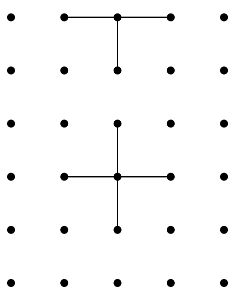
8
Surface tension

At the interface between two materials physical properties change rapidly over distances comparable to the molecular separation scale. The transition layer is, from a macroscopic point of view, an infinitely thin sheet coinciding with the interface. Although the transition layer in the continuum limit thus appears to be a mathematical surface, it may nevertheless possess macroscopic physical properties, such as energy. And where energy is found, forces are not far away. Surface energy is necessarily accompanied by surface forces, because work has to performed if the area of an interface and thus its surface energy is increased. The surface energy per unit of area or equivalently the force per unit of length is called *surface tension*.

Surface tension depends on the physical properties of both of the interfacing materials, which is quite different from other material constants, for example the bulk modulus, that normally depend only on the physical properties of just one material. Surface tension creates a finite jump in pressure across the interface, but the typical magnitude of surface tension limits its influence to fluid bodies much smaller than the huge planets and stars discussed in the preceding chapters. When surface tension does come into play, as it does for a drop of water hanging at the tip of an icicle, the shape of a fluid body bears little relation to the gravitational equipotential surfaces that dominate the large scale systems. The characteristic length scale where surface tension matches standard gravity in strength, the *capillary length*, is merely three millimeters for the water-air interface. This is the length scale of champagne bubbles, droplets of rain, insects walking on water, and many other phenomena.

In this chapter surface tension is introduced together with the accompanying concept of *contact angle*, and applied to the capillary effect, and to bubbles and droplets. In chapter 22 we shall study its influence on surface waves.

8.1 Definition of surface tension



Two-dimensional cross section of a primitive three-dimensional model of a material interfacing to vacuum. A molecule at the surface has only five bonds compared to the six that tie a molecule in the interior.

The apparent paradox that a mathematical surface with no volume can possess energy may be resolved by considering a primitive three-dimensional model of a material in which the molecules are placed in a cubic grid with grid length L_{mol}. Each molecule in the interior has six bonds to its neighbors with a total binding energy of $-\epsilon$, but a surface molecule will only have five bonds when the material is interfacing to vacuum. The (negative) binding energy of the missing bond is equivalent to an extra positive energy $\epsilon/6$ for a surface molecule relative to an interior molecule, and thus an extra surface energy density,

$$\alpha \approx \frac{1}{6}\frac{\epsilon}{L_{\mathsf{mol}}^2} \ . \tag{8-1}$$

The binding energy may be estimated from the specific enthalpy of evaporation H of the material as $\epsilon \approx H M_{\mathsf{mol}}/N_A$. Notice that the unit for surface tension is $\mathsf{J/m^2} = \mathsf{kg/s^2}$.

Example 8.1.1: For water the specific evaporation enthalpy is $H \approx 2.2\times 10^6$ J/kg, leading to the estimate $\alpha \approx 0.12$ J/m^2. The measured value of the surface energy for water/air interface is in fact $\alpha \approx 0.073$ J/m^2 at room temperature. Less than a factor of 2 wrong is not a bad estimate at all!

	α[mN/m]
Water	*72*
Methanol	*22*
Ethanol	*22*
Bromine	*41*
Mercury	*485*

Surface tension of some liquids against air at 1 atm *and* 25°C *in units of millinewton per meter (from [3]).*

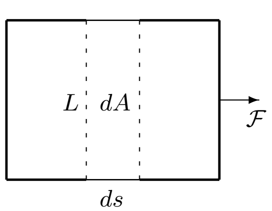
Surface energy and surface tension

Increasing the area of the interface by a tiny amount dA, takes an amount of work equal to the surface energy contained in the extra piece of surface,

$$\boxed{dW = \alpha\, dA \ .} \tag{8-2}$$

This is quite analogous to the mechanical work $dW = -p\, dV$ performed against pressure when the volume of the system is expanded by dV. But where a volume expansion under positive pressure takes negative work, increasing the surface area takes positive work. This resistance against extension of the surface shows that the interface has a permanent internal tension, called *surface tension*[1] which we shall now see equals the energy density α.

Formally, surface tension is defined as the force per unit of length that acts orthogonally to an imaginary line drawn on the interface. Suppose we wish to stretch the interface along a straight line of length L by a uniform amount ds. Since the area is increased by $dA = Lds$, it takes the work $dW = \alpha L ds$, implying that the force acting orthogonally to the line is $\mathcal{F} = \alpha L$, or $\mathcal{F}/L = \alpha$. Surface tension is thus identical to the surface energy density. This is also reflected in the equality of the natural units for the two quantities, N/m = J/m^2.



An external force $\mathcal{F}$ performs the work $dW = \mathcal{F}\,ds$ to stretch the surface by ds. Since the area increase is $dA = Lds$, the force is $\mathcal{F} = \alpha\, L$. The force per unit of length, $\alpha = \mathcal{F}/L$, is the surface tension.

[1] There is no universally agreed-upon symbol for surface tension which is variously denoted α, γ, σ, S, Υ and even T. We shall use α, even if it collides with other uses, for example the thermal expansion coefficient.

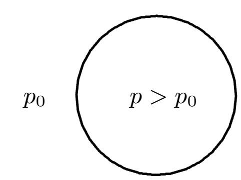
Since the interface has no macroscopic thickness, it may be viewed as being locally flat everywhere, implying that the energy density cannot depend on the macroscopic curvature, but only on the microscopic properties of the interface. If the interfacing fluids are homogeneous and isotropic — as they normally are — the value of the surface energy density will be the same everywhere on the surface, although it may vary with the local temperature. Surface tension depends as mentioned on the physical properties of both of the interfacing materials, which is quite different from other material constants that normally depend only on the physical properties of just one material.

Fluid interfaces in equilibrium are usually quite smooth, implying that α must always be positive. For if α were negative, the system could produce an infinite amount of work by increasing the interface area without limit. The interface would fold up like crumbled paper and mix the two fluids thoroughly, instead of separating them. Formally, one may in fact view the rapid dissolution of ethanol in water as due to negative interfacial surface tension between the two liquids. The general positivity of α guarantees that fluid interfaces seek towards the minimal area consistent with the other forces that may be at play, for example pressure forces and gravity. Small raindrops and champagne bubbles are for this reason nearly spherical. Larger raindrops are also shaped by viscous friction, internal flow, and gravity, giving them a much more complicated shape.

Pressure excess in a sphere

Consider a spherical ball of liquid of radius a, for example hovering weightlessly in a spacecraft. Surface tension will attempt to contract the ball but is stopped by the build-up of an extra pressure Δp inside the liquid. If we increase the radius by an amount da we must perform the work $dW_1 = \alpha\, dA = \alpha d(4\pi a^2) = \alpha 8\pi a\, da$ against surface tension. This work is compensated by the thermodynamic work against the pressure excess $dW_2 = -\Delta p\, dV = -\Delta p\, 4\pi a^2\, da$. In equilibrium there should be nothing to gain, $dW_1 + dW_2 = 0$, leading to,

$$\Delta p = \frac{2\alpha}{a} \; . \tag{8-3}$$



Surface tension increases the pressure inside a spherical droplet or bubble.

The pressure excess is inversely proportional to the radius of the sphere.

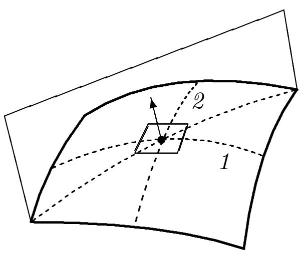
It should be emphasized that the pressure excess is equally valid for a spherical raindrop in air and a spherical air bubble in water. A spherical soap bubble of radius a has two spherical surfaces, one from air to soapy water and one from soapy water to air. Each gives rise to a pressure excess of $2\alpha/a$, such that the total pressure inside a soap bubble is $4\alpha/a$ larger than outside.

> **Example 8.1.2:** A spherical raindrop of diameter 1 mm has an excess pressure of only about 300 Pa, which is tiny compared to atmospheric pressure (10^5 Pa). A spherical air bubble the size of a small bacterium with diameter 1 μm acquires a pressure excess due to surface tension a thousand times larger, about 3 atm.

When can we disregard the influence of gravity on the shape of a raindrop? For a spherical air bubble or raindrop of radius a, the condition must be that the change in hydrostatic pressure across the drop should be negligible compared to the pressure excess due to surface tension, *i.e.* $\rho_0 g_0 2a \ll 2\alpha/a$, where ρ_0 is the density of water (minus the negligible density of air). Consequently, we must require

$$a \ll R_c = \sqrt{\frac{\alpha}{\rho_0 g_0}}\ , \tag{8-4}$$

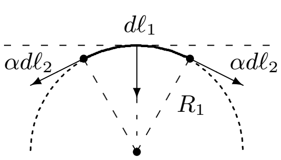
where the critical radius R_c is called the *capillary constant* or *capillary radius.* It equals 2.7 mm for water and 1.9 mm for mercury.



A plane containing the normal in a point intersects the surface in a planar curve with a signed radius of curvature in the point. The extreme values of the signed radii of curvature define the principal directions. The small rectangle has sides parallel with the principal directions.

Pressure discontinuity due to surface tension

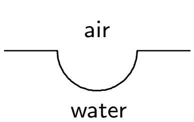
A smooth surface may in a given point be intersected with an infinity of planes containing the normal to the surface. In each normal plane the intersection is a smooth planar curve which at the given point may be approximated by a circle centered on the normal. The center of this circle is called the *center of curvature* and its radius the *radius of curvature* of the intersection. Usually the radius of curvature is given a sign depending on which side of the surface the center of curvature is situated. As the intersection plane is rotated, the center of curvature moves up and down the normal between extreme values R_1 and R_2 of the signed radius of curvature, called the *principal radii of curvature.* It may be shown (problem 8.2) that the corresponding principal intersection planes are orthogonal, and that the radius of curvature along any other normal intersection may be calculated from the principal radii.



The rectangular piece of the surface of size $d\ell_1 \times d\ell_2$ is exposed to two tension forces along the 1-direction resulting in a normal force pointing towards the center of the circle of curvature. The tension forces in the 2-direction also contribute to the normal force.

Consider now a small rectangle $d\ell_1 \times d\ell_2$ with its sides aligned with the principal directions, and let us to begin with assume that R_1 and R_2 are positive. In the 1-direction surface tension acts with two nearly opposite forces of magnitude $\alpha d\ell_2$, but because of the curvature of the surface there will be a resultant force in the direction of the center of the principal circle of curvature. Each of the tension forces forms an angle $d\ell_1/2R_1$ with the tangent, and projecting both on the normal we obtain the total inwards force $2\alpha d\ell_2 \times d\ell_1/2R_1$. Since the force is proportional to the area $d\ell_1 d\ell_2$ of the rectangle, it represents an excess in pressure $\Delta p = \alpha/R_1$ on the side of the surface containing the center of curvature. Finally, adding the contribution from the 2-direction we obtain the *Young-Laplace* law for the pressure discontinuity due to surface tension,

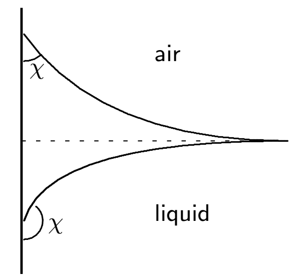
$$\boxed{\Delta p = \alpha \left(\frac{1}{R_1} + \frac{1}{R_2} \right)\ .} \tag{8-5}$$



Sketch of the meniscus formed by evaporation of water from the surface of a plant leaf, resulting in a high negative pressure in the water, capable of lifting the sap to great heights.

For the sphere we have $R_1 = R_2 = a$ and recover the preceding result (8-3). The Young-Laplace law may be extended to signed radii of curvature, provided it is remembered that *a contribution to the pressure discontinuity is always positive on the side of the surface containing the center of curvature, otherwise negative.*

Example 8.1.3 (How sap rises in plants): Plants evaporate water through tiny pores on the surface of the leaves. This creates a hollow air-to-water surface in the shape of a half-sphere of the same diameter as the pore. Both radii of curvature are negative $R_1 = R_2 = -a$ because the center of curvature lies outside the water, leading to a negative pressure excess in the water. For a pore of diameter $2a \approx 1\ \mu\mathsf{m}$ the excess pressure inside the water will be about $\Delta p \approx -3\ \mathsf{atm}$, capable of lifting sap through a height of 30 m. In practice, the lifting height is considerably smaller because of resistance in the xylem conduits of the plant through which the sap moves. Taller plants and trees need correspondingly smaller pore sizes to generate sufficient negative pressures, even down to -100 atm! Recent research has confirmed this astonishing picture (see M. T. Tyree, Nature **423**, 923 (2003)).



An air/liquid interface meeting a wall. The upper curve makes an acute contact angle, like water, whereas the lower curve makes an obtuse contact angle, like mercury.

8.2 Contact angle

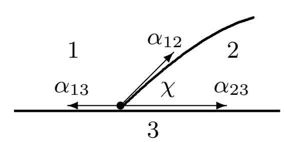
An interface between two fluids is a two-dimensional surface which makes contact with a solid wall along a one-dimensional line. Locally the plane of the fluid interface forms a certain *contact angle* χ with the wall. For the typical case of a liquid/air interface, χ is normally defined as the angle inside the liquid. Water and air against glass meet in a small acute contact angle, $\chi \approx 0$, whereas mercury and air meets glass at an obtuse contact angle of $\chi \approx 140°$. Due to its small contact angle, water is very efficient in *wetting* many surfaces, whereas mercury has a tendency to make pearls. It should be emphasized that the contact angle is extremely sensitive to surface properties, fluid composition, and additives.

In the household we regularly use surfactants that are capable of making dishwater wet greasy surfaces where it otherwise would tend to pearl. After washing our cars we apply a wax which makes rainwater pearl and prevents it from wetting the surface, thereby diminishing rust and corrosion.

The contact angle is a material constant which depends on the properties of all three materials coming together. Whereas material adhesion can sustain a tension normal to the wall, the tangential tension has to vanish. This yields an equilibrium relation between the three surface tensions,

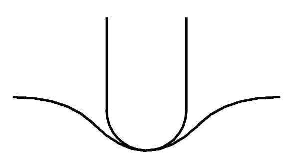
$$\alpha_{13} = \alpha_{23} + \alpha_{12} \cos \chi \ , \tag{8-6}$$

This relation is, however, not particularly useful because of the sensitivity of χ to surface properties, and it is better to view χ as an independent material constant.



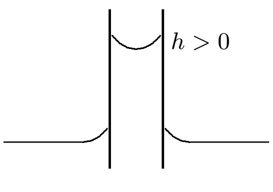
Two fluids meeting at a solid wall in a line orthogonal to the paper. The tangential component of surface tension must vanish.

Example 8.2.1 (Walking on water): Insects capable of walking on the surface of water must "wax" their feet to obtain an obtuse contact angle and avoid getting wet. Since they are carried by surface tension we may estimate an insect's ability to walk on water by the so-called *Jesus number* [70] $\mathsf{Je} = \alpha L / M g_0$ where M is the mass of the insect and L the length of the circumference of all the contact regions. Thus, to obtain $\mathsf{Je} > 1$ an insect with $M = 10$ mg must have $L > 1.3$ mm.


An insect foot making contact with the water surface at an obtuse angle.

Capillary effect

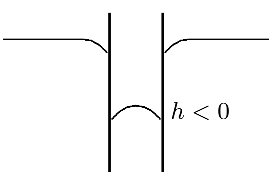
Water has a well-known tendency to rise above the ambient water level in a narrow vertical glass tube which is lowered into the liquid. Closer inspection reveals that the surface inside the tube is concave. This is called the *capillary effect* and is caused by the acute contact angle of water in conjunction with its surface tension which creates a negative pressure just below the liquid surface, balancing the weight of the raised water column. Mercury with its obtuse contact angle displays instead a convex surface shape, creating a positive pressure just below the surface which forces the liquid down to a level where the pressure equals the pressure at the ambient level.



Water rises above the ambient level in a glass tube and displays a concave surface inside the tube. Mercury behaves oppositely and sinks with a convex surface.

Let us first calculate the effect for an acute angle of contact. At the center of the tube the radii of curvature are equal, and since the center of curvature lies outside the liquid, they are also negative, $R_1 = R_2 = -R_0$ where R_0 is positive. Hydrostatic balance at the center of the tube then takes the form, $\rho_0 g_0 h = 2\alpha/R_0$ where h is the central height, such that

$$h = \frac{2\alpha}{\rho_0 g_0 R_0} = 2\frac{R_c^2}{R_0} \; . \tag{8-7}$$

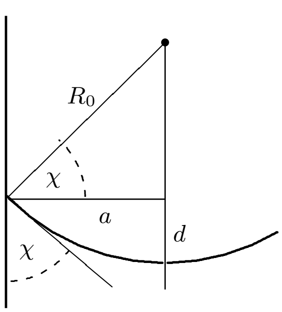


Mercury sinks below the general level in a capillary glass tube.

It should be noticed that this is an exact relation which does not depend on the surface being spherical. It also covers the case of an obtuse contact angle by taking R_0 to be negative.

Assuming now that the surface is in fact spherical, which should be the case for $a \lesssim R_c$ where gravity has no effect on the shape, a simple geometric construction shows that $a = R_0 \cos\chi$, and thus,

$$\boxed{h = 2\frac{R_c^2}{a}\cos\chi \; .} \tag{8-8}$$



Approximatively spherical surface with acute contact angle in a circular tube.

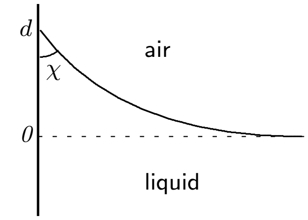
It is as expected positive for acute and negative for obtuse contact angles. From the same geometry it also follows that the depth of the central point of the surface is $d = R_0(1 - \sin\chi)$, or

$$\boxed{d = a\frac{1 - \sin\chi}{\cos\chi} \; ,} \tag{8-9}$$

Both of these expressions are modified for larger radius, $a \gtrsim R_c$ where the surface flattens.

> **Example 8.2.2:** A capillary tube has diameter $2a = 1$ mm. Water with $\chi \approx 0$ rises $h = +30$ mm with a surface depth $d = +0.5$ mm . Mercury with contact angle $\chi \approx 140°$ sinks on the other hand to $h = -11$ mm and $d = -0.2$ mm under the same conditions.

8.3 Capillary effect at a vertical wall

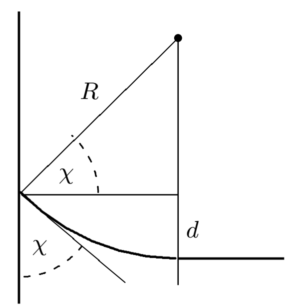


The interface at a vertical wall with an acute angle of contact.

In the limit of infinite tube radius the capillary effect only deforms the liquid surface close to the nearly flat vertical wall to accommodate the finite contact angle. Far from the wall the surface is perfectly flat, and there will be no pressure jump due to surface tension, and consequently no general capillary rise of the surface above the ambient level. This is an exactly solvable case which nicely illustrates the mathematics of planar curves.

The rise or drop at the wall may be estimated by a geometric argument of the same kind as at the end of the preceding section. Assuming that the shape is a circle of radius R, the pressure change due to surface tension inside the liquid is $\Delta p = -\alpha/R$ roughly in the middle at $z = d/2$. Hydrostatic balance thus requires $\rho_0 g_0 d/2 \approx \alpha/R$, and since the radius R as before is related by geometry to the depth by $d = R(1 - \sin\chi)$, we find for an acute angle of contact,

$$d \approx R_c\sqrt{2(1-\sin\chi)} = 2R_c \sin\frac{90^\circ - \chi}{2} \ . \qquad (8\text{-}10)$$



Approximatively circular geometry of a liquid surface with acute contact angle near a vertical wall.

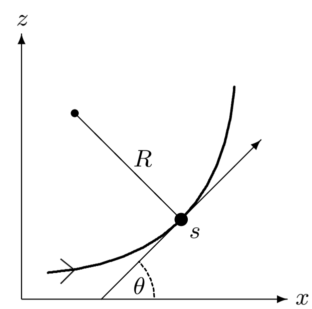
The last expression is also valid for an obtuse angle of contact. We shall see below that this expression is in fact identical to the exact result.

For water with nearly vanishing angle of contact, we find $d \approx \sqrt{2}R_c \approx 3.9$ mm whereas for mercury with $\chi = 140^\circ$ we get $d \approx -1.6$ mm.

Geometry of planar curves

Taking the x-axis orthogonal to the wall, and the z-axis vertical, the surface shape may be assumed to be independent of y and described by a simple curve in the xz-plane. The best way to handle the geometry of a planar curve is to use two auxiliary parameters: the arc length s along the interface curve, and the elevation angle θ between the x-axis and the oriented tangent to the curve. From this definition of θ we obtain immediately,

$$\frac{dx}{ds} = \cos\theta \ , \qquad\qquad \frac{dz}{ds} = \sin\theta \ . \qquad (8\text{-}11)$$



The geometry of a planar curve. The curve is parameterized by the arc length s along the curve. A small change in s generates a change in the elevation angle θ determined by the local radius of curvature. Here the radius of curvature is positive.

The radius of curvature may conveniently be defined as,

$$R = \frac{ds}{d\theta} \ . \qquad (8\text{-}12)$$

Evidently this *geometric radius of curvature* is positive if s is an increasing function of θ, otherwise negative. One should be aware that this sign convention may not agree with the physical sign convention for the Young-Laplace law (8-5). Depending on the arrangement of liquid and air, it may be necessary to introduce an explicit sign to get the physics right.

Hydrostatic balance

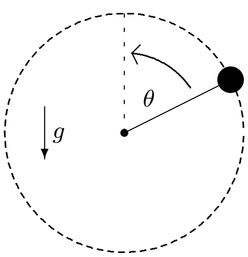
Assuming that the air pressure is constant, $p = p_0$, the pressure in the liquid just below the surface is $p = p_0 + \Delta p$ where Δp is given by the Young-Laplace (8-5) law. Denoting the local geometric radius of curvature by R we have for an acute angle of contact $R_1 = -R$ and $R_2 = \infty$, because the center of curvature lies outside the liquid. The pressure is thus negative $\Delta p = -\alpha/R$ just below the surface, and the hydrostatic pressure of the raised surface must balance the drop in pressure, $\rho_0 g_0 z = \alpha/R$, everywhere on the surface. Introducing the capillary radius (8-4), this may be written as $1/R = z/R_c^2$, and we find from (8-12)

$$\frac{d\theta}{ds} = \frac{z}{R_c^2} \ . \tag{8-13}$$

This equation together with the two definitions (8-11) determine x, z and θ as functions of s.

There are several different types of solutions, depending on the boundary conditions. For the surface near the wall the boundary conditions are $x = 0$ and $\theta = \chi - 90°$ for $s = 0$, and $z \to 0$ for $s \to \infty$. Having obtained the solution we may then determine the depth $z = d$ for $x = 0$.

The pendulum connection



Inverted mathematical pendulum with angle θ moving towards the unstable equilibrium at $\theta = 0$. This sketch corresponds to a liquid with acute contact angle. If the contact angle is obtuse, the pendulum has to start from the other side of the unstable equilibrium.

Since R_c is a constant for the liquid, we may without loss of generality choose the unit of length such that $R_c = 1$. Differentiating (8-13) once more after s, we obtain the equation of motion for an *inverted mathematical pendulum*,

$$\boxed{\frac{d^2\theta}{ds^2} = \sin\theta \ .} \tag{8-14}$$

The boundary conditions correspond to starting the pendulum at an angle $\theta = \theta_0 = \chi - 90°$ with velocity $d\theta/ds = d$, according to (8-13) (for $R_c = 1$). The depth d must be chosen precisely such that the pendulum eventually comes to rest in the unstable equilibrium at $\theta = 0$.

> If the velocity is chosen larger than the depth, the pendulum will continue through the unstable equilibrium, and the liquid surface will start to rise again. When the pendulum reaches the angle $\theta = -\theta_0$, another vertical wall may be placed there, forming the same angle of contact with the liquid surface. This is the planar analogue of the capillary effect in a circular tube, but this problem is not solvable in terms of elementary functions. The periodic pendulum solutions obtained by letting the pendulum move through the stable equilibrium at $\theta = \pi$ correspond to a strip of liquid hanging at the lower edge of the vertical plate.

To find the solution for the problem at hand, the surface shape near a single wall, we multiply the pendulum equation of motion by $d\theta/ds$ and integrate, to get

$$\frac{1}{2}\left(\frac{d\theta}{ds}\right)^2 = 1 - \cos\theta \ ,$$

where the constant 1 has been determined from the condition that $d\theta/ds = 0$ and $\theta = 0$ for $s \to \infty$. From this equation and (8-13) we derive that,

$$\boxed{z = -2\sin\frac{\theta}{2}\ ,} \tag{8-15}$$

independently of whether the contact angle is acute or obtuse. Taking $\theta = \chi - 90°$ we recover indeed (8-10).

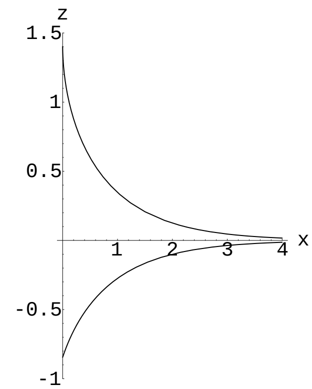
The dependence of x on θ is calculated from,

$$\frac{dx}{d\theta} = \frac{dx/ds}{d\theta/ds} = \frac{\cos\theta}{-2\sin\frac{\theta}{2}} = \sin\frac{\theta}{2} - \frac{1}{2\sin\frac{\theta}{2}}\ .$$

This differential equation integrates to

$$\boxed{x = x_0 - 2\cos\frac{\theta}{2} - \log\left|\tan\frac{\theta}{4}\right|\ ,} \tag{8-16}$$

where $x_0 = 2\cos(\theta_0/2) + \log|\tan(\theta_0/4)|$ and $\theta_0 = \chi - 90°$. Together with (8-15) this constitutes a parametric form for the surface shape.



Capillary surface shape of water and mercury in units where $R_c = 1$. Notice the exaggerated vertical scale.

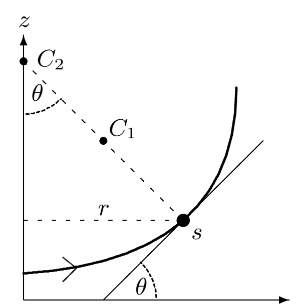
8.4 Axially invariant shapes

Many static interfaces — capillary surfaces in circular tubes, droplets and bubbles — are invariant under rotations around an axis, allowing us to establish a fairly simple formalism for the shape of the equilibrium surface.

Geometry of axially invariant interfaces

In cylindrical coordinates an axially invariant interface is a planar curve in the rz-plane. Using again the arc length s along the curve and the angle of elevation θ for its slope, we find as in the planar case,

$$\frac{dr}{ds} = \cos\theta\ , \qquad \frac{dz}{ds} = \sin\theta\ , \tag{8-17}$$



The interface curve is parameterized by the arc length s. A small change in s generates a change in the elevation angle θ determined by the local radius of curvature R_1 with center C_1. The second radius of curvature R_2 lies on the z-axis with center C_2 (see problem 8.3).

The first principal radius of curvature may be directly taken over from the planar case, whereas it takes some work to show that the second center of curvature lies on the z-axis (see problem 8.3), such that

$$R_1 = \frac{ds}{d\theta}\ , \qquad R_2 = \frac{r}{\sin\theta}\ . \tag{8-18}$$

One should be aware that this sign convention for these *geometric radii of curvature* may not agree with the physical sign convention for the Young-Laplace law (8-5), and that it may be necessary to introduce explicit signs to get the physics right. This will become clear in the calculations that follow.

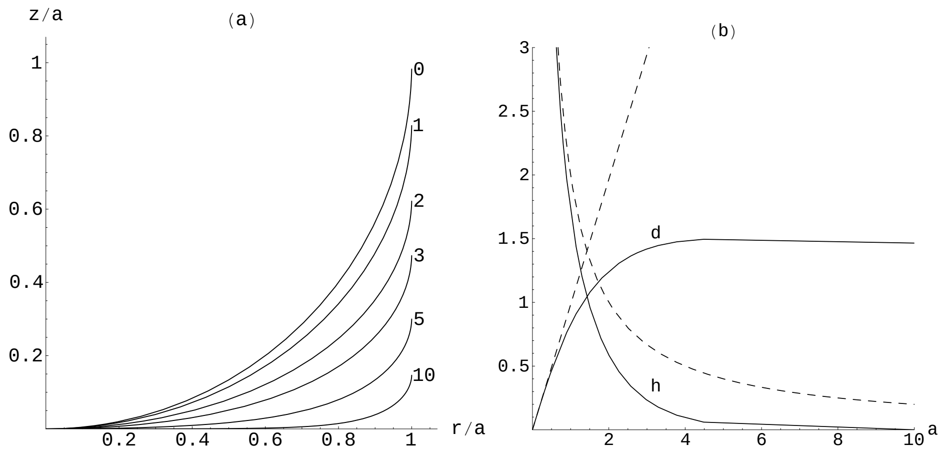
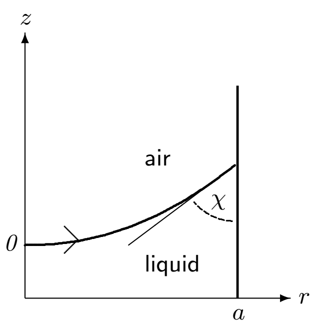


Figure 8.1: *Capillary effect in water for a circular tube of radius a in units where $R_c = 1$.* **(a)** *Surface shape $z(r)/a$ plotted as a function of r/a for $\chi_c = 1^\circ$ and $a = 0, 1, 2, 3, 5, 10$. Notice how the shape becomes gradually spherical as the tube radius a approaches 1. For $a \lesssim 1$ the shape is constant.* **(b)** *Computed capillary rise h and depth d as functions of a (fully drawn). For $a \gtrsim 1$ the computed values deviate from the spherical surface results (8-8) and (8-9) (dashed).*



For the capillary with acute angle of contact both centers of curvature lie outside the liquid.

The capillary surface

For the rising liquid/air capillary surface with acute contact angle both geometric radii of curvature, R_1 and R_2, are positive. Since both centers of curvature lie outside the liquid, the physical radii will be $-R_1$ and $-R_2$ in the Young-Laplace law (8-5). Assuming that the air pressure is constant, hydrostatic balance demands that $g_0 z + \Delta p/\rho_0$ be constant, or

$$g_0 z - \frac{\alpha}{\rho_0}\left(\frac{d\theta}{ds} + \frac{\sin\theta}{r}\right) = -\frac{2\alpha}{R_0} \ .$$

The value of the constant has been determined from the initial condition in the center, where $r = z = \theta = 0$ and the geometric radii of curvature are equal to the central radius of curvature, $R_1 = R_2 = R_0$. Solving for $d\theta/ds$ we find,

$$\frac{d\theta}{ds} = \frac{2}{R_0} - \frac{\sin\theta}{r} + \frac{z}{R_c^2} \ , \tag{8-19}$$

where R_c is the capillary constant (8-4). In the second term one must remember that $r/\theta \to R_0$ for $\theta \to 0$.

Together with the two equations (8-17) we have obtained three first order differential equations for r, z, and θ. Since s does not occur explicitly, and since θ grows monotonically with s, one may eliminate s and instead use θ as the running parameter. Unfortunately these equations cannot be solved analytically, but given R_0 they may be solved numerically with the boundary conditions $r = z = 0$

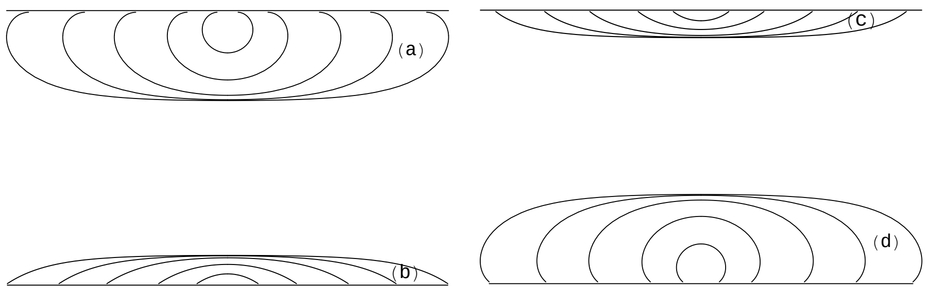
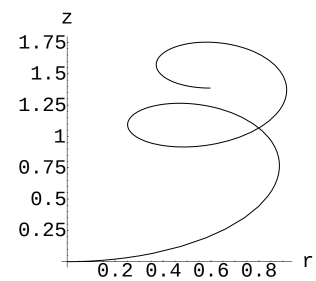


Figure 8.2: *Shapes of stable air bubbles and droplets of water ($R_c = 2.7$ mm, $\chi_c = 1°$) and mercury ($R_c = 1.9$ mm, $\chi_c = 140°$).* **(a)** *Air bubbles in water under a lid (to scale).* **(b)** *Water droplet on table plotted with vertical scale enlarged 40 times.* **(c)** *Air bubbles in mercury (to scale).* **(d)** *Mercury droplets on a table (to scale).*

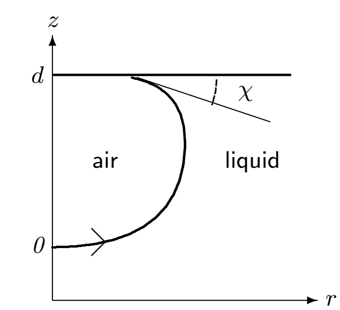
for $\theta = 0$. The solutions are quasi-periodic curves that spiral upwards forever. The physical solution must however stop at the wall $r = a$ for $\theta = \theta_0 = 90° - \chi$, and that fixes R_0. The numeric solutions are displayed in fig. 8.1.



The numeric solution for $R_0 = R_c = 1$ in the interval $0 < \theta < 4\pi$. The spiral is unphysical.

Sessile bubbles and droplets

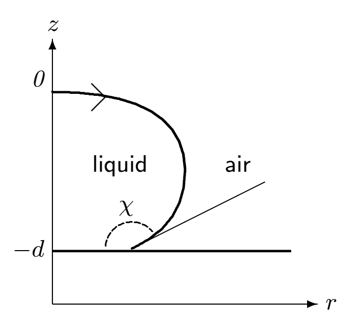
If a horizontal plate (a "lid") is inserted into water, air bubbles may come up against its underside, and remain stably sitting (sessile) there. The bubbles are pressed against the plate by buoyancy forces that in addition tend to flatten bubbles larger than the capillary radius. The shape may be obtained from the above solution to the capillary effect by continuing it to $\theta_0 = 180° - \chi$.



An air bubble in under a horizontal lid with acute angle of contact.

Mercury sitting on the upper side of a horizontal plate likewise forms small nearly spherical droplets which may be brought to merge and form large flat puddles of "quick silver". In this case the geometric radii of curvature will both be negative while the physical radii of curvature are both positive because the centers of curvature lie inside the liquid. The formalism is consequently exactly the same as before, except that the central radius of curvature R_0 is now negative. The shapes are nearly the same as for air bubbles, except for the different angle of contact.

In fig. 8.2 the four sessile configurations of bubbles and droplets are displayed. The depth approaches in all cases a constant value for large central radius of curvature R_0, which may be estimated by the same methods as before to be $d = R_c\sqrt{2(1 \pm \cos\chi)}$ for bubbles(+) and droplets(−). Notice that the depth of the water droplet (frame 8.2b) is enlarged by a factor 40. If water really has contact angle $\chi = 1°$, the maximal depth of a water droplet on a flat surface is only $d = 0.018R_c \approx 50$ μm. This demonstrates how efficient water is in wetting a surface, because of its small contact angle.



A droplet on a horizontal plate with an obtuse angle of contact.

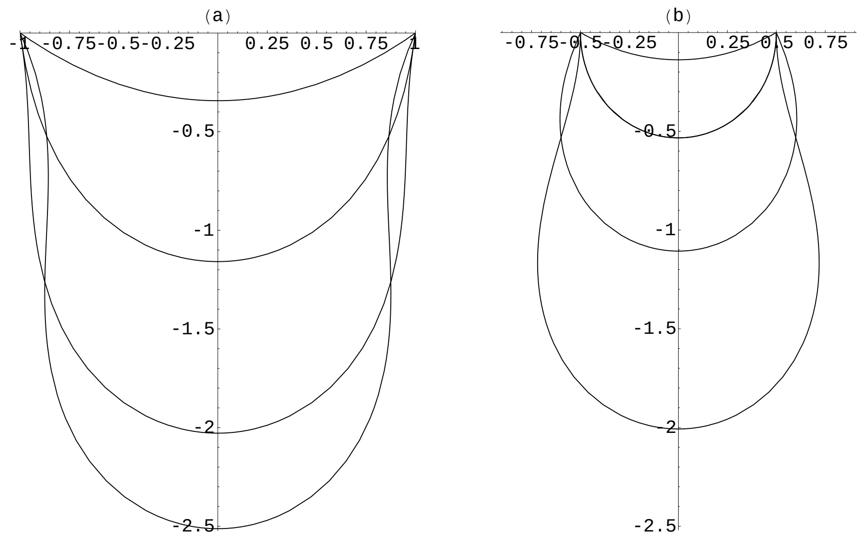
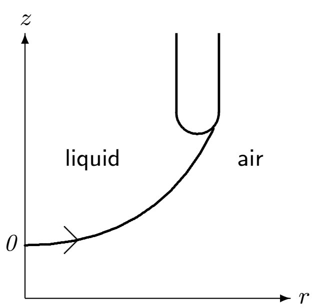


Figure 8.3: *Static droplet shapes at the mouth of a circular tube in units of $R_c = 1$. There are no solutions with larger volumes than the largest ones shown here. All contact angles are assumed to be possible at the mouth of the tube.* **(a)** *Tube with radius $a = 1$ which is larger the critical radius ($a_1 = 0.918$).* **(b)** *Tube with radius $a = 0.5$ which is smaller than the critical radius.*



A liquid drop hanging from a tube. Any contact angle can be accommodated by the 180° turn at the end of the tube's material.

Pending droplets

Whereas sessile droplets in principle can have unlimited size, hanging liquid droplets will fall if they become too large. Here we shall investigate the shape of a droplet hanging at the end of a thin glass tube, for example a pipette provided with a rubber bulb which allows us to vary the pressure. The column of fluid in the tube may be held static by using the bulb to create a sufficiently negative pressure. When the bulb is slowly squeezed, a droplet emerges at the end of the tube and eventually falls when it becomes large enough.

Both the geometric and physical radii of curvature are positive in this system, such that we get (for $R_c = 1$),

$$\frac{d\theta}{ds} = \frac{2}{R_0} - \frac{\sin\theta}{r} - z \ , \qquad (8\text{-}20)$$

with a negative sign of z. In this case θ is not a monotonic function of s, and we may not eliminate s. Assuming that the tube material is very thin, the boundary conditions may be taken to be $r = z = \theta = 0$ for $s = 0$, because the rounded end of the tube material is able to accommodate any angle of contact. The condition that the liquid surface must always make contact with the end of the glass tube at $r = a$ then determines the total curve length s_0 as a function of the central curvature R_0, and thereby the height $d = z(s_0)$.

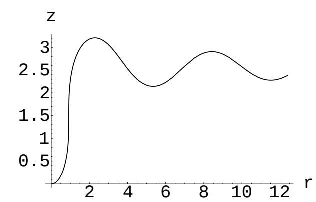
The volume of a droplet,

$$V = \int_0^d \pi r^2 \, dz \ , \qquad (8\text{-}21)$$

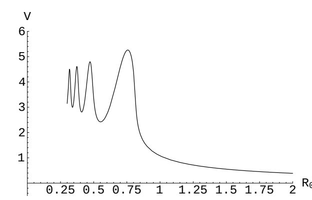
is a function of R_0. As the bulb is squeezed slowly, the volume of the droplet must grow continuously through a sequence of hydrostatic shapes. At some point instability sets in and the drop falls. It is not possible to determine the point of instability in a purely hydrostatic calculation, but as it turns out the droplet can only grow continuously through hydrostatic solutions to a certain maximum volume, beyond which it has to jump discontinuously to reach even larger volumes. We shall take this to indicate that instability has surely set in.

The solutions fall in two classes. If R_0 is larger than a certain critical value, $R_0 > R_{01} = 0.778876\ldots$, the radial distance $r(s)$ will grow monotonically with s, but if $R_0 < R_{01}$ the surface will be shaped like an old-fashioned bottle with one or more waists. The critical solution at $R_0 = R_{01}$ has a turning point with vertical tangent, allowing us to locate the critical point by solving $r'(s) = r''(s) = 0$. The result is that at the critical point the curve length is $s_1 = 1.95863\ldots$, the radius $a_1 = 0.917622\ldots$ and the depth $d_1 = 1.47804\ldots$.

In fig. 8.3a is shown the family of shapes for a droplet with tube radius $a = 1$. For large central radius of curvature R_0 the shape is flat, but as R_0 diminishes the droplet grows in volume and develops a "waist". It finally reaches a maximum volume of $5.26R_c^3$, beyond which it cannot pass continuously. In fig. 8.3b is shown a family of shapes for a droplet with tube radius $a = 0.5$. In this case the droplet may expand beyond the radius of the tube until it reaches a maximal volume of $2.32R_c^3$.



Critical solution for $R_0 \approx$ 0.78.



The variation of the volume with R_0 for a tube with radius $a = 1$. Notice the maximum for $R_0 \approx 0.75$.

Problems

8.1 A soap bubble of diameter 6 cm floats in the air. What is the pressure excess inside the bubble when the surface tension between water and air is taken to be $\alpha = 0.15$ N/m? How would you define the capillary length in this case, and how big is it? Do you expect the bubble to keep its spherical shape?

* **8.2** Consider a quadratic surface $z = ax^2 + by^2 + 2cxy$ with a unique extremum at $x = y = 0$. For a suitable choice of coordinates, a smooth function may always be approximated with such a function in any given point. **(a)** Determine the radius of curvature of the surface along a line in the xy-plane forming an angle ϕ with the x-axis. **(b)** Determine the extrema of the radius of curvature as a function of ϕ and show that they correspond to orthogonal directions.

* **8.3** Determine the radii of curvature in section 8.4 by expanding the shape $z = f(r)$ with $r = \sqrt{x^2 + y^2}$ to second order around $x = x_0$, $y = 0$, and $z = z_0$.

