two flat parallel solid surfaces separated by a distance h, hosting a *capillary bridge* of radius $R \gg h$. We want to know the force exerted by the capillar bridge on the top plate. The radius of curvature r_{c} of the capillary bridge is obtained from the geometric relation $r_{\text{c}}\cos(\theta) = h/2$, where θ is the contact angle, and the Laplace pressure in the liquid is

$$p = \gamma\left(\frac{1}{R} - \frac{1}{r_{\text{c}}}\right) \simeq -\frac{\gamma}{r_{\text{c}}} = -\frac{2\gamma\cos(\theta)}{h}, \tag{34}$$

where γ is the liquid-air surface tension. The force exerted by the pressure on the top plate is

$$F_{\text{p}} = \pi R^2 p = -\frac{2\pi R^2\gamma\cos(\theta)}{h}. \tag{35}$$

The capillary force is attractive if $\theta < \pi/2$. The force exerted by the contact line on the top plate is

$$F_{\text{c}} = 2\pi R\gamma\sin(\theta) \ll F_{\text{p}}. \tag{36}$$

The expression (35) for the capillary adhesion force can also be obtained from energetic arguments. The volume of the drop $V = Ah = \pi R^2 h$ is constant; as a consequence, by moving the surfaces appart, we reduce the area of the drop. The surface energy of the system is given by

$$U = 2A(\gamma_{\text{s-l}} - \gamma_{\text{s-a}}) = -\frac{2V}{h}\gamma\cos(\theta). \tag{37}$$

The force on the top plate is

$$F = -\frac{\mathrm{d}U}{\mathrm{d}h} = -\frac{2V}{h^2}\gamma\cos(\theta), \tag{38}$$

which is the previous result (35).

Capillary adhesion plays a key role, for instance, in the cohesion of sand castles. Assuming grains with a radius of 0.2 mm, with a volumic mass of $2 \times 10^3\,\mathrm{kg\,m^{-3}}$ and water brigdes of thickness $h \simeq 5\,\mu\mathrm{m}$, the capillary adhesion force is $|F_\mathrm{p}| \simeq 1\,\mathrm{mN}$. We have assumed $R \simeq 0.1\,\mathrm{mm}$ in the optimal scenario $\theta = 0$. For comparison, the weight of a grain is $F_\mathrm{grav} \simeq 1\,\mu\mathrm{N}$.

4 Liquids under gravity

4.1 Capillary length, meniscus, puddle

Capillary length. We saw that liquid droplets tend to adopt a spherical shape to minimize the area of their interface. This is true in the absence of gravity, and it is clear that the puddles of water are not spherical. Instead, the puddles of water, and all the water-air interfaces from the centimetric scale up to the sea scale tend to be flat because of gravity. To understand the transition from spherical to flat, we need to compare the constant driving capillarity, the liquid-air surface tension γ, to the constant driving gravity, ρg, where g is the gravitational acceleration and ρ is the density difference between the liquid and the air. The ratio of these two quantities is the square of a length, leading us to define the *capillary length*

$$\ell_\mathrm{c} = \sqrt{\frac{\gamma}{\rho g}}. \tag{39}$$

For water on Earth, the capillary length is $\ell_\mathrm{c} \simeq 2.7\,\mathrm{mm}$.

Gravity dominates for lengths above ℓ_c, and capillarity dominates for lengths below it. To describe more precisely the shape of a puddle of water or a meniscus, we need to combine the Laplace law (6) with the hydrostatic pressure $-\rho g h$, where h is the height. We assume that the height of the interface h depends only on its distance x from the contact line. We denote s the arc length from the contact line along the interface and ϕ the local angle between the horizontal and the interface.

Equation of a meniscus. We take the height to be zero where the interface is flat; there, the pressure drop across the interface is zero. The pressure drop across the interface at a height h is $\rho g h$, and the mean curvature of the interface is

$$H = \frac{1}{2}\frac{\mathrm{d}\phi}{\mathrm{d}s}. \tag{40}$$

The Laplace law (6) thus gives

$$\rho g h = \gamma \frac{\mathrm{d}\phi}{\mathrm{d}s}, \tag{41}$$

which could be rewritten with the capillary length

$$\frac{\mathrm{d}\phi}{\mathrm{d}s} = \frac{h}{\ell_\mathrm{c}^2}. \tag{42}$$

Using the relation between h and ϕ, $\mathrm{d}h/\mathrm{d}s = \sin(\phi)$, we can obtain a closed equation for $\phi(s)$:

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}s^2} = \ell_\mathrm{c}^{-2} \sin(\phi(s)). \tag{43}$$

This equation is non-linear and difficult to solve.

Small slope limit. We can make progress in the small slope limit where $\sin(\phi) \simeq \phi$, so that Eq. (43) reduces to

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}s^2} = \ell_\mathrm{c}^{-2}\phi(s), \tag{44}$$

which integrates into, keeping only the non-diverging part for $s \to \infty$,

$$\phi(s) = \phi(0)\exp(-s/\ell_\mathrm{c}). \tag{45}$$

Here we see that the capillary length sets the size of the region of the interface that is affected by the boundary. In the small slope limit, we can also obtain the height profile $h(x)$ through $\mathrm{d}s = \sqrt{1 + (\mathrm{d}h/\mathrm{d}x)^2}\mathrm{d}x \simeq \mathrm{d}x$ and $\mathrm{d}h/\mathrm{d}x \simeq \phi$. We obtain that $h(x) = h(0)\exp(-x/\ell_\mathrm{c})$.

Height of a meniscus, thickness of a puddle. If we are interested in the thickness of a puddle of water or the height of a meniscus, we can get it without approximation by multiplying both sides by $\mathrm{d}h/\mathrm{d}s = \sin(\phi)$:

$$\sin(\phi(s))\frac{\mathrm{d}\phi(s)}{\mathrm{d}s} = \frac{\mathrm{d}h(s)}{\mathrm{d}s}\frac{h}{\ell_\mathrm{c}^2}, \tag{46}$$

$$\frac{\mathrm{d}}{\mathrm{d}s}\left[-\cos(\phi(s))\right] = \frac{\mathrm{d}}{\mathrm{d}s}\left[\frac{h(s)^2}{2\ell_c^2}\right]. \tag{47}$$

From the last line, we identify a quantity that is constant along the interface:

$$\frac{h(s)^2}{2\ell_c^2} + \cos(\phi(s)) = A. \tag{48}$$

We now distinguish between the puddle, where the substrate is horizontal, and the meniscus against a vertical wall. In both cases, where the interface is flat, $h = 0$ and $\phi = 0$, so that $A = 1$. At the contact line of a puddle of thickness h_puddle, $h(0) = -h_0$ and $\phi(0) = \theta_\mathrm{YD}$, where θ_YD is the Young-Dupré contact angle, which is the solution of Eq. (18). We thus have

$$\frac{h_\mathrm{puddle}^2}{2\ell_\mathrm{c}^2} + \cos(\theta_\mathrm{YD}) = 1, \tag{49}$$

so that

$$h_\mathrm{puddle} = \ell_\mathrm{c}\sqrt{2\left[1-\cos(\theta_\mathrm{YD})\right]}. \tag{50}$$

For a meniscus against a flat wall, $\phi(0) = \theta_\mathrm{YD} - \pi/2$. Following the same steps, we find its height $h_\mathrm{meniscus} = h(0)$ to be

$$h_\mathrm{meniscus} = \ell_\mathrm{c}\sqrt{2\left[1-\sin(\theta_\mathrm{YD})\right]}. \tag{51}$$

Energetic approach. We can also obtain the thickness h of a puddle of volume V by comparing the interfacial and gravitational energies. Introducing the area of the puddle, $A = V/h$, the energies are

$$E_\mathrm{int} = A(\gamma_\mathrm{s\text{-}l} + \gamma_\mathrm{s\text{-}a} - \gamma_\mathrm{s\text{-}a}), \tag{52}$$

$$E_\mathrm{grav} = A\frac{\rho g h^2}{2}. \tag{53}$$

We now write the total energy as a function of the thickness h, with $\Delta\gamma = \gamma_\mathrm{s\text{-}l} + \gamma_\mathrm{s\text{-}a} - \gamma_\mathrm{s\text{-}a} = \gamma_\mathrm{l\text{-}a}[1 - \cos(\theta_\mathrm{YD})]$:

$$E_\mathrm{tot} = V\left(\frac{\rho g h}{2} + \frac{\Delta\gamma}{h}\right). \tag{54}$$

Differentiating with respect to h, we find that the energy is minimal for $h = \sqrt{2\Delta\gamma/(\rho g)}$, which is the same result as Eq. (50).

The energetic approach clarifies the fact that the shape of the interface close to the contact does not really matter.

4.2 Meniscus around a wire

In contact with a flat wall, a liquid forms a meniscus whose width and height given by the capillary length. We discuss the contrast with a meniscus formed in contact with a wire with diameter $d \ll \ell_\mathrm{c}$ with scaling arguments. We assume that the width of the meniscus is still given by the capillary length and evaluate its height h. The interface energy of this meniscus is $\sim dh(\gamma_\mathrm{s\text{-}l} - \gamma_\mathrm{s\text{-}a}) < 0$, while its gravitational energy is $\sim \rho g h^2 \ell_\mathrm{c}^2 = \gamma h^2$. Equating these two energies, we find $h \sim d$, which is much lower than the rise against a wall.

4.3 Capillary rise

We have seen that, due to gravity, liquids do not spread indefinitely on a substrate, and keep a finite thickness due to surface tension, which is proportional to the capillary length. However, dipping a sugar cube in a cup of tea, one can see the tea rising much above the capillary length. To model this phenomenon, we replace the sugar cube, a porous medium, by a vertical tube with diameter $d \ll \ell_\mathrm{c}$, and

compute the level of the rise h. As for the puddle thickness, there are two ways to do this calculation: either by using the Laplace law and determining the geometry of the meniscus in the tube, or minimizing the sum of the gravitational and surface energies. Both methods give the same result, we thus choose the energy minimization, which is simpler.

The interface and gravitational energies are

$$E_{\text{int}} = \pi d h(\gamma_{\text{s-l}} - \gamma_{\text{s-a}}) = \pi d h \Delta\gamma, \tag{55}$$

$$E_{\text{grav}} = \rho g \times \frac{\pi d^2}{4} \times \frac{h^2}{2}. \tag{56}$$

We have introduced $\Delta\gamma = \gamma_{\text{s-l}} - \gamma_{\text{s-a}} = -\gamma_{\text{l-a}} \cos(\theta_{\text{YD}})$. Because we have assumed that $d \ll \ell_{\text{c}}$, we neglect the variation of height in the meniscus. Differentiating the total energy with respect to the height h, we get

$$\frac{\partial E_{\text{tot}}}{\partial h} = \pi d \left(\Delta\gamma + \frac{\rho g d h}{4} \right). \tag{57}$$

We thus obtain the height of the rise

$$h_{\text{rise}} = -\frac{4\Delta\gamma}{\rho g d} = \frac{4\ell_{\text{c}}^2 \cos(\theta_{\text{YD}})}{d}. \tag{58}$$

This is the *Jurin law*, discovered experimentally in 1718 and explained by Laplace in 1806.

Complete wetting. The case of complete wetting, $\gamma_{\text{s-l}} - \gamma_{\text{s-a}} > \gamma_{\text{l-a}}$ should be treated carefully. From the energetic argument above, it could be expected that the capillary rise could be

$$h_{\text{rise}} = \frac{4(\gamma_{\text{s-a}} - \gamma_{\text{s-l}})}{\rho g d} > \frac{4\gamma_{\text{l-a}}}{\rho g d}. \tag{59}$$

However, the maximal curvature of the meniscus is $2/d$, which sets the minimal pressure in the liquid to $p_{\text{min}} = -4\gamma/d$. The capillary rise obtained by matching this pressure with the one obtained from hydrostatics, $p_{\text{hydro}} = -\rho g h_{\text{rise}}$, is

$$h_{\text{rise}} = \frac{4\gamma_{\text{l-a}}}{\rho g d}. \tag{60}$$

This is the capillary rise at complete wetting. In this situation, a thin liquid film forms that covers the substrate above h_{rise}.

5 Mixtures and interfaces

5.1 Solutes at interfaces

Up to this point, we have only considered pure liquids. When solute molecules are present in a solvent, they may preferentially go at the interface with another medium, for instance air. We are interested in the relation between the bulk concentration of the solute c, its surface concentration c_{s}, and the effect on the surface tension of mixture γ.

Relation between bulk and surface concentrations. We first address the relation between the bulk and surface concentrations. If each solute molecule has a substantial energy gain at the interface, the surface concentration can be large while the bulk concentration remains small. The simplest model taking that into account is the *Langmuir adsorption model*. Considering the adsorption of a solute molecule as a "reaction" of a bulk solute molecule with a free space at the interface, equilibrium of adsorption and desorption events reads

$$k_{\text{a}}(1 - a c_{\text{s}})c = k_{\text{d}} c_{\text{s}}, \tag{61}$$

where a is the area of a molecule and k_{a} and k_{d} are the adsorption and desorption rates. Solving for the surface concentration, we obtain

$$c_{\text{s}} = \frac{k_{\text{a}} c}{k_{\text{d}} + a k_{\text{a}} c} = c_{\text{s}}^{\max} \frac{Kc}{1 + Kc}, \tag{62}$$

where we have defined the constant K, which may depend on temperature, and $c_{\mathrm{s}}^{\max} = 1/a$ is the maximal surface concentration. This model assumes that the only interactions of solvent molecules at the interface are steric.

The Langmuir relation (62) can also be expressed in terms of chemical potentials. Assuming that the solute behaves as a perfect gas in the bulk, its chemical potential in the bulk takes the form

$$\mu = \mu_0 + k_{\mathrm{B}}T \ln(vc), \tag{63}$$

where v is the volume of a solute molecule. At equilibrium, the bulk chemical potential should be equal to the surface chemical potential μ_{s}. Inverting the Langmuir relation (62), we find $c = c_{\mathrm{s}}/[K(c_{\mathrm{s}}^{\max} - c_{\mathrm{s}})]$, so that

$$\mu_{\mathrm{s}} = \mu_0 + k_{\mathrm{B}}T \ln(vc) = \mu_0 + k_{\mathrm{B}}T \ln\left(\frac{vc_{\mathrm{s}}}{K(c_{\mathrm{s}}^{\max} - c_{\mathrm{s}})}\right) = \mu_{\mathrm{s}0} + k_{\mathrm{B}}T \ln\left(\frac{c_{\mathrm{s}}}{c_{\mathrm{s}}^{\max} - c_{\mathrm{s}}}\right). \tag{64}$$

This provides an expression of the surface chemical potential as a function of the surface concentration that is compatible with the Langmuir adsorption law.

Effect on the surface tension. To investigate the effect of the solution on the surface tension, we use the Gibbs-Duhem relation at interfaces:

$$\mathrm{d}\gamma = -c_{\mathrm{s}}\mathrm{d}\mu_{\mathrm{s}}, \tag{65}$$

where we have assumed a constant temperature. This relation is general. With the Langmuir model, we have

$$\mathrm{d}\gamma = -k_{\mathrm{B}}Tc_{\mathrm{s}}^{\max}\frac{\mathrm{d}c_{\mathrm{s}}}{c_{\mathrm{s}}^{\max} - c_{\mathrm{s}}} = k_{\mathrm{B}}Tc_{\mathrm{s}}^{\max}\mathrm{d}\left[\ln\left(1 - \frac{c_{\mathrm{s}}}{c_{\mathrm{s}}^{\max}}\right)\right], \tag{66}$$

leading after integration to

$$\gamma - \gamma_0 = k_{\mathrm{B}}Tc_{\mathrm{s}}^{\max}\log\left(1 - \frac{c_{\mathrm{s}}}{c_{\mathrm{s}}^{\max}}\right) \leq 0. \tag{67}$$

With the relation (62), we can also express the surface tension as a function of the bulk concentration:

$$\gamma - \gamma_0 = -k_{\mathrm{B}}Tc_{\mathrm{s}}^{\max}\log(1 + Kc). \tag{68}$$

The surface tension is thus reduced with respect to the pure interface. This consequence just relies on the fact that the chemical potential increases with the concentration.

5.2 Surfactants

Very useful solutes are *surfactants*, *amphiphilic molecules*, which have an hydrophilic head and a lipophilic, or hydrophobic, tail. In solution, they can form spheres with their hydrophilic heads facing water and their hydrophobic tails "hidden" inside the sphere; these spheres are called *micelles*.

Critical micellar concentration. The number p of molecules in a micelle can be computed from geometrical arguments and has a typical value of $p \approx 100$. To determine when micelles form, we can write the chemical potential of a molecule in a micelle:

$$\mu_{\mathrm{m}} = \mu_{\mathrm{m}0} + \frac{k_{\mathrm{B}}T}{p}\ln\left(\frac{vc}{p}\right). \tag{69}$$

This chemical potential grows slower with the concentration than the chemical potential of lonely molecules (63); they cross at a critical concentration c^*. As a consequence, the molecules remain lonely for $c < c^*$ and they start to form micelles when $c > c^*$; for $c > c^*$, the concentration of lonely molecules remain close to c^*, and the exceeding molecules go into the micelles. The equation for the *critical micellar concentration* c^* is thus

$$\mu_0 + k_{\mathrm{B}}T \ln(vc^*) = \mu_{\mathrm{m}0} + \frac{k_{\mathrm{B}}T}{p}\ln\left(\frac{vc^*}{p}\right). \tag{70}$$

Since $p \gg 1$, we can neglect the second term on the right hand side and get the critical concentration

$$c^* = v^{-1}\exp\left(\frac{\mu_{\mathrm{m}0} - \mu_0}{k_{\mathrm{B}}T}\right). \tag{71}$$

Effect on the surface concentration. A consequence of the formation of micelles is that the concentration of free molecules is bounded by c^*. Thus, the surface concentration c_s does not increase anymore when c reaches c_s because, most of the time, the micellar chemical potential is lower than the surface chemical potential.

References

[1] Pierre-Gilles De Gennes, Françoise Brochard-Wyart, and David Quéré. *Capillarity and Wetting Phenomena*. Springer New York, New York, NY, 2004.