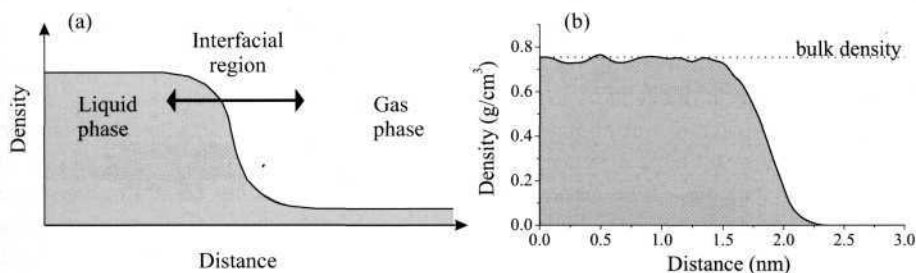


## 2 Liquid surfaces

### 2.1 Microscopic picture of the liquid surface

A surface is not an infinitesimal sharp boundary in the direction of its normal, but it has a certain thickness. For example, if we consider the density  $\rho$  normal to the surface (Fig. 2.1), we can observe that, within a few molecules, the density decreases from that of the bulk liquid to that of its vapor [11].



**Figure 2.1:** Density of a liquid versus the coordinate normal to its surface: (a) is a schematic plot; (b) results from molecular dynamics simulations of a *n*-tridecane ( $C_{13}H_{28}$ ) at  $27^\circ C$  adapted from Ref. [12]. Tridecane is practically not volatile. For this reason the density in the vapor phase is negligible.

The density is only one criterion to define the thickness of an interface. Another possible parameter is the orientation of the molecules. For example, water molecules at the surface prefer to be oriented with their negative sides “out” towards the vapor phase. This orientation fades with increasing distance from the surface. At a distance of 1–2 nm the molecules are again randomly oriented.

Which thickness do we have to use? This depends on the relevant parameter. If we are for instance, interested in the density of a water surface, a realistic thickness is in the order of 1 nm. Let us assume that a salt is dissolved in the water. Then the concentration of ions might vary over a much larger distance (characterized by the Debye length, see Section 4.2.2). With respect to the ion concentration, the thickness is thus much larger. In case of doubt, it is safer to choose a large value for the thickness.

The surface of a liquid is a very turbulent place. Molecules evaporate from the liquid into the vapor phase and vice versa. In addition, they diffuse into the bulk phase and molecules from the bulk diffuse to the surface.

- **Example 2.1.** To estimate the number of gas molecules hitting the liquid surface per second, we recall the kinetic theory of ideal gases. In textbooks of physical chemistry the rate of effusion of an ideal gas through a small hole is given by [13]

$$\frac{PA}{\sqrt{2\pi mk_B T}} \quad (2.1)$$

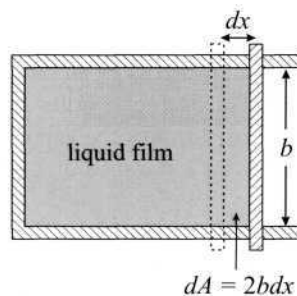
Here,  $A$  is the cross-sectional area of the hole and  $m$  is the molecular mass. This is equal to the number of water molecules hitting a surface area  $A$  per second. Water at 25°C has a vapor pressure  $P$  of 3168 Pa. With a molecular mass  $m$  of  $0.018 \text{ kg mol}^{-1}/6.02 \times 10^{23} \text{ mol}^{-1} \approx 3 \times 10^{-26} \text{ kg}$ ,  $10^7$  water molecules per second hit a surface area of  $10 \text{ \AA}^2$ . In equilibrium the same number of molecules escape from the liquid phase.  $10 \text{ \AA}^2$  is approximately the area covered by one water molecule. Thus, the average time a water molecule remains on the surface is of the order of  $0.1 \text{ \mu s}$ .

## 2.2 Surface tension

The following experiment helps us to define the most fundamental quantity in surface science: the surface tension. A liquid film is spanned over a frame, which has a mobile slider (Fig. 2.2). The film is relatively thick, say  $1 \text{ \mu m}$ , so that the distance between the back and front surfaces is large enough to avoid overlapping of the two interfacial regions. Practically, this experiment might be tricky even in the absence of gravity but it does not violate a physical law so that it is in principle feasible. If we increase the surface area by moving the slider a distance  $dx$  to the right, work has to be done. This work  $dW$  is proportional to the increase in surface area  $dA$ . The surface area increases by twice  $b \cdot dx$  because the film has a front and back side. Introducing the proportionality constant  $\gamma$  we get

$$dW = \gamma \cdot dA \quad (2.2)$$

The constant  $\gamma$  is called surface tension.



**Figure 2.2:** Schematic set-up to verify Eq. (2.2) and define the surface tension.

Equation (2.2) is an empirical law and a definition at the same time. The empirical law is that the work is proportional to the change in surface area. This is not only true for infinitesimal small changes of  $A$  (which is trivial) but also for significant increases of the surface area:  $\Delta W = \gamma \cdot \Delta A$ . In general, the proportionality constant depends on the composition of the liquid and the vapor, temperature, and pressure, but it is independent of the area. The definition is that we call the proportionality constant “surface tension”.

The surface tension can also be defined by the force  $F$  that is required to hold the slider in place and to balance the surface tensional force:

$$|F| = 2\gamma b \quad (2.3)$$

Both forms of the law are equivalent, provided that the process is reversible. Then we can write

$$F = -\frac{dW}{dx} = -2\gamma b \quad (2.4)$$

The force is directed to the left while  $x$  increases to the right. Therefore we have a negative sign.

The unit of surface tension is either  $\text{J/m}^2$  or  $\text{N/m}$ . Surface tensions of liquids are of the order of  $0.02$ – $0.08 \text{ N/m}$  (Table 2.1). For convenience they are usually given in  $\text{mN/m}$  (or  $10^{-3} \text{ N/m}$ ), where the first “m” stands for “milli”.

The term “surface tension” is tied to the concept that the surface stays under a tension. In a way, this is similar to a rubber balloon, where also a force is required to increase the surface area of its rubber membrane against a tension. There is, however, a difference: while the expansion of a liquid surface is a plastic process the stretching of a rubber membrane is usually elastic.

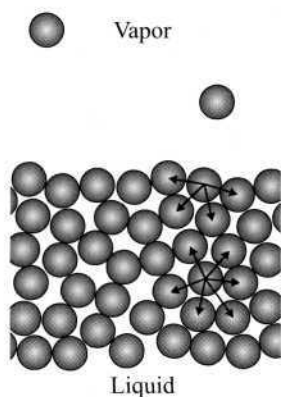
**Table 2.1:** Surface tensions  $\gamma$  of some liquids at different temperatures  $T$ .

Substance	$T$	$\gamma$ ( $\text{mNm}^{-1}$ )	Substance	$T$	$\gamma$ ( $\text{mNm}^{-1}$ )		
Water	$10^\circ\text{C}$	74.23	Mercury	$25^\circ\text{C}$	485.48		
	$25^\circ\text{C}$	71.99		Phenol	$50^\circ\text{C}$	38.20	
	$50^\circ\text{C}$	67.94			Benzene	$25^\circ\text{C}$	28.22
	$75^\circ\text{C}$	63.57				Toluene	$25^\circ\text{C}$
	$100^\circ\text{C}$	58.91			Dichloromethane		$25^\circ\text{C}$
Argon	$90 \text{ K}$	11.90	$n$ -pentane	$25^\circ\text{C}$		15.49	
	Methanol	$25^\circ\text{C}$	22.07	$n$ -hexane	$25^\circ\text{C}$	17.89	
Ethanol		$10^\circ\text{C}$	23.22	$n$ -heptane	$25^\circ\text{C}$	19.65	
	$25^\circ\text{C}$	21.97	$n$ -octane	$10^\circ\text{C}$	22.57		
	$50^\circ\text{C}$	19.89		$25^\circ\text{C}$	21.14		
1-propanol	$25^\circ\text{C}$	23.32		$50^\circ\text{C}$	18.77		
	1-butanol	$25^\circ\text{C}$	24.93	$75^\circ\text{C}$	16.39		
2-butanol		$25^\circ\text{C}$	22.54	$100^\circ\text{C}$	14.01		
	Acetone			$25^\circ\text{C}$	23.46	Formamide	$25^\circ\text{C}$

□ **Example 2.2.** If a water film is formed on a frame with a slider length of 1 cm, then the film pulls on the slider with a force of

$$2 \times 0.01 \text{ m} \times 0.072 \text{ Jm}^{-2} = 1.44 \times 10^{-3} \text{ N}$$

That corresponds to a weight of 0.15 g.



**Figure 2.3:** Schematic molecular structure of a liquid–vapor interface.

How can we interpret the concept of surface tension on the molecular level? For molecules it is energetically favorable to be surrounded by other molecules. Molecules attract each other by different interactions such as van der Waals forces or hydrogen bonds (for details see Chapter 6). Without this attraction there would not be a condensed phase at all, there would only be a vapor phase. The sheer existence of a condensed phase is evidence for an attractive interaction between the molecules. At the surface, molecules are only partially surrounded by other molecules and the number of adjacent molecules is smaller than in the bulk (Fig. 2.3). This is energetically unfavorable. In order to bring a molecule from the bulk to the surface, work has to be done. With this view  $\gamma$  can be interpreted as the energy required to bring molecules from inside the liquid to the surface and to create new surface area. Therefore often the term “surface energy” is used for  $\gamma$ . As we shall see in the next chapter this might lead to some confusion. To avoid this we use the term surface tension.

With this interpretation of the surface tension in mind we immediately realize that  $\gamma$  has to be positive. Otherwise the Gibbs free energy of interaction would be repulsive and all molecules would immediately evaporate into the gas phase.

□ **Example 2.3.** Estimate the surface tension of cyclohexane from the energy of vaporization  $\Delta_{vap}U = 30.5$  kJ/mol at 25°C. The density of cyclohexane is  $\rho = 773$  kg/m<sup>3</sup>, its molecular weight is  $M = 84.16$  g/mol.

For a rough estimate we picture the liquid as being arranged in a cubic structure. Each molecule is surrounded by 6 nearest neighbors. Thus each bond contributes roughly  $\Delta_{vap}U/6 = 5.08$  kJ/mol. At the surface one neighbor and hence one bond is missing. Per mole we therefore estimate a surface tension of 5.08 kJ/mol.

To estimate the surface tension we need to know the surface area occupied by one molecule. If the molecules form a cubic structure, the volume of one unit cell is  $a^3$ , where  $a$  is the distance between nearest neighbors. This distance can be calculated from the density:

$$a^3 = \frac{M}{\rho N_A} = \frac{0.08416 \text{ kg/mol}}{773 \text{ kg/m}^3 \cdot 6.02 \times 10^{23} \text{ mol}^{-1}} = 1.81 \times 10^{-28} \text{ m}^3 \Rightarrow$$

$$a = 0.565 \text{ nm}$$

The surface area per molecule is  $a^2$ . For the surface energy we estimate

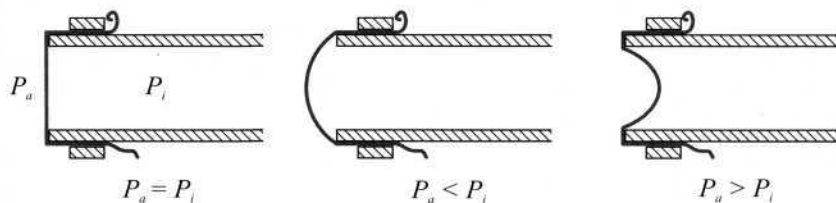
$$\gamma = \frac{\Delta_{\text{vap}}U}{6N_A a^2} = \frac{5080 \text{ J mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1} \cdot (0.565 \times 10^{-9} \text{ m})^2} = 0.0264 \frac{\text{J}}{\text{m}^2}$$

For such a rough estimate the result is surprisingly close to the experimental value of  $0.0247 \text{ J/m}^2$ .

## 2.3 Equation of Young and Laplace

### 2.3.1 Curved liquid surfaces

We start by describing an important phenomenon: If in equilibrium a liquid surface is curved, there is a pressure difference across it. To illustrate this let us consider a circular part of the surface. The surface tension tends to minimize the area. This results in a planar geometry of the surface. In order to curve the surface, the pressure on one side must be larger than on the other side. The situation is much like that of a rubber membrane. If we, for instance, take a tube and close one end with a rubber membrane, the membrane will be planar (provided the membrane is under some tension) (Fig. 2.4). It will remain planar as long as the tube is open at the other end and the pressure inside the tube is equal to the outside pressure. If we now blow carefully into the tube, the membrane bulges out and becomes curved due to the increased pressure inside the tube. If we suck on the tube, the membrane bulges inside the tube because now the outside pressure is higher than the pressure inside the tube.



**Figure 2.4:** Rubber membrane at the end of a cylindrical tube. An inner pressure  $P_i$  can be applied, which is different than the outside pressure  $P_a$ .

The Young<sup>1</sup>–Laplace<sup>2</sup> equation relates the pressure difference between the two phases  $\Delta P$  and the curvature of the surface:

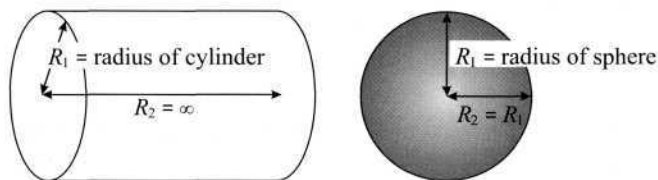
$$\Delta P = \gamma \cdot \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2.5)$$

$R_1$  and  $R_2$  are the two principal radii of curvature.  $\Delta P$  is also called Laplace pressure. Equation (2.5) is also referred to as the Laplace equation.

<sup>1</sup> Thomas Young, 1773–1829. English physician and physicist, professor in Cambridge.

<sup>2</sup> Pierre-Simon Laplace, Marquis de Laplace, 1749–1827. French natural scientist.

It is perhaps worthwhile to describe the radii of curvature in a little bit more detail. The curvature  $1/R_1 + 1/R_2$  at a point on an arbitrarily curved surface is obtained as follows. At the point of interest we draw a normal through the surface and then pass a plane through this line and the intersection of this line with the surface. One angle of orientation of this plane is not defined and can be chosen conveniently. The line of intersection will, in general, be curved at the point of interest. The radius of curvature  $R_1$  is the radius of a circle inscribed to the intersection at the point of interest. The second radius of curvature is obtained by passing a second plane through the surface also containing the normal, but perpendicular to the first plane. This gives the second intersection and leads to the second radius of curvature  $R_2$ . So the planes defining the radii of curvature must be perpendicular to each other and contain the surface normal. Otherwise their orientation is arbitrary. A law of differential geometry says that the value  $1/R_1 + 1/R_2$  for an arbitrary surface is invariant and does not depend on the orientation, as long as the radii are determined in perpendicular directions.



**Figure 2.5:** Illustration of the curvature of a cylinder and a sphere.

Let us illustrate the curvature for two examples. For a cylinder of radius  $r$  a convenient choice is  $R_1 = r$  and  $R_2 = \infty$  so that the curvature is  $1/r + 1/\infty = 1/r$ . For a sphere with radius  $R$  we have  $R_1 = R_2$  and the curvature is  $1/R + 1/R = 2/R$  (Fig. 2.5).

□ **Example 2.4.** How large is the pressure in a spherical bubble with a diameter of 2 mm and a bubble of 20 nm diameter in pure water, compared with the pressure outside? For a bubble the curvature is identical to that of a sphere:  $R_1 = R_2 = R$ . Therefore

$$\Delta P = \frac{2\gamma}{R} \quad (2.6)$$

With  $R = 1$  mm we get

$$\Delta P = 0.072 \frac{\text{J}}{\text{m}^2} \times \frac{2}{10^{-3}\text{m}} = 144 \text{ Pa}$$

With  $R = 10$  nm the pressure is  $\Delta P = 0.072 \text{ J/m}^2 \times 2/10^{-8} \text{ m} = 1.44 \times 10^7 \text{ Pa} = 144 \text{ bar}$ . The pressure inside the bubbles is therefore 144 Pa and  $1.44 \times 10^7 \text{ Pa}$ , respectively, higher than the outside pressure.

The Young–Laplace equation has several fundamental implications:

- If we know the shape of a liquid surface we know its curvature and we can calculate the pressure difference.
- In the absence of external fields (e. g. gravity), the pressure is the same everywhere in the liquid; otherwise there would be a flow of liquid to regions of low pressure. Thus,  $\Delta P$  is constant and Young–Laplace equation tells us that in this case the surface of the liquid has the same curvature everywhere.

- With the help of the Young–Laplace Eq. (2.5) it is possible to calculate the equilibrium shape of a liquid surface. If we know the pressure difference and some boundary conditions (such as the volume of the liquid and its contact line) we can calculate the geometry of the liquid surface.

In practice, it is usually not trivial to calculate the geometry of a liquid surface with Eq. (2.5). The shape of the liquid surface can mathematically be described by a function  $z = z(x, y)$ . The  $z$  coordinate of the surface is given as a function of its  $x$  and  $y$  coordinate. The curvature involves the second derivative. As a result, calculating the shape of a liquid surface involves solving a partial differential equation of second order, which is certainly not a simple task.

In many cases we deal with rotational symmetric structures. Assuming that the axis of symmetry is identical to the  $z$  axis, then  $z = z(r)$  describes the liquid surface, where  $r$  is the radial coordinate.

Let us assume the  $z$ -axis is vertical and in the plane of the paper. Then it is convenient to put one radius of curvature also in the plane of the paper. This radius is given by

$$\frac{1}{R_2} = \frac{z'}{r\sqrt{1+z'^2}} \quad (2.7)$$

The other principal radius of curvature is in a plane perpendicular to the plane of the paper and oriented parallel to  $R_2$ . It is given by

$$\frac{1}{R_1} = \frac{z''}{\sqrt{(1+z'^2)^3}}, \quad (2.8)$$

where  $z'$  and  $z''$  are the first and second derivatives with respect to  $r$ .

### 2.3.2 Derivation of the Young–Laplace equation

To derive the equation of Young and Laplace we consider a small part of a liquid surface. This part should be so small that the curvature does not change significantly. First, we pick a point X and draw a line around it which is characterized by the fact that all points on that line are the same distance  $d$  away from X (Fig. 2.6). It is the cross section that the studied surface will have with a sphere with its center in X and with a radius  $d$ . If the liquid surface is planar, this would be a flat circle. On this line we take two cuts that are perpendicular to each other (AXB and CXD). Consider in B a small segment on the line of length  $dl$ . The surface tension pulls with a force  $\gamma dl$ . The vertical force on that segment is  $\gamma dl \sin \alpha$ . For small surface areas ( $d \ll R_1, R_2$ ) and small  $\alpha$  we have  $\sin \alpha \approx d/R_1$  where  $R_1$  is the radius of curvature along AXB. The vertical force component is

$$\gamma \cdot dl \cdot \frac{d}{R_1} \quad (2.9)$$

The sum of the four vertical components of the forces related to the small line segments  $dl$  at points A, B, C, and D is

$$\gamma \cdot dl \cdot \left( \frac{2d}{R_1} + \frac{2d}{R_2} \right) = \gamma \cdot dl \cdot 2d \cdot \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2.10)$$

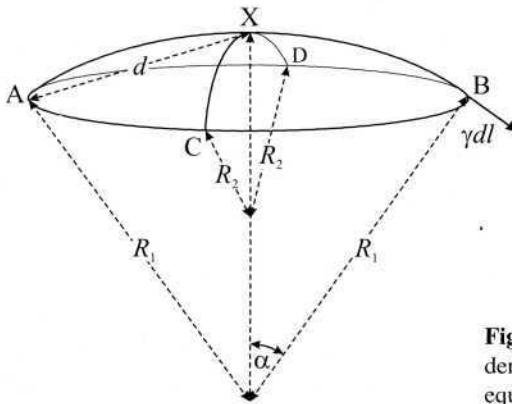
The value of  $1/R_1 + 1/R_2$  is independent of the particular orientation. This means that although developed for the ABCD orientation, Eq. (2.10) is valid for any orientation of the cross-sectional planes as long as they are orthogonal to the surface at X and mutually orthogonal. Integration over the borderline (only  $90^\circ$  rotation of the four segments) gives the total vertical force, caused by the surface tension:

$$\pi d^2 \cdot \gamma \cdot \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2.11)$$

In equilibrium, this downward force must be compensated by an equal force in the opposite direction. This upward force is caused by an increased pressure  $\Delta P$  on the concave side of  $\pi d^2 \Delta P$ . Equating both forces leads to

$$\Delta P \cdot \pi d^2 = \pi d^2 \cdot \gamma \cdot \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \Rightarrow \Delta P = \gamma \cdot \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2.12)$$

These considerations are valid for any small part of the liquid surface. Since the part is arbitrary the Young–Laplace equation must be valid everywhere.



**Figure 2.6:** Diagram used for deriving the Young–Laplace equation.

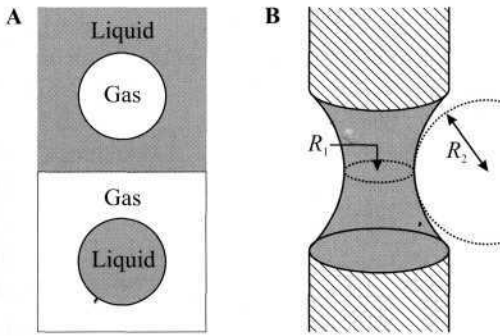
### 2.3.3 Applying the Young–Laplace equation

When applying the equation of Young and Laplace to simple geometries it is usually obvious at which side the pressure is higher. For example, both inside a bubble and inside a drop, the pressure is higher than outside (Fig. 2.7). In other cases this is not so obvious because the curvature can have an opposite sign. One example is a drop hanging between the planar ends of two cylinders (Fig. 2.7). Then the two principal curvatures, defined by

$$C_1 = \frac{1}{R_1} \quad \text{and} \quad C_2 = \frac{1}{R_2}, \quad (2.13)$$

can have a different sign. We count it positive if the interface is curved towards the liquid. The pressure difference is defined as  $\Delta P = P_{liquid} - P_{gas}$ .





**Figure 2.7:** (A) A gas bubble in liquid and a drop in a gaseous environment. (B) A liquid meniscus with radii of curvature of opposite sign between two solid cylinders.

- **Example 2.5.** For a drop in a gaseous environment, the two principal curvatures are positive and given by  $C_1 = C_2 = 1/R$ . The pressure difference is positive, which implies that the pressure inside the liquid is higher than outside.

For a bubble in a liquid environment the two principal curvatures are negative:  $C_1 = C_2 = -1/R$ . The pressure difference is negative and the pressure inside the liquid is lower than inside the bubble.

For a drop hanging between the ends of two cylinders (Fig. 2.7B) in a gaseous environment, one curvature is conveniently chosen to be  $C_1 = 1/R_1$ . The other curvature is negative,  $C_2 = -1/R_2$ . The pressure difference depends on the specific values of  $R_1$  and  $R_2$ .

The shape of a liquid surface is determined by the Young–Laplace equation. In large structures we have to consider also the hydrostatic pressure. Then the equation of Young and Laplace becomes

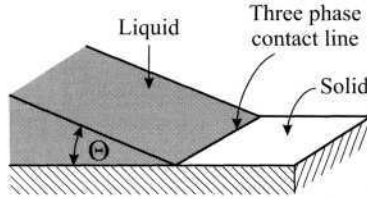
$$\Delta P = \gamma \cdot \left( \frac{1}{R_1} + \frac{1}{R_2} \right) + \rho gh \quad (2.14)$$

Here,  $g$  is the acceleration of free fall and  $h$  is the height coordinate.

What is a large and what is a small structure? In practice this is a relevant question because for small structures we can neglect  $\rho gh$  and use the simpler equation. Several authors define the capillary constant  $\sqrt{2\gamma/\rho g}$  (as a source of confusion other authors have defined  $\sqrt{\gamma/\rho g}$  as the capillary constant). For liquid structures whose curvature is much smaller than the capillary constant the influence of gravitation can be neglected. At 25°C the capillary constant is 3.8 mm for water and 2.4 mm for hexane.

## 2.4 Techniques to measure the surface tension

Before we can discuss the experimental techniques used to measure the surface tension, we need to introduce the so called contact angle  $\Theta$ . When we put a drop of liquid on a solid surface the edge usually forms a defined angle which depends only on the material properties of the liquid and the solid (Fig. 2.8). This is the contact angle. Here we only need to know what it is. In Chapter 7, contact angle phenomena are discussed in more detail. For a wetting surface we have  $\Theta = 0$ .



**Figure 2.8:** Rim of a liquid drop on a planar solid surface with its contact angle  $\Theta$ .

There are several techniques used to measure the surface tension of liquids. The most common technique is to measure optically the contour of a **sessile drop** resting on table. The measured contour is then fitted with a contour calculated using the Young–Laplace Eq. (2.14). The only parameter required is the density of the liquid. From this fit the surface tension is obtained, assuming that the shape is rotational symmetric around a vertical axis. The sessile drop method is only one technique in which the drop shape is analysed to measure the surface tension. Other geometries are

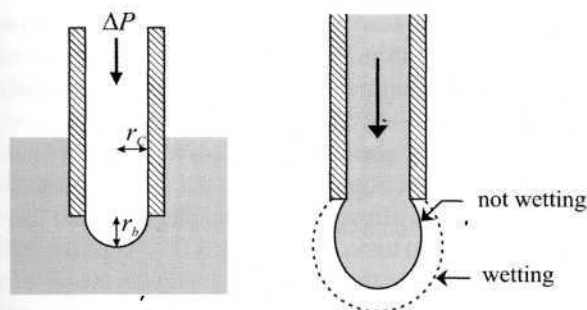
- **pendant drops**, in which the shape of a hanging drop with its familiar tear-drop shape hanging down from a solid (typically the end needle) is analysed,
- **pendant bubbles**, in which the shape of a bubble at the end of a needle in the liquid is analysed, and
- **sessile bubbles**, in which a bubble is floated against the top of a container.

For all drop (and bubble) shape methods an implicit assumption is that the drop is not in motion and viscosity and inertia do not play a role. Surface tension and gravity are the only forces shaping the drop. Using a bubble ensures that the vapor pressure is 100%, a requirement for doing experiments in thermodynamic equilibrium. Often problems caused by contamination are reduced.

In the **bubble pressure method** the surface tension is determined from the value of the pressure which is necessary to push a bubble out of a capillary against the Laplace pressure. Therefore a capillary tube, with inner radius  $r_C$ , is immersed into the liquid (Fig. 2.9). A gas is pressed through the tube, so that a bubble is formed at its end. If the pressure in the bubble increases, the bubble is pushed out of the capillary more and more. In that way, the curvature of the gas–liquid interface increases according to the Young–Laplace equation. The maximum pressure is reached when the bubble forms a half-sphere with a radius  $r_b = r_C$ . This maximum pressure is related to the surface tension by  $\gamma = r_C \Delta P / 2$ . If the volume of the bubble is further increased, the radius of the bubble would also have to become larger. A larger radius corresponds to a smaller pressure. The bubble would thus become unstable and detach from the capillary tube.

**Drop-weight method.** Here, the liquid is allowed to flow out from the bottom of a capillary tube. Drops are formed which detach when they reach a critical dimension. The weight of a drop falling out of a capillary is measured. To get a precise measure, this is done for a number of drops and the total weight is divided by this number.

As long as the drop is still hanging at the end of the capillary, its weight is more than balanced by the surface tension. A drop falls off when the gravitational force  $mg$ , determined by the mass  $m$  of the drop, is no longer balanced by the surface tension. The surface tensional

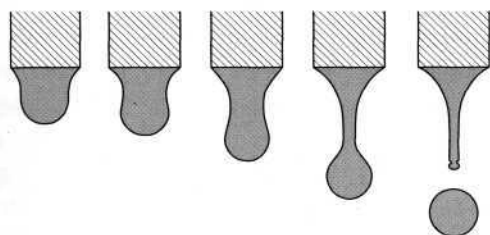


**Figure 2.9:** Maximal bubble pressure and drop-weight method to measure the surface tension of liquids.

force is equal to the surface tension multiplied by the circumference. This leads to

$$mg = 2\pi r_c \gamma \quad (2.15)$$

Thus, the mass is determined by the radius of the capillary. Here, we have to distinguish between the inner and outer diameter of the capillary. If the material of which the capillary is formed is not wetted by the liquid, the inner diameter enters into Eq. (2.15). If the surface of the capillary tube is wetted by the liquid, the external radius of the capillary has to be taken. For completely nonwetting surfaces (contact angle higher than  $90^\circ$ ) the internal radius determines the drop weight. Experimentally, Tate already observed in 1864 that “other things being the same, the weight of a drop of a liquid is proportional to the diameter of the tube in which it is formed” [14].



**Figure 2.10:** Release of a liquid drop from a capillary.

In practice, the equation is only approximately valid, and a weight less than the ideal value is measured. The reason becomes evident when the process of drop formation is observed closely (Fig. 2.10): A thin neck is formed before the drop is released. Correction factors  $f$  are therefore used and Eq. (2.15) becomes:  $mg = 2\pi f r_c \gamma$ .

We have to admit that the maximum bubble pressure and the drop-weight methods are not very common for measuring the surface tension. Nevertheless we described them because the underlying phenomena, that is bubbling a gas into liquid and pressing a liquid out of a capillary, are very important. A common device used to measure  $\gamma$  is the **ring tensiometer**, called also the **Du-Nouy**<sup>3</sup> tensiometer [15]. In a ring tensiometer the force necessary to detach a ring from the surface of a liquid is measured (Fig. 2.11). The force required for the detachment is

$$2\pi \cdot (r_i + r_a) \cdot \gamma \quad (2.16)$$

<sup>3</sup> Pierre Lecomte du Nouÿ, 1883–1974. French scientist who worked in New York and Paris.

A necessary condition is that the ring surface must be completely wetting. A platinum wire is often used which can be annealed for cleaning before the measurement. Even in the early measurements it turned out that Eq. (2.16) was generally in serious error and that an empirical correction function is required [16, 17].

A widely used technique is the **Wilhelmy<sup>4</sup>-plate method**. A thin plate of glass, platinum, or filter paper is vertically placed halfway into the liquid. In fact, the specific material is not important, as long as it is wetted by the liquid. Close to the three-phase contact line the liquid surface is oriented almost vertically (provided the contact angle is  $0^\circ$ ). Thus the surface tension can exert a downward force. One measures the force required to prevent the plate from being drawn into the liquid. After subtracting the gravitational force this force is  $2l\gamma$ , where  $l$  is the length of the plate. In honor of Ludwig Wilhelmy, who studied the force on a plate in detail, the method was named after him [18]. The Wilhelmy-plate method is simple and no correction factors are required. Care has to be taken to keep the plates clean and prevent contamination in air.

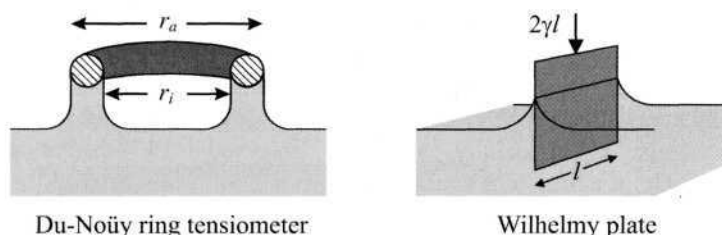


Figure 2.11: Du-Noüy ring tensiometer and Wilhelmy-plate method.

Finally there are dynamic methods to measure the surface tension. For example, a liquid jet is pushed out from a nozzle, which has an elliptic cross-section. The relaxation to a circular cross-section is observed. An advantage of this method is that we can measure changes of the surface tension, which might be caused by diffusion of amphiphilic substances to the surface.

## 2.5 The Kelvin equation

In this chapter we get to know the second essential equation of surface science — the Kelvin<sup>5</sup> equation. Like the Young–Laplace equation it is based on thermodynamic principles and does not refer to a special material or special conditions. The subject of the Kelvin equation is the vapor pressure of a liquid. Tables of vapor pressures for various liquids and different temperatures can be found in common textbooks or handbooks of physical chemistry. These vapor pressures are reported for vapors which are in thermodynamic equilibrium with liquids having planar surfaces. When the liquid surface is curved, the vapor pressure changes. The vapor pressure of a drop is higher than that of a flat, planar surface. In a bubble the vapor

<sup>4</sup> Ludwig Ferdinand Wilhelmy, 1812–1864. German physicochemist.

<sup>5</sup> William Thomson, later Lord Kelvin, 1824–1907. Physics professor at the University of Glasgow.

pressure is reduced. The Kelvin equation tells us how the vapor pressure depends on the curvature of the liquid.

The cause for this change in vapor pressure is the Laplace pressure. The raised Laplace pressure in a drop causes the molecules to evaporate more easily. In the liquid, which surrounds a bubble, the pressure with respect to the inner part of the bubble is reduced. This makes it more difficult for molecules to evaporate. Quantitatively the change of vapor pressure for curved liquid surfaces is described by the Kelvin equation:

$$RT \cdot \ln \frac{P_0^K}{P_0} = \gamma V_m \cdot \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2.17)$$

$P_0^K$  is the vapor pressure of the curved,  $P_0$  that of the flat surface. The index "0" indicates that everything is only valid in thermodynamic equilibrium. Please keep in mind: in equilibrium the curvature of a liquid surface is constant everywhere.  $V_m$  is the molar volume of the liquid. For a sphere-like volume of radius  $r$ , the Kelvin equation can be simplified:

$$RT \cdot \ln \frac{P_0^K}{P_0} = \frac{2\gamma V_m}{r} \quad \text{or} \quad P_0^K = P_0 \cdot e^{\frac{2\gamma V_m}{RT r}} \quad (2.18)$$

The constant  $2\gamma V_m/RT$  is 1.03 nm for Ethanol ( $\gamma = 0.022$  N/m,  $V_m = 58$  cm<sup>3</sup>/mol) and 1.05 nm for Water ( $\gamma = 0.072$  N/m,  $V_m = 18$  cm<sup>3</sup>/mol) at 25°C.

To derive the Kelvin equation we consider the Gibbs free energy of the liquid. The molar Gibbs free energy changes when the surface is being curved, because the pressure increases due to the Laplace pressure. In general, any change in the Gibbs free energy is given by the fundamental equation  $dG = VdP - SdT$ . The increase of the Gibbs free energy per mole of liquid, upon curving, at constant temperature is

$$\Delta G_m = \int_0^{\Delta P} V_m dP = \gamma V_m \cdot \left( \frac{1}{R_1} + \frac{1}{R_2} \right), \quad (2.19)$$

We have assumed that the molar volume remains constant, which is certainly a reasonable assumption because most liquids are practically incompressible for the pressures considered. For a spherical drop in its vapor, we simply have  $\Delta G_m = 2\gamma V_m/r$ . The molar Gibbs free energy of the vapor depends on the vapor pressure  $P_0$  according to

$$G_m = G_m^0 + RT \cdot \ln P_0 \quad (2.20)$$

For a liquid with a curved surface we have

$$G_m^K = G_m^0 + RT \cdot \ln P_0^K \quad (2.21)$$

The change of the molar Gibbs free energy inside the vapor due to curving the interface is therefore

$$\Delta G_m = G_m^K - G_m = RT \cdot \ln \frac{P_0^K}{P_0} \quad (2.22)$$

Since the liquid and vapor are supposed to be in equilibrium, the two expressions must be equal. This immediately leads to the Kelvin equation.

When applying the Kelvin equation, it is instructive to distinguish two cases: A drop in its vapor (or more generally: a positively curved liquid surface) and a bubble in liquid (a negatively curved liquid surface).

**Drop in its vapor:** The vapor pressure of a drop is higher than that of a liquid with a planar surface. One consequence is that an aerosol of drops (fog) should be unstable. To see this, let us assume that we have a box filled with many drops in a gaseous environment. Some drops are larger than others. The small drops have a higher vapor pressure than the large drops. Hence, more liquid evaporates from their surface. This tends to condense into large drops. Within a population of drops of different sizes, the bigger drops will grow at the expense of the smaller ones — a process called Ostwald ripening<sup>6</sup>. These drops will sink down and, at the end, bulk liquid fills the bottom of the box.

For a given vapor pressure, there is a critical drop size. Every drop bigger than this size will grow. Drops at a smaller size will evaporate. If a vapor is cooled to reach over-saturation, it cannot condense (because every drop would instantly evaporate again), unless nucleation sites are present. In that way it is possible to explain the existence of over-saturated vapors and also the undeniable existence of fog.

**Bubble in a liquid:** From Eq. (2.19) we see that a negative sign has to be used for a bubble because of the negative curvature of the liquid surface. As a result we get

$$RT \cdot \ln \frac{P_0^K}{P_0} = -\frac{2\gamma V_m}{r} \quad (2.23)$$

Here,  $r$  is the radius of the bubble. The vapor pressure inside a bubble is therefore reduced. This explains why it is possible to overheat liquids: When the temperature is increased above the boiling point (at a given external pressure) occasionally, tiny bubbles are formed. Inside the bubble the vapor pressure is reduced, the vapor condenses, and the bubble collapses. Only if a bubble larger than a certain critical size is formed, is it more likely to increase in size rather than to collapse. As an example, vapor pressures for water drops and bubbles in water are given in Table 2.2.

$r$ (nm)	$P_0^K/P_0$ drop	$P_0^K/P_0$ bubble
1000	1.001	0.999
100	1.011	0.989
10	1.114	0.898
1	2.950	0.339

**Table 2.2:** Relative equilibrium vapor pressure of a curved water surface at 25°C for spherical drops and bubbles of radius  $r$ .

At this point it is necessary to clarify several questions which sometimes cause confusion. When do we use the term “vapor” instead of “gas”? Vapor is used when the liquid is present in the system and liquid evaporation and vapor condensation take place. This distinction is not always clear cut because, when dealing with adsorption (Chapter 9) we certainly take

<sup>6</sup> In general, Ostwald ripening is the growth of large objects at the expense of smaller ones. Wilhelm Ostwald, 1853–1932. German physicochemist, professor in Leipzig, Nobel price for chemistry 1909.

the two corresponding processes — adsorption and desorption — into account but still talk about gas. How does the presence of an additional background gas change the properties of a vapor? For example, does pure water vapor behave differently from water vapor at the same partial pressure in air (in the presence of nitrogen and oxygen)? Answer: To a first approximation there is no difference as long as phenomena in thermodynamic equilibrium are concerned. “First approximation” means, as long as interactions between the vapor molecules and the molecules of the background gas are negligible. However, time-dependent processes and kinetic phenomena such as diffusion can be completely different and certainly depend on the background gas. This is, for instance, the reason why drying in a vacuum is much faster than drying in air.

## 2.6 Capillary condensation

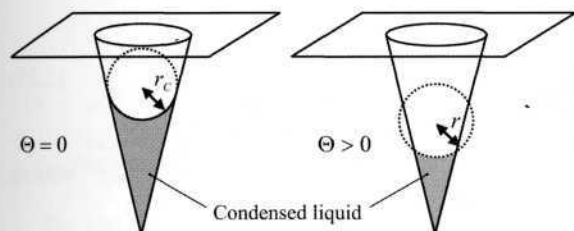
An important application of the Kelvin equation is the description of capillary condensation. This is the condensation of vapor into capillaries or fine pores even for vapor pressures below  $P_0$ ;  $P_0$  is the equilibrium vapor pressure of the liquid with a planar surface. Lord Kelvin was the one who realized that the vapor pressure of a liquid depends on the curvature of its surface. In his words this explains why “moisture is retained by vegetable substances, such as cotton cloth or oatmeal, or wheat-flour biscuits, at temperatures far above the dew point of the surrounding atmosphere” [19].

Capillary condensation can be illustrated by the model of a conical pore with a totally wetting surface (Fig. 2.12). Liquid will immediately condense in the tip of the pore. Condensation continues until the bending radius of the liquid has reached the value given by the Kelvin equation. The situation is analogous to that of a bubble and we can write

$$RT \cdot \ln \frac{P_0^K}{P_0} = -\frac{2\gamma V_m}{r_C} \quad (2.24)$$

The vapor pressure of the liquid inside the pore decreases to  $P_0^K$ , with  $r_C$  being the capillary radius at the point where the meniscus is in equilibrium.

Many surfaces are not totally wetted, but they form a certain contact angle  $\Theta$  with the liquid. In this case the radius of curvature increases. It is not longer equal to the capillary radius, but to  $r = r_C / \cos \Theta$ .



**Figure 2.12:** Capillary condensation into a conical pore with wetting and partially wetting surfaces.

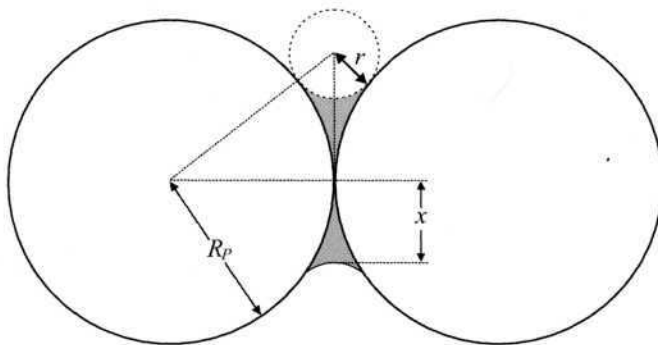
□ **Example 2.6.** We have a porous solid with pores of all dimensions. It is in water vapor at 20°C. The humidity is 90%. What is the size of the pores, which fill up with water?

$$r_C = -\frac{2\gamma V_m}{RT \cdot \ln 0.9} = -\frac{2 \cdot 0.072 \text{ Jm}^{-2} \cdot 18 \times 10^{-6} \text{ m}^3}{8.31 \text{ JK}^{-1} \cdot 293 \text{ K} \cdot \ln 0.9} = 10 \text{ nm}$$

Attention has to be paid as to which radius is inserted into the Kelvin equation. Generally there is no rotational symmetric geometry. Then  $2/r_C$  has to be substituted by  $1/R_1 + 1/R_2$ . In a fissure or crack, one radius of curvature is infinitely large. Instead of  $2/r_C$  there should be  $1/r$  in the equation, with  $r$  being the bending radius vertical to the fissure direction.

Capillary condensation has been studied by various methods, and the validity of the previous description has been confirmed for several liquids and radii of curvature down to a few nanometers [20–23].

An important consequence of capillary condensation is that liquids are strongly adsorbed into porous materials. Another important consequence is the existence of the capillary force, also called the meniscus force. Capillary condensation often strengthens the adhesion of fine particles and in many cases determines the behavior of powders. If, for instance, two particles come into contact, liquid (usually water) will condense into the gap of the contact zone [25]. The meniscus is curved. As a consequence, the Laplace pressure in the liquid is negative, and the particles attract each other.



**Figure 2.13:** Two spherical particles with liquid meniscus.

To calculate the capillary force we take a simple but important example. Two spherical particles of identical radius  $R_P$  are in contact (Fig. 2.13). We further assume that the liquid wets the surface of the particles. This is the case for clays and many other minerals, and water. The total radius of curvature of the liquid surface  $1/R_1 + 1/R_2$  is

$$\frac{1}{x} - \frac{1}{r} \approx -\frac{1}{r} \quad (2.25)$$

In most practical cases we can safely assume that  $x \gg r$ . The pressure is therefore  $\Delta P = \gamma/r$  lower in the liquid than in the outer vapor phase. It acts upon a cross-sectional area  $\pi x^2$  leading to an attractive force of  $\pi x^2 \Delta P$ . We use Pythagoras' theorem to express  $x^2$  by  $r$ :

$$\begin{aligned} (R_P + r)^2 &= (x + r)^2 + R_P^2 \Rightarrow R_P^2 + 2rR_P + r^2 = x^2 + 2xr + r^2 + R_P^2 \\ &\Rightarrow 2rR_P = x^2 + 2xr \approx x^2 \end{aligned} \quad (2.26)$$



For the last approximation we assumed that  $x \gg 2r$ . From this follows  $x^2 = 2rR_P$ . Therefore the attractive capillary force is

$$F = 2\pi\gamma R_P \quad (2.27)$$

The force only depends on the radius of the particles and the surface tension of the liquid. It does not depend on the actual radius of curvature of the liquid surface nor on the vapor pressure! This is at first sight a surprising result, and is due to the fact that, with decreasing vapor pressure the radius of curvature, and therefore also  $x$ , decreases. At the same time the Laplace pressure increases as  $1/r$  increases by the same amount. In addition, there is also a surface tensional force acting between the spheres. Its magnitude  $2\pi x\gamma$  is, however, usually much smaller than the Laplace pressure force.

□ **Example 2.7.** A quartz sphere hangs on a second similar sphere. Some water vapor is in the room which leads to a capillary force. Small particles are held by the capillary force, large particles fall down due to the dominating gravitational force. Beyond which particle radius is gravity strong enough to separate the two spheres? For quartz ( $\text{SiO}_2$ ) we assume a density of  $\rho = 3000 \text{ kgm}^{-3}$ . The weight of the sphere is

$$\frac{4}{3}\pi R_P^3 \rho g = 1.23 \times 10^5 \frac{\text{kg}}{\text{m}^2 \text{s}^2} \cdot R_P^3$$

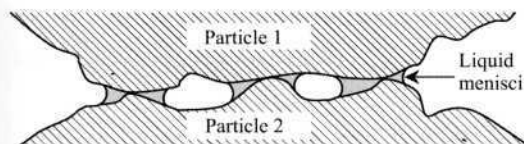
The capillary force is

$$2\pi \cdot 0.072 \frac{\text{J}}{\text{m}^2} \cdot R_P = 0.45 \frac{\text{kg}}{\text{s}^2} \cdot R_P$$

Both are equal for

$$R_P = \sqrt{\frac{0.45}{1.23 \times 10^5} \text{m}^2} = 1.9 \text{ mm}$$

In reality the capillary force is often much smaller than the calculated value. This can be explained by the roughness of the surfaces. The particle surfaces are usually rough and touch only at some points. Capillary condensation takes place only at these points, as illustrated in Fig. 2.14.



**Figure 2.14:** Two particles with rough surfaces in contact.

The surface tension of the liquid itself gives a further direct contribution to the attraction of  $F = 2\pi x\gamma$ . Since  $x \ll R_P$  this contribution is usually small. A calculation of the distance dependence of the capillary force and of adhesion can be found in Refs [24, 26–28].

## 2.7 Nucleation theory

The change of vapor pressure with the curvature of a liquid surface has important consequences for condensation and the formation of bubbles during boiling. The formation of new phase in the absence of an external surface is called homogeneous nucleation. In homogeneous nucleation first small clusters of molecules are formed. These clusters grow due to the condensation of other molecules. In addition, they aggregate to form larger clusters. Finally macroscopic drops form. Usually this happens only if the vapor pressure is significant above the saturation vapor pressure. In most practical situations we encounter heterogeneous nucleation, where a vapor condenses onto a surface such as a dust particle. A well known example of heterogeneous nucleation is the formation of bubbles when pouring sparkling water (or if you prefer beer) into a glass. Bubbles nucleate at the glass surface, grow in size and eventually rise.

Here we only discuss homogeneous nucleation. Though it is less common, the mathematical treatment and the concepts developed are important and are also used for other applications. The classical theory of homogeneous nucleation was developed around 1920-1935 [29, 30]. In order to describe nucleation, we calculate the change in the Gibbs free energy for the condensation of  $n$  moles vapor at a vapor pressure  $P$ , into a drop. Please note that  $n$  is much smaller than one. Keep also in mind that in this chapter,  $P$  is not the total pressure. The total pressure might be higher than the vapor pressure due to the presence of other gases. To calculate the change in Gibbs free energy we first consider  $G_L - G_V$ . Here,  $G_L$  is the Gibbs free energy of the liquid drop and  $G_V$  is the Gibbs free energy of the corresponding number of molecules in the vapor phase.  $G_V$  is given by

$$G_V = nG^0 + nRT \cdot \ln P \quad (2.28)$$

assuming that the vapor behaves as an ideal gas. It is more difficult to obtain an expression for  $G_L$ . To calculate  $G_L$  we use the fact that it is equal to the Gibbs free energy of a (hypothetical) vapor, which is in equilibrium with the liquid drop. This hypothetical vapor has a pressure  $P_0^K$  and its Gibbs free energy is

$$G_L = G_V^{\text{hypothetical}} = nG^0 + nRT \cdot \ln P_0^K \quad (2.29)$$

Since the drops have a curved surface of radius  $r$  the vapor pressure  $P_0^K$  is higher than that of the flat liquid surface. Thus, the difference in the Gibbs energies is

$$G_L - G_V = nRT \cdot \ln P_0^K - nRT \cdot \ln P = -nRT \cdot \ln \frac{P}{P_0^K} \quad (2.30)$$

This, however, is not the whole energy difference. In addition, the drop has a surface tension which has to be considered. The total change in the Gibbs free energy is

$$\Delta G = -nRT \cdot \ln \frac{P}{P_0^K} + 4\pi\gamma r^2 \quad (2.31)$$

In a drop of radius  $r$  there are  $n = 4\pi r^3 / 3V_m$  moles of molecules, where  $V_m$  is the molar volume of the liquid phase. Inserting leads to

$$\Delta G = -\frac{4\pi RT r^3}{3V_m} \cdot \ln \frac{P}{P_0^K} + 4\pi\gamma r^2 \quad (2.32)$$

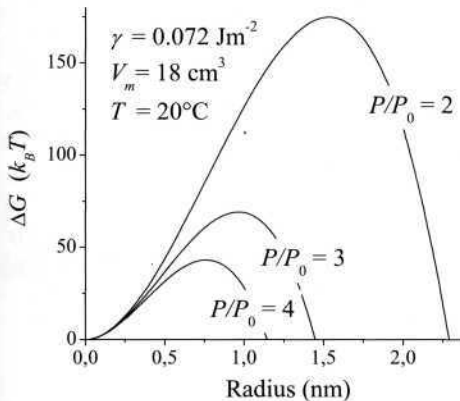
This is the change in Gibbs free energy upon condensation of a drop from a vapor phase with partial pressure  $P$ .

Let us analyse Eq. (2.32) in more detail. For  $P < P_0^K$ , the first term is positive and therefore  $\Delta G$  is positive. Any drop, which is formed by randomly clustering molecules will evaporate again. No condensation can occur. For  $P > P_0^K$ ,  $\Delta G$  increases with increasing radius, has a maximum at the so-called critical radius  $r^*$  and then decreases again. At the maximum we have  $d\Delta G/dr = 0$ , which leads to a critical radius of

$$r^* = \frac{2V_m\gamma}{RT \cdot \ln(P/P_0^K)} \quad (2.33)$$

One (at first sight) surprising fact, is that Eq. (2.32) is equal to the Kelvin equation (2.18). The Kelvin equation applies to systems in thermodynamic equilibrium. Since  $d\Delta G/dr = 0$  the system is formally in equilibrium.

As an example, Fig. 2.15 shows a plot of  $\Delta G$  versus the drop radius for water at different supersaturations. Supersaturation is the actual vapor pressure  $P$  divided by the vapor pressure  $P_0$  of a vapor, which is in equilibrium with a liquid having a planar surface.



**Figure 2.15:** Change of Gibbs free energy for the condensation of vapor to a drop of a certain radius.

□ **Example 2.8.** For water at  $T = 0^\circ\text{C}$  and a supersaturation  $P/P_0 = 4$ , the critical radius is  $R^* = 8 \text{ \AA}$ . This corresponds approximately to 70 molecules. There  $\Delta G_{max} = 1.9 \times 10^{-19} \text{ J}$ .

How does nucleation proceed? In a vapor there are always a certain number of clusters. Most of them are very small and consist only of a few molecules. Others are a little larger. When the actual partial pressure  $P$  becomes higher than the equilibrium vapor pressure  $P_0$ , large clusters occur more frequently. If a cluster exceeds the critical size, thermal fluctuations tend to enlarge it even more, until it becomes “infinitely” large and the liquid condenses.

The aim of any theory of nucleation is to find a rate  $J$  with which clusters of critical size are formed. This number is proportional to the Boltzmann factor  $\exp(-\Delta G_{max}/k_B T)$ .

A complete description of the classical theory of nucleation is not possible within this book. The result is:

$$J = \sqrt{\frac{2\gamma}{\pi m}} \cdot v_m \cdot \left(\frac{P}{k_B T}\right)^2 \cdot \exp\left[-\frac{16\pi v_m^2 \gamma^3}{3 \cdot (k_B T)^3 \cdot \ln^2(P/P_0)}\right] \quad (2.34)$$

Here,  $m$  is the mass and  $v_m = V_m/N_A$  the volume of one molecule.

Classical nucleation theory is the basis for understanding condensation and it predicts the dependencies correctly. Unfortunately, quantitatively the predictions often do not agree with experimental results [31,32]. Theory predicts too low nucleation rates at low temperatures. At high temperatures the calculated rates are too high. Empirical correction functions can be used and then very good agreement is achieved [33]. Ref. [34] reviews experimental methods. General overviews are Refs [35–37].

Experimentally nucleation rates can be determined in expansion chambers [38]. The vapor is expanded in a fast and practically adiabatic process. Then it cools down. Since at low temperatures, the equilibrium vapor pressure is much lower, supersaturation is reached. Partially, this is compensated for by the pressure reduction during the expansion, but the temperature effect dominates. The density of nuclei can be measured by light scattering.

□ **Example 2.9.** The nucleation of water is analysed in an expansion chamber. A vapor at an initial pressure of 2330 Pa at 303 K is expanded to a final pressure of 1575 Pa. In this process it cools down to 260 K. At 260 K the equilibrium vapor pressure is 219 Pa. Thus, the supersaturation reaches  $P/P_0 = 7.2$ . What is the nucleation rate?

At 260 K the surface tension extrapolated from values above 0°C is  $\gamma \approx 77 \text{ mNm}^{-1}$ . The molecular volume is  $v_m = m/\rho = 2.99 \times 10^{-26} \text{ kg}/1000 \text{ kgm}^{-3} = 2.99 \times 10^{-29} \text{ m}^3$ , where  $m$  is the mass of a water molecule. Inserting these values into Eq. (2.34) leads to a nucleation rate of

$$\begin{aligned} J &= \sqrt{\frac{2 \cdot 0.077 \text{ Nm}^{-1}}{\pi \cdot 2.99 \times 10^{-26} \text{ kg}}} \cdot 2.99 \times 10^{-29} \text{ m}^3 \cdot \left(\frac{1575 \text{ Pa}}{3.59 \times 10^{-21} \text{ J}}\right)^2 \\ &\cdot \exp\left\{-\frac{16\pi \cdot (2.99 \times 10^{-29} \text{ m}^3)^2 \cdot (0.077 \text{ Nm}^{-1})^3}{3 \cdot (3.59 \times 10^{-21} \text{ J})^3 \cdot \ln^2 7.2}\right\} \\ &\approx 1.28 \times 10^{12} \text{ s}^{-1} \cdot 2.99 \times 10^{-29} \text{ m}^3 \cdot 1.92 \times 10^{47} \text{ m}^{-6} \cdot e^{-37.9} \\ &= 2.54 \times 10^{14} \text{ s}^{-1} \text{ m}^{-3} \end{aligned}$$

In most practical situations nucleation occurs at certain nucleation sites [39]. One example is the formation of bubbles in champagne [40]. At the end of the fermentation process, the  $\text{CO}_2$  pressure in a bottle of champagne is around 6 atm. When the bottle is opened, the pressure in the vapor phase suddenly drops and an oversaturation of typically 5 is reached. After pouring the champagne into a glass the dissolved  $\text{CO}_2$  molecules escape by forming bubbles (only a small part escapes by diffusion to the surface). Several kinds of particles, which are stuck on the glass wall, are able to entrap gas pockets during the filling of the glass. These particles are responsible for the repetitive production of bubbles rising in the form of bubble trains

(Fig. 2.16). Most of these particles are cellulose fibers coming from the surrounding air or remaining from the wiping process.



**Figure 2.16:** CO<sub>2</sub> bubbles nucleating from champagne at the bottom of a glass. Here, gas pockets entrapped inside cellulose particles serve as nucleation sites. The images, taken with a high speed video microscope, were kindly provided by G. Liger-Belair [40].

## 2.8 Summary

- The surface tension of a liquid is defined as the work required to produce a new surface per unit area:

$$dW = \gamma \cdot dA$$

- Surface tensions of liquids are typically 20–80 mN/m.
- In equilibrium and neglecting gravity, the curvature of a liquid surface is constant and given by the Young–Laplace equation:

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

For a liquid surface with a net curvature there is always a pressure difference across the interface. The pressure on the concave side is higher.

- Important techniques to measure the surface tension of liquids are the sessile drop method, the pendant or sessile bubble method, the Du–Noüy ring tensiometer, and the Wilhelmy-plate method.
- The vapor-pressure of a liquid depends on the curvature of its surface. For drops it is increased compared to the vapor pressure of a planar surface under the same conditions. For bubbles it is reduced. Quantitatively this is described by the Kelvin equation.
- One consequence of the curvature dependence of the vapor pressure is capillary condensation, that is the spontaneous condensation of liquids into pores and capillaries. Capillary condensation plays an important role for the adsorption of liquids into porous materials and powders. It also causes the adhesion of particles. The condensing liquid forms a meniscus around the contact area of two particles which causes the meniscus force.

## 2.9 Exercises

1. We would like to study a clean solid surface. Lets assume we have produced a pure clean surface in UHV (ultrahigh vacuum). We would like to analyze it for 1 h and we can tolerate a contamination of 10% of a monolayer. Estimate to which value we have to reduce the pressure in the UHV chamber. You can assume that on a clean solid surface most of the gas molecules which hit the surface are adsorbed.
2. To apply the sitting or pendant drop method to measure the surface tension of a liquid the drop must be large enough so that gravitation plays a significant role. Why? Could you determine the surface tension from the shape of a tiny drop?
3. A plastic box is filled with water to a height  $h = 1$  m. A hole of radius 0.1 mm is drilled into the bottom. Does all water run out? The plastic is nonwetting.
4. Wilhelmy-plate method. What is the force on a plate of 1 cm width having a contact angle of  $45^\circ$  in water?
5. Drop-weight method. To determine the surface tension of a hexadecane ( $C_{16}H_{34}$ ) you let it drop out of a capillary with 4 mm outer and 40  $\mu\text{m}$  inner diameter. Hexadecane wets the capillary. Its density is  $773 \text{ kg/m}^3$ . 100 drops weigh 2.2 g. Calculate the surface tension of hexadecane using the simple Eq. (2.15) and the correction factor  $f$ . It was concluded that  $f$  should be a function of  $r_c/V^{1/3}$ , with  $V$  being the volume of the drop. Values for the correction factor are listed in the following table (from Ref. [1], p. 19). Is it necessary to use the correction?

$r_c/V^{1/3}$	$f$	$r_c/V^{1/3}$	$f$	$r_c/V^{1/3}$	$f$
0.00	1.0000	0.75	0.6032	1.25	0.652
0.30	0.7256	0.80	0.6000	1.30	0.640
0.35	0.7011	0.85	0.5992	1.35	0.623
0.40	0.6828	0.90	0.5998	1.40	0.603
0.45	0.6669	0.95	0.6034	1.45	0.583
0.50	0.6515	1.00	0.6098	1.50	0.567
0.55	0.6362	1.05	0.6179	1.55	0.551
0.60	0.6250	1.10	0.6280	1.60	0.535
0.65	0.6171	1.15	0.6407		
0.70	0.6093	1.20	0.6535		

6. A hydrophilic sphere of radius  $R_P = 5 \mu\text{m}$  sits on a hydrophilic planar surface. Water from the surrounding atmosphere condenses into the gap. What is the circumference of the meniscus? Make a plot of radius of circumference  $x$  versus humidity. At equilibrium the humidity is equal to  $P_0^K/P_0$ .
7. To measure the surface tension of a liquid a wire of  $r = 1$  mm radius and  $l = 1$  cm length is dipped horizontally into the liquid. The force required to pull the wire out of the completely wetting liquid is measured to be 0.49 mN. What is the surface tension of the

liquid? What if the liquid forms a certain contact angle  $\Theta > 90^\circ$  with the solid surface of the wire? Derive the relationship between force, surface tension, and contact angle. Keep in mind that the three-phase contact line is moving over the surface while pulling the wire out of the liquid.

