# 5 Interfacial Phenomena

Interfacial phenomena are behaviors that occur at the interface or boundary surface between a suspended particle and the continuous phase material in which it is suspended. For this reason, interfacial phenomena are almost always associated with disperse systems. Recall from Chapter 3 that disperse systems consist of discrete particle phases surrounded by a continuous phase medium. The particles can be in the solid, liquid or gaseous phase; and the continuous phase medium can also be solid, liquid or gas. Thus, disperse systems can exist in any one of nine different combinations of particle phase and continuous phase. Some examples of cases where interfaces can be formed are given in Table 5.1.

The key feature of any disperse system is that the two phases cannot be soluble (or miscible) with each other. They must be immiscible, meaning they are incapable of dissolving in each other to form a solution. For example, if we dissolve a small amount of salt or sugar crystals in a glass of water, the crystals disappear, and we have a clear (miscible) solution. The same would be true of mixing alcohol in water. Although two different substances are being mixed together in these examples, the resulting mixtures remain as single phase systems (miscible solutions). They do not have two separate phases. Thus, no interface is formed, and no interfacial phenomena occur.

On the other hand, if we try to mix salad oil (or any oil) in a glass of water, the oil will not mix or dissolve in the water. The oil will separate into small droplets (particle phase) that remain suspended and visible in the continuous water phase. This is an example of a two-phase disperse system. In this type of system, an interface exists between the surface of each droplet (particle phase) and the surrounding liquid (continuous phase) in contact with the particle surface. The various reactions and behaviors that can take place at these types of interfaces are the phenomena to be studied in this chapter.

fluid-fluid interfaces		solid-fluid/solid interfaces		
liquid-gas	e.g. beer – CO <sub>2</sub>	solid-gaseous	e.g. powders, grains (in air)	
liquid-liquid	e.g. water–oil	solid-liquid	e.g. sugar–oil	
gas–liquid	e.g. whipped cream, foam on beer	solid-solid	e.g. glass-plastic (acrylics)	

Table 5.1. Examples of cases where interfaces are formed (based on three aggregate states)

When either one of the phases in a two-phase disperse system is a solid (solid-gas, solid-liquid, solid-solid), the interfaces at the boundary surfaces between particle phase and continuous phase are considered to be rigid interfaces (nonflexible). Rigid interfaces of this type were discussed earlier in the chapters on water activity and geometrical properties about size and shape of disperse systems. In this chapter, we will focus on interfaces between only fluids (gas-liquid), in which the boundary surface between particle phase and continuous phase involves flexible interfaces (nonrigid). These are called fluid interfaces.

Molecules within the interior of the particle or continuous phase material are surrounded by a microenvironment made up of similar neighboring molecules with similar properties. This is different from the microenvironment surrounding molecules on the particle surface at an interface between the two material phases, where their neighbors may be different molecules with different properties. For this reason, molecules at an interface will have different properties from those within the interior material of either phase, such as vapor pressure. Sometimes the region at the interface is called the interfacial phase [1]. Recall from Chapter 1 on water activity, that when water vapor molecules are adsorbed onto a solid food surface, the water molecules accumulating at the solid/liquid interface are in a liquid state, but they do not behave like normal liquid water because they are bound at the interface. In this example, the interface (and the situation of molecular binding at the interface) plays an important role in governing the physical properties of the solid material [2].

More dramatic examples of how interfacial phenomena affect physical properties of materials are when bipolar molecules of surfactants and emulsifiers are adsorbed on interfaces. They can totally change the behavior of the two-phase material to which they are added, such as when soap or detergent (surfactant) is added to suspended particles in water to get a permanent miscible disperse gas and liquid system (foam), or when an emulsifier like lecithin is added to an oil and water disperse system to get a permanent miscible emulsion (mayonnaise). These complex situations occurring at the interface between the surfaces of both phases can be characterized by the forces involved in interfacial tension, more commonly called "surface tension" in the cases of solid–gas and liquid–gas interfaces.

## 5.1 Interfacial Surface Tension

Figure 5.1 illustrates the different microenvironments surrounding molecules on the surface at an interface, and those deep within the interior of a material. A molecule *M* in the interior of the material has neighbors all of the same nature. So, forces of attraction and repulsion are the same in all directions, and the net force acting on the molecule is zero. However, a molecule at the interface will be surrounded by different neighboring molecules at the surface with lesser



**Figure 5.1.** Intermolecular forces at an interface. A molecule M is driven inward away from the interface by the resultant intermolecular force F (surface tension)

attracting forces, like gases. In this case, the net force will not be zero, but will be in the direction into the interior of the phase of interest. Therefore, in order to attract a molecule from the interior to an interface at the surface, this net force acting inward needs to be overcome. As a consequence, the molecules at the interface have a higher energy level than molecules within the interior of the material.

This is the reason why altering conditions at an interface (or a surface) requires input of work or energy, such as in making foams or emulsions. This is also the reason why materials try to minimize the available surface area at their interfaces (minimize the energy required). Liquid droplets take the form of an enclosed volume with minimal surface area (spherical shape). Solids cannot do this, so they are not always in a spherical shape. In that case we characterize their shape with form factors (see Section 3.1.6), which are normally not needed for liquids. Although the interfacial energy requirement is a minimum for spherical droplets, sometimes liquid droplets are not spherical because of other forces acting them, such as falling rain drops are not spheres because of gravimetric weight, drag, and inertia forces acting on them simultaneously.

Recall that in order to attract a molecule from the interior to an interface at the surface, the net force acting inward (surface tension) needs to be overcome. This is illustrated as work energy in Figure 5.2. In order to create an additional segment of interface  $dA = s \cdot db$ , we have to move the piston rod against this force *F* by distance d*b*. This is an element of work energy (force multiplied by distance, or  $dE = F \cdot dB$ ). The energy divided by the newly created area *dA* is called specific interfacial energy  $\sigma$  (specific with respect to a unit of area, not mass).

Thus:

$$\sigma = \lim_{\Delta A \to 0} \frac{\Delta E}{\Delta A} = \frac{dE}{dA}$$
(5.1)  
$$\sigma = \frac{F \cdot db}{s \cdot db} = \frac{F}{s}$$
(5.2)

where

 $\begin{array}{ll} F & \text{interfacial force in N} \\ A & \text{area in m}^2 \\ \sigma & \text{specific interface energy in N} \cdot \text{m}^{-1} \\ db & \text{length in m} \\ s & \text{width in m} \end{array}$ 





The SI units are: 
$$\frac{J}{m^2} = \frac{N \cdot m}{m^2} = \frac{N}{m}$$

The specific interfacial energy  $\sigma$  is also called interfacial stress in the case of surface tension with gases, and is not to be confused with the type of stress (axial or shear) discussed in the chapter on rheology.

So in the engineering design of systems or methods to produce or enlarge an interfacial area, the energy needed can be calculated by:

$$dE = \sigma \cdot dA \tag{5.3}$$

or

$$\Delta E = \sigma \cdot \Delta A \tag{5.4}$$

It is evident that lowering the specific interfacial energy  $\sigma$  would decrease the total energy needed to achieve the new system with the larger interfacial area, and it will be more stable [1,2].

## 5.1.1 Curved (Convex / Concave) Interfaces

When a beaker is overfilled with water, a curved interface is formed at the top surface, and the water reaches a slightly higher level than the rim of the beaker. It looks as though an invisible thin skin would retain the water at the top of the beaker. The reason for this "skin" is what we call "surface tension," and is a result of the interfacial energy discussed previously. This phenomenon is also the reason why the molecules in the inner volume are exposed to a slight pressure which would not be there without that "skin." This pressure is called capillary pressure.

Assume we wish to slightly enlarge a small liquid droplet (increase its volume), as shown in Figure 5.3. An incremental amount of work energy is needed by applying pressure to increase V by dV. This incremental work can be expressed as  $dW = -p \cdot dV$ . Since increasing the volume requires work to flow out of the system, it must be mathematically negative. This type of work is called volume work. To make the volume larger we have to overcome the capillary pressure  $p_{\sigma}$  at the interface.

Thus:

$$\mathrm{d}W_P = -p_\sigma \cdot \mathrm{d}V \tag{5.5}$$



Figure 5.3. Volume increase of a liquid droplet (needs energy because of surface tension)

#### where

 $\begin{array}{ll} W_P & \text{volume work in N} \cdot m \\ W_\sigma & \text{interfacial work in N} \cdot m \\ p_\sigma & \text{capillary pressure in N} \cdot m^{-2} \\ V & \text{volume in m}^3 \end{array}$ 

Considering  $\frac{dV}{dr}$  for a sphere, and taking the volume  $V = \frac{3}{4}\pi \cdot r^3$  of a sphere:

$$\frac{\mathrm{d}V}{\mathrm{d}r} = \frac{\mathrm{d}d}{\mathrm{d}dr} \cdot \left(\frac{4}{3}\pi \cdot r^3\right) = 4\pi \cdot r^2 \tag{5.6}$$

so

$$\mathrm{d}W_P = -p_\sigma \cdot 4\pi \cdot r^2 \cdot \mathrm{d}r \tag{5.7}$$

A larger interface results from increasing the radius of the droplet. The work needed for this enlargement is interfacial work  $dW_{\sigma}$ .

With reference to equation (5.3):

$$\mathrm{d}W_{\sigma} = \sigma \cdot \mathrm{d}A \tag{5.8}$$

For a sphere with  $A = 4\pi \cdot r^2$ :

$$\frac{\mathrm{d}A}{\mathrm{d}r} = \frac{\mathrm{d}}{\mathrm{d}r} \cdot \left(4\pi \cdot r^2\right) = 8\pi \cdot r \tag{5.9}$$

so

 $\mathrm{d}W_{\sigma} = \sigma \cdot 8\pi \cdot r \cdot \mathrm{d}r \tag{5.10}$ 

Applying the law of energy conservation:

$$\mathrm{d}W_{\sigma} + \mathrm{d}W_P = 0 \tag{5.11}$$

respectively,

 $\mathrm{d}W_{\sigma} = -\mathrm{d}W_{P}$ 

so, from equations (5.7) and (5.10) follows

$$\sigma_{12} \cdot 8\pi \cdot r \cdot dr = p_{\sigma} \cdot 4\pi \cdot r^2 \cdot dr \tag{5.12}$$

which means

$$p_{\sigma} = \frac{2\sigma_{12}}{r} \tag{5.13}$$

This is called the capillary pressure after LAPLACE. It is also called "pressure because of curvature." The radius r is the radius of curvature, and is influenced by the capillary pressure. The surrounding pressure outside the droplet " $p_{\sigma}$ " is an over pressure. The LAPLACE equation gives the pressure difference between inside and outside the droplet.

When there is a convex shaped interface on one phase (1) with a radius of curvature  $r_1$  then the pressure difference between this one phase and the surrounding phase (2) is:

$$p_1 - p_2 = \frac{2\sigma_{12}}{r_1} = p_\sigma \tag{5.14}$$

where

$\sigma_{12}$	surface tension (between phase 1 and phase 2) in N $\cdot$ m <sup>-1</sup>
$r_1$	radius of curvature (phase 1) in m
$p_1$	absolute pressure in phase 1 (droplet) in Pa
$p_2$	absolute pressure in phase 2 (surrounding) in Pa
pσ	"over" pressure (= capillary pressure) of phase 1 in Pa

From equation (5.14) it can be seen that the smaller the radius the higher is the capillary pressure.

When the radius *r* is very high, the curvature of the interface is very low. For  $r = \infty$ , the interface is flat. For flat interfaces, LAPLACE's equation gives:  $p_1 - p_2 = p_{\sigma} = 0$  meaning there is no difference in pressure when the interface has no curvature.

The curvature of an interface can be convex or concave. LAPLACE's equation is valid for both types:

The interface of an overfilled glass beaker is convex; so, r > 0. The pressure in the liquid volume is higher than the pressure outside in the surrounding air. The higher this pressure, the smaller will be r. When an interface has a concave curvature, this is indicated by a negative value of r. LAPLACE's equation gives:  $p_1 - p_2 < 0$ . That means the pressure in the phase with the concave interface is lower than the pressure in the surrounding phase. We often see this when measuring a liquid level in a graduated cylinder. The liquid surface at the interface is concave. Now we see the origin of equation (1.1) in Chapter 1 which we used to calculate the water vapor pressure above a capillary filled with water. In a dispersed system of water air, an air bubble in water is an example of a concave surface with respect to the water phase. However, a water droplet in air is an example of a convex surface with respect to the water phase. Table 5.2 shows a systematic approach.

**Problem 5.1.** There are two droplets of different particle size having different capillary pressures. When they touch each other, the different pressures will start to equilibrate. What will happen?

Interface curvature	curvature is	curvature is	no curvature
curvature (of phase1)	concave	convex	flat
	phase 2	phase2	phase 2
looks like (schematic)			
	phase 1	phase 1	phase 1
radius of curvature $r_1$ is	$r_{1} < 0$	$r_1 > 0$	$r_1 = \infty$
$p_1 - p_2 = \frac{2\sigma_{12}}{r_1}$	< 0	> 0	0
in words: in phase 1			
there is	lower pressure than in phase 2	higher pressure than in phase 2	same pressure than in phase 2
examples:	a bubble of gas (air) (phase 2) in water (phase 1). Water (phase 1) –air (phase 2) interface in a capillary	a droplet of wa- ter (phase 1) in air (phase 2)	flat water-air surface

Table 5.2. Capillary pressure at interfaces of different curvature

a) the bigger droplet will decrease in size

b) the smaller droplet will decrease in size

c) both droplets are going to have the same size

For a spherical interface, the radius of curvature r is the same in the x- and y-direction of that interface. Nonspherical interfaces have different radii in the x- and y-direction. LAPLACE's equation is also valid for these interfaces, and then should be used as:

$$p_{\sigma} = \sigma \cdot \left(\frac{1}{r_x} + \frac{1}{r_y}\right) \tag{5.15}$$

With  $r_x = r_y = r$  (sphere) we have again equation (5.13).

#### 5.1.2 Temperature Dependency

Temperature has a significant effect on surface tension (specific interfacial energy). Interfacial energy will decrease with increasing temperature, and will

decrease to zero when a critical temperature is reached at which there is no longer any interface between liquid and gas phases.

A linear mathematical function (model) was developed by Eörvös for predicting the decrease of interfacial energy as a function of temperature for temperature ranges far beyond the critical temperature [1]. However, for this purpose, interfacial energy was based on the amount of substance (in moles), and was not the specific interfacial energy (divided by area) defined earlier.

Let's assume for a moment that a liquid consists of cubic molecules with length *l*. Then, the volume of 1 mole of liquid can be expressed as:

$$V_m = N_A \cdot l^3 \tag{5.16}$$

One of these cubic molecules at an interface would need the space:

$$l^2 = \left(\frac{V_m}{N_A}\right)^{\frac{2}{3}} \tag{5.17}$$

so, 1 mole of the substance would need an interfacial area of:

$$A_m = N_A \cdot l^2 = N_A^{\frac{1}{3}} \cdot V_m^{\frac{2}{3}}$$
(5.18)

so, the interfacial energy can be calculated:

$$\sigma_m = \sigma \cdot A_m = \sigma \cdot N_A^{\frac{1}{3}} \cdot V_m^{\frac{2}{3}}$$
(5.19)

with the volume of a mole of these molecules,

$$V_m = \frac{M}{\rho} \tag{5.20}$$

then

$$\sigma_m = \sigma \cdot N_A^{\frac{1}{3}} \left(\frac{M}{\rho}\right)^{\frac{2}{3}}$$
(5.21)

For this quantity, Eötvös found a linear temperature dependency:

$$\sigma_m = k_E \cdot (T_C - T_\theta - T) \tag{5.22}$$

Substituting (5.19) for the volume into (5.20):

$$\sigma \cdot N_A^{\frac{1}{3}} \cdot M^{\frac{2}{3}} \cdot \rho^{-\frac{2}{3}} = k_E \cdot (T_C - T_\theta - T)$$
(5.23)

and so

$$\sigma = N_A^{-\frac{1}{3}} \cdot M^{-\frac{2}{3}} \cdot \rho^{+\frac{2}{3}} \cdot k_E \cdot (T_C - T_\theta - T)$$
(5.24)

This is the equation after RAMSEY and SHIELD [115] for the temperature dependency of surface tension. For materials like water which have an abnormally high tendency for molecular association, a specific factor  $\chi$  is introduced:

$$\sigma = N_A^{-\frac{1}{3}} \cdot \left(M \cdot \chi\right)^{-\frac{2}{3}} \cdot \rho^{+\frac{2}{3}} \cdot k_E \cdot (T_C - T_\theta - T)$$
(5.25)

.

where	
$k_E$	Eötvös constant
Т	absolute temperature in K
$T_C$	critical temperature in K
$T_{\theta}$	material constant in K
$N_A$	Avogadro's constant
$V_m$	volume of a mole in $m^3 \cdot mol^{-1}$
ρ	density in kg $\cdot$ m <sup>-3</sup>
$\sigma$	surface tension in N $\cdot$ m <sup>-1</sup>
Μ	molar mass in kg $\cdot$ mol <sup>-1</sup>
χ	molecular association factor

Figure 5.4 illustrates the linear relationship between surface tension and temperature after equation (5.25).



**Figure 5.4.** Temperature dependency of surface tension after Eötvös resp. after RAMSEY and SHIELD

*Example 5.1. Surface tension of water-air at 20*  $^{\circ}C$  Using equation (5.25) with the following data:

	for H <sub>2</sub> O
$k_E$	7.5 J · K <sup>-1</sup> mol <sup>-1</sup> (at 20 $^{\circ}$ C)
$T_C$	647.15 K
$T_{\theta}$	6 K
$N_A$	$6.023 \cdot 10^{23} \text{ mol}^{-1}$
ρ	1000 kg $\cdot$ m <sup>-3</sup> (at 20 $^{\circ}$ C)
Μ	$18 \cdot 10^{-3} \mathrm{kg} \cdot \mathrm{mol}^{-1}$
X	0.47

gives:

$$\sigma = \frac{\left(1000 \,\mathrm{kg} \cdot \mathrm{m}^{-3}\right)^{\frac{2}{3}} \cdot 7.5 \,\mathrm{N} \cdot \mathrm{m} \cdot \mathrm{K}^{-1} \cdot \mathrm{mol}^{-1}}{\left(6.023 \cdot 10^{23} \,\mathrm{mol}^{-1}\right)^{\frac{1}{3}} \cdot \left(0.47 \cdot 18 \cdot 10^{3} \,\mathrm{kg} \cdot \mathrm{mol}^{-1}\right)^{\frac{2}{3}}} \cdot \left(647.15 \,\mathrm{K} - 6 \,\mathrm{K} - \mathrm{T/K}\right)$$

This can be simplified to:

$$\sigma = 0.2133 \frac{\mathrm{mN}}{\mathrm{m}} \cdot (368 - \vartheta/^{\circ}\mathrm{C})$$
(5.26)

So, for 20 °C we get  $\sigma = 74.2 \text{ mN} \cdot \text{m}^{-1}$ .

Another way is to measure values of surface tension for different temperatures, and then find a mathematical function to fit this relationship. Two approaches of this type are the following equations: equation (5.27) is a simple linear regression (from [106]). Equation (5.28) is a polynomial regression recommended by the International Association for the Properties of Steam [108].

$$\sigma/\mathrm{mN} \cdot \mathrm{m}^{-1} = 76.056 - 0.1675 \cdot \vartheta/^{\circ}\mathrm{C}$$
 (5.27)

$$\sigma = B \cdot \left(\frac{T_C - T}{T_C}\right)^{\mu} \cdot \left(1 + b \cdot \left(\frac{T_C - T}{T_C}\right)\right)$$
(5.28)

For water:

$$B = 235.8 \cdot 10^{-3} \text{N} \cdot \text{m}^{-1}$$
  

$$b = 0.625$$
  

$$\mu = 1.256$$
  

$$T_C = 647.15 \text{ K}$$

A comparison of the predicted values calculated from these equations with measured experimental data is shown in Table 5.3.

A comparison of experimentally measured data with calculated values shows that equation (5.28) performs best by delivering the best "goodness of fit." It can also be seen that the simple linear regression in equation (5.27) provides predicted values with smaller differences than those predicted by equation (5.26). So we see that the mathematical polynomial fitting provides better predicted values than equation (5.26). However, equation (5.26) is the one which was derived from a theoretical basis. It was developed by considering the simple geometric space needed on a molecular scale. A factor "association

Table 5.3. Surface tension of water: Comparison of measured data with calculated values.

	measured [106]	calculated b	oy (5.26)	calculated l	oy (5.27)	calculated b	oy (5.28)
$\vartheta/^{\circ}C$	$\sigma_{exp}/\mathrm{mN}\cdot\mathrm{m}^{-1}$	$\sigma_{cal}/\mathrm{mN}\cdot\mathrm{m}^{-1}$	difference	$\sigma_{cal}/\mathrm{mN}\cdot\mathrm{m}^{-1}$	difference	$\sigma_{cal}/{ m mN} \cdot { m m}^{-1}$	difference
0.01	75.65	78.50	3.8%	76.05	0.5%	75.65	-0.001%
10	74.22	76.37	2.9%	74.38	0.2%	74.22	0.006%
20	72.74	74.24	2.1%	72.71	0.0%	72.74	0.000%
30	71.20	72.11	1.3%	71.03	-0.2%	71.20	-0.003%
40	69.60	69.97	0.5%	69.36	-0.4%	69.60	0.001%
50	67.95	67.84	-0.2%	67.68	-0.4%	67.95	-0.002%
60	66.24	65.71	-0.8%	66.01	-0.4%	66.24	0.005%
70	64.49	63.57	-1.4%	64.33	-0.2%	64.49	-0.006%
80	62.68	61.44	-2.0%	62.66	0.0%	62.68	-0.003%
90	60.82	59.30	-2.5%	60.98	0.3%	60.82	0.003%
100	58.92	57.17	-3.0%	59.31	0.7%	58.92	-0.004%

constant" was introduced, but no consideration was given to the fact that the factor is dependent on temperature. Moreover, the density was also considered independent of temperature. So, there are opportunities to further improve the "goodness of fit" of (5.26).

These models provide an impression of what options are available for engineering purposes in process simulation. We can obtain experimental data and develop mathematical equations to model these data. We can start with fundamental equations derived from a theoretical basis, and then improve the precision ("goodness of fit") with appropriate mathematical regression analysis. Recall all these options are approximations. The approximations have different "grades of goodness." Even the experimental data carry a given uncertainty because of experimental errors. Often, more complicated equations are needed for improved precision. The choice we make will depend on the question to be answered. For a rough estimate, a simple linear regression equation may suffice, and the more complicated equations are unnecessary. On the other hand, if we make computer simulations for process development, there is no problem for the computer to use the best (even the most complicated) equation in order to obtain results with the greatest precision.

Decisions of these types involve determining what level of precision is needed, what level of computational power is readily available, what time limitations are imposed, what will be the economic impact of lack of precision, etc.

#### 5.1.3 Concentration Dependency

Concentration dependency is important in substances which tend to adsorb at their interfaces. This adsorption significantly influences the surface tension, and for this reason these substances are called "interfacially active" substances. The most common of these substances are emulsifiers and surfactants. An emulsifier is an amphiphilic (bipolar) molecule that will strongly adsorb to an interface between water and air or between water and oil. An amphiphilic molecule is bipolar because one end of the molecule is attracted to one phase in the dispersion, and the opposite end is attracted to the other phase. Thus, these molecules have both lyophilic ("loving or attracting the solvent") and lyophobic ("fearing or rejecting the solvent") properties. In the specific case of water molecules, they are called hydrophilic and hydrophobic properties.

In the case of emulsifiers, this adsorption can lead to a dramatic reduction in the surface tension, even when very small amounts are used. This is because the molecules will reorient themselves within the interfacial layer to reach the lowest energy level possible. This reduces the interfacial energy and thus, the surface tension. Adsorption of additional emulsifier molecules at the interface further decreases the surface tension until all available spaces for these molecules at the interface are occupied. At this point, any further addition of emulsifier molecules will cause them to associate forming micelles. This creates an interface within the system leading to a lower energy state in which interactions with "unfriendly" parts of the molecules are minimized. This association is governed by the size and geometry of the polar groups in the newly formed micelle. There are spherical micelles (see Figure 5.7) and inverse spherical micelles. But, there are also other types like lamellar and hexagonal types [3,136], which are not discussed in any detail here.

So, adsorption of an emulsifier or surfactant leads to a decrease in surface tension with increasing concentration of emulsifier or surfactant until a critical point is reached when micelles begin to form. Then there will be no further decrease in surface tension with further increase in concentration. This critical point in concentration is called the critical micelle formation concentration (cmc). The relation between the surface tension and the emulsifier concentration in the aqueous phase is well known, and is shown graphically, along with the critical micelle formation concentration (cmc) zone in Figure 5.5.

The same graph with  $\sigma - c$  curve is shown with a series of beakers beneath it in Figure 5.6. The beakers beneath the graph indicate the situation at the interface at the different stages of concentration.

Assuming that surfactants form a monolayer between two immiscible phases the amount of surfactant needed (the monolayer concentration) can be calculated using the adsorption models we learned about in Section 1.2, e.g. the FREUNDLICH OF LANGMUIR model (see Section 1.2.3) [136].

SZYSZKOWSKI's equation allows the calculation of the interfacial surface tension as a function of surfactant concentration [22]:

$$\sigma_0 - \sigma = a \cdot \ln\left(1 + \frac{c}{b}\right) \tag{5.29}$$

where

 $\begin{aligned} \sigma & \text{surface tension in N} \cdot \text{m}^{-1} \\ \sigma_0 & \text{surface tension at } c = 0 \\ c & \text{concentration of surfactant in kg} \cdot \text{m}^{-3} \\ b & \text{material specific constant in m}^3 \cdot \text{kg}^{-1} \\ a & \text{material specific constant in N} \cdot \text{m}^{-1} \end{aligned}$ 

In contrast to the addition of emulsifiers which leads to decreased surface tension, there are materials which increase the surface tension when added to



Figure 5.5. Surface tension as function of emulsifier concentration



**Figure 5.6.** After reaching the monolayer at the critical concentration point, cmc, the surface tension remains constant with increasing concentration.



Figure 5.7. Spherical micelle (schematic). The lyophobic parts (drawn as lines) of the molecules are inside the micelle, covered from the surrounding solvent by the lyophilic parts (drawn as balls) of the molecules.

a dispersed system. In the case of aqueous systems these are strong electrolytes (inorganic salts) and hydroxyl compounds like carbohydrates [2]. The increase in surface tension comes about because of strong interaction between these substances and the solvent. This interaction is called negative adsorption or depletion and is a form of hydration which prevents these molecules from adsorption at the interface, and keeps them well within the interior of the continuous phase volume. Strong depletion can lead to forming an interface between two different aqueous phases [16].

## 5.1.4 Liquid–Liquid–Gas Systems

The shape of a liquid droplet dispersed within another liquid in a three-phase system is determined by the interfacial tensions between the phases. Such a droplet is shown in Figure 5.8. The droplet consists of phase 3, and is dispersed at the interface between phases 2 and 1. In this situation, three interfacial tensions are acting on the droplet,  $\sigma_{12}$ ,  $\sigma_{13}$  and  $\sigma_{23}$ , which are causing the shape of the droplet not be a sphere.



Figure 5.8. Interfacial tensions at the point where three phases are in contact. For example, phase1 is a gas, phase 2 is liquid A, and phase 3 is liquid B.

Figure 5.9. Addition of vectors in Figure 5.8

The values of the vectors  $\sigma_{12}$ ,  $\sigma_{13}$  and  $\sigma_{23}$  are governed by the substances of which phases 1, 2, 3 are made, but the direction of each vector is a matter of static equilibrium. The equilibrium is reached when tension  $\sigma_{12}$  at the point of contact has the same value as the resulting vector resolved from addition of  $\sigma_{13}$  and  $\sigma_{23}$ . That means that the resulting contact angle  $\varphi_3$  can have only one possible value, as shown in Figure 5.9.

With the help of the cosine function for an obtuse angle:

$$c^{2} = a^{2} + b^{2} - 2a \cdot b \cdot \cos \gamma \tag{5.30}$$

according to Figure 5.9 we can write

$$\sigma_{12}^{2} = \sigma_{13}^{2} + \sigma_{23}^{2} - 2\sigma_{13} \cdot \sigma_{23} \cdot \cos \gamma$$
(5.31)

because of

 $\alpha + \beta = \varphi_3 \tag{5.32}$ 

and

$$\gamma + \varphi_3 = 180^\circ \tag{5.33}$$

or

$$\gamma = 180^{\circ} - \varphi_3 \tag{5.34}$$

then

 $\cos \gamma = -\cos \varphi_3 \tag{5.35}$ 

and therefore

$$\sigma_{12}^{2} = \sigma_{13}^{2} + \sigma_{23}^{2} - 2\sigma_{13} \cdot \sigma_{23} \cdot \cos \varphi_{3}$$
(5.36)

so

$$\cos\varphi_3 = \frac{\sigma_{12}^2 - (\sigma_{13}^2 + \sigma_{23}^2)}{2 \cdot \sigma_{13} \cdot \sigma_{23}}$$
(5.37)

case	$\varphi_3$	$\cos \varphi_3$	shape of phase 3	example
Ι	pprox 0	is $\approx 1$	film on phase 2	gasoline on water
II	$0^{\circ}-90^{\circ}$	is positive and $\ll 1$	lens on phase 2	olive oil on water
III	$90^{\circ}$ – $180^{\circ}$	is negative	sphere on phase 2	water on silicone oil

Table 5.4. Typical cases of contact angles on a liquid underlying phase

For equation (5.37) we want to distinguish three cases: contact angle  $\varphi_3$  above 90°, below 90° or equal to zero. In Table 5.4 the consequences for these three cases are listed.

Let us focus on the droplet behavior from an energetic point of view: In case I, formation of a film, an increased adhesion between phases 2 and 3 takes place. Adhesion energy is released. In cases II and III, formation a lens or sphere, instead of adhesion now cohesion of phase 3 is taking place. Cohesion energy is released. The difference between adhesion energy and cohesion energy characterizes the ability of the system to form a film on the underlying phase and is called spreading pressure. This pressure characterizes the tendency for forming a film on the underlying phase. When a small amount of this liquid is dropped on the underlying phase, the liquid spreads along the interface forming a thin film. The thickness of this film can be decreased down as far as the monolayer thickness. The spreading pressure also drives the spreading rate when surfactant molecules spread onto newly generated interfaces e.g. during foaming or emulsifying processes [136].

#### 5.1.5 Solid–Liquid–Gas systems

When a liquid droplet forms onto a solid interface, the shape of the droplet is governed by the interfacial tensions of the phases in contact (see Figure 5.10).



Figure 5.10. Interfacial tensions at the point of contact between three phases with phase 2 being solid. For example, phase 3 is a liquid and phase 1 is a gas.

We can derive the following from Figure 5.10:

In equilibrium we have

 $\sigma_{12} = \sigma_{23} + \sigma_{13} \cdot \cos \varphi_3 \tag{5.38}$ 

This is called YOUNG's equation.

With the abbreviation  $\varphi \equiv \varphi_3$ , this means

$$\cos\varphi = \frac{\sigma_{12} - \sigma_{23}}{\sigma_{13}} \tag{5.39}$$

case		$\cos \varphi$	$\varphi$	consequence
Ι	$\sigma_{12} - \sigma_{23} \geq \sigma_{13}$	$\cos \varphi \ge 1$	= 0	complete wetting, phase 3 forms a film on a solid surface
II	$0 > \sigma_{12} - \sigma_{23} < \sigma_{13}$	$0 > \cos \varphi > -1$	$90^\circ > \varphi > 180^\circ$	partial wetting, phase 3 forms flat wet spots on solid surface
III	$0 < \sigma_{12} - \sigma_{23} < \sigma_{13}$	$0 < \cos \varphi < 1$	$90^\circ > arphi > 0^\circ$	no wetting, phase 3 forms droplets on a solid sur- face

Table 5.5. Typical cases of contact angles on a solid underlying phase



Figure 5.11. A liquid on a solid interface: I: complete wetting (film forming), II: partial wetting, III: no wetting

**Figure 5.12.** Contact angle  $\varphi$  below 90° (left), and above 90° (right)

Let us again focus on three cases where the contact angle  $\varphi$  is above or below 90° or equal to zero. In Table 5.5 these cases and their consequences are listed. In Figure 5.11 and Figure 5.12 the different behaviors are illustrated.

## 5.1.6 Kinetics of Interfacial Phenomena

The effect of decreasing the interfacial tension by adsorption of polar (amphiphilic) molecules at the interface is an equilibrium state. Until the equilibrium is reached these molecules must do the following:

- (eventually) detach from a micelle
- find their way to the interface (diffusion)
- adjust to the proper orientation in order to adsorb
- find available space at the interface for adsorption.

For engineering processes like formation of bubbles (foaming) and forming of droplets (emulsifying), it is important to have information about the kinetics of these steps (speed or rate in which they occur) [4,15]. The kinetics of interfacial adsorption can be studied by measurement of interfacial tension over time, as discussed in the following subsection.

#### 5.1.7 Adsorption Kinetics at Solid Interfaces

When molecules from a liquid phase are going to become adsorbed onto a solid interface, they must undergo the same procedural steps listed above. Let us imagine macromolecules like proteins which are to be adsorbed onto a solid. They must first undergo diffusion to the interface before they can be adsorbed. Then they have to adjust to the right spatial orientation, and then they must find an available space on the interface. Because of the bonding forces between such a macromolecule and the solid surface, the adsorption isotherm (see Section 1.2) often has the form of the LANGMUIR isotherm, which has the typical profile for adsorption at the monolayer, with maximum interfacial concentration (see Table 1.4). The kinetics of processes like this can also be studied by interfacial tension measurement over time. The opposite case, in which desorption of macromolecules from the interface into the volume of the liquid occurs, is called depletion. It can be identified by an increase of interfacial tension over time.

## 5.2 Measurement

#### 5.2.1 Measuring Interfacial Tension

One of the methods used for measurement of interfacial (surface) tension is known as the bow wire method. Figure 5.13 shows a schematic of how this method is applied. A piece of wire of length l is lifted for a distance dh out of a liquid interface. This causes the interfacial surface area to increase by  $dA = 2 \cdot l \cdot dh$ . The force F necessary for lifting the wire is measured and used to calculate the surface tension.

An alternative is the "ring method" after Du Nouy. In this method, a ring made of platinum wire is used. Like in Figure 5.13 the wire ring is lifted a distance dh, resulting in the interfacial area increasing by  $dA = 2 \cdot l \cdot dh$  with the circumference of the ring. Measuring *F* and using equation (5.2) the following expressions can be derived:



Figure 5.13. Schematic for measuring surface tension with the bow wire. 1: forcemeter, 2: bow wire, 3: horizontal piece of wire, 4: liquid sample

$$\sigma = \frac{\mathrm{d}E}{\mathrm{d}A} = \frac{F \cdot \mathrm{d}h}{2 \cdot l \cdot \mathrm{d}h} = \frac{F}{2 \cdot \pi \cdot d}$$
(5.40)

Another possibility is using a vertical plate instead of a wire ring or straight wire. In Figure 5.14 the so-called WILHELMY plate is shown. The interfacial force on a plate like this is:

$$F = \sigma \cdot 2 \cdot l \cdot \cos \varphi \tag{5.41}$$

where

 $\sigma \qquad surface tension in N \cdot m^{-1}$  $F \qquad force in N$  $E \qquad interface energy in N \cdot m$  $A \qquad interface area in m^2$  $l \qquad length in m$  $h \qquad height in m$  $d \qquad diameter in m$ 

The wire ring and vertical plate techniques after DE NOUY and WILHELMY are often used to measure the surface tension of aqueous solutions. However, they can also be used to measure the interfacial tension between two liquids. Then, in that case, the effects from buoyancy and wetting properties have to be taken into account. In equation (5.40) it was assumed that the liquid in Figure 5.13 was wetting the ring or the plate in an ideal manner, i.e. the contact angle  $\varphi = 0$  (see Figure 5.14). For interfaces between water and hydrophilic solids this approximation is mostly valid.

Another method of approach for measuring interfacial tension is to use capillary pressure. When a glass capillary tube is dipped vertically into a beaker with water, water will flow up the capillary tube to a certain height forming a concave meniscus at the air-water interface (Figure 5.15).

The height depends on the capillary diameter, interfacial tension and contact angle between liquid and solid material. The evaluation is based on LAPLACE's equation. Recall in a liquid with a concave interface, there is lower pressure compared to the phase behind the interface (in this case, air). The lower pressure sucks the liquids into the capillary until the equilibrium vertical height is reached. The equilibrium is reached when the pressure on both sides of the meniscus (interface with curvature in Table 5.2 is the same. That



Figure 5.14. WILHELMY plate



**Figure 5.15.** Capillary action (rise in liquid level in capillary tube) to evaluate interfacial tension

occurs when the hydrostatic pressure of the water in the capillary (below the interface) reaches the capillary pressure.

To calculate the capillary rise, we first calculate the specific interfacial energy to raise the liquid in the capillary:

$$dE = F_A \cdot \cos \varphi \cdot dh \tag{5.42}$$

With the wetted area in the capillary

$$\mathrm{d}A = 2\pi \cdot r_K \cdot \mathrm{d}h \tag{5.43}$$

the specific interfacial energy is:

$$\sigma = \frac{dE}{dA} = \frac{F \cdot dh}{2 \cdot \pi \cdot r_K \cdot dh} = \frac{F_A \cdot \cos \varphi}{2\pi \cdot r_K}$$
(5.44)

With the interfacial force acting on the liquid

$$F = 2\pi \cdot r_K \cdot \sigma \tag{5.45}$$

and its vertical component is

$$F_A = F \cdot \cos \varphi = 2\pi \cdot r_K \cdot \sigma \cdot \cos \varphi \tag{5.46}$$

The contact angle  $\varphi$  in Figure 5.15 between the wall of the capillary and the liquid interface – sometimes called the wetting angle – depends of the materials used. Materials with ideal wetting properties have zero contact angle ( $\varphi = 0$ ). In that case,  $\cos \varphi = 1$ , and there is no influence on the calculated value in equation (5.51).

The weight force of the liquid in the capillary is

$$F_G = \pi \cdot r_K^2 \cdot h \cdot g \cdot \Delta \rho \tag{5.47}$$

In case of a liquid-air surface, it is

$$\Delta \rho = (\rho_{Fluid} - \rho_{air}) \approx \rho_{Fluid} \tag{5.48}$$

so

$$F_G = \pi \cdot r_K^2 \cdot h \cdot g \cdot \rho_{Fluid} \tag{5.49}$$

At equilibrium, this force is equal to that in (5.46)

(5.50)

$$\pi \cdot r_K^2 \cdot h \cdot g \cdot \rho_{Fluid} = 2\pi \cdot r_K \cdot \sigma \cdot \cos \varphi$$

and, therefore

$$\sigma = \frac{h \cdot r_K \cdot g \cdot \rho_{Fluid}}{2 \cdot \cos \varphi}$$
(5.51)

with the ideal case  $\varphi = 0$  i.e.  $\cos \varphi = 1$ 

$$\sigma = \frac{h \cdot r_K \cdot g \cdot \rho_{Fluid}}{2} \tag{5.52}$$

where

$\sigma$	interfacial tension in N $\cdot$ m <sup>-1</sup>
$F_A$	interfacial force in N
$F_G$	weight force in N
Ε	specific interfacial energy in N $\cdot$ m <sup>-1</sup>
Α	interface area in m <sup>2</sup>
$r_K$	capillary radius in m
f	correction factor for droplet radius
h	height in m
g	acceleration of gravity in $m \cdot s^{-2}$
$\rho_{Fluid}$	density of fluid in kg $\cdot$ m <sup>-3</sup>
φ	contact angle
т	mass of a droplet in kg
V	volume of a droplet in m <sup>3</sup>
	-

There are further possibilities for measuring the interfacial tension based on capillary action. The general principle is to measure geometric quantities like diameter, radius or volume of droplets or bubbles, and calculate  $\sigma$  by applying LAPLACE's equation.

A simple technique is to form droplets with a pipette of given orifice. By measuring the volume of the droplets, the interfacial tension can be calculated. This type of drop forming pipette is called a stalagmometer, Figure 5.16 shows an example. An easy way of working with a stalagmometer is to drop a known volume, count the number of drops and calculate the average volume of one drop. Another way is to drip a fixed number of drops, e.g. 20 into a beaker on a balance and measure the average mass of a drop.

The evaluation of interfacial tension is based on the equilibrium of weight force of a drop and force of adhesion to the capillary: With the weight force  $m \cdot g$  of a drop and the adhesion force  $2\pi \cdot r_K \cdot f \cdot \sigma$  in equilibrium it is

$$m \cdot g = 2\pi \cdot r_K \cdot f \cdot \sigma \tag{5.53}$$

called TATE's law and so

$$\sigma = \frac{m \cdot g}{2\pi \cdot r_K \cdot f} \tag{5.54}$$

in case the drop volume was measured:

$$\sigma = \frac{\rho \cdot V \cdot g}{2\pi \cdot r_K \cdot f} \tag{5.55}$$





When drops are formed out of a small capillary, the droplet radius is larger than the capillary radius. A correction factor f (which is available from tables) is introduced to take account for this.

Other techniques based on this principle also compare gravitational force with adhesive force. They are called the pendant drop method and sessile drop method (see Figure 5.17). It is important to note that LAPLACE's equation is valid for both convex and concave interfaces. So, instead of a sessile or pendant drop, these experiments can be performed with a sessile bubble or a pendant bubble. In case of bubbles (see bubble point tensiometer in Figure 5.18) the buoyancy force has to be taken as gravitational force. By reading the pressure p in the capillary and using equation (5.15) we can get the surface tension between gas and liquid of interest.

When a drop is rotated, its shape is changed until centrifugal forces and interfacial forces are in equilibrium. The microscopic observation of a rotating drop to measure the interfacial tension is called the spinning drop method (Figure 5.19). Because of temperature dependency (recall Section 5.1.2) all measurements of these types must be carried out under good temperature control.

*Example 5.2.* A liquid in a glass capillary of 1 mm diameter rises to a height of 28 mm. What is the surface tension of the liquid?

Using equation (5.51) and assuming contact angle to be zero and it is:

$$\sigma = \frac{10^3 \,\mathrm{kg} \cdot \mathrm{m}^{-3} \cdot 28 \cdot 10^{-3} \,\mathrm{m} \cdot 9.81 \,\mathrm{m} \cdot \mathrm{s}^{-2} \cdot 0.5 \cdot 10^{-3} \,\mathrm{m}}{2} = 68.7 \,\mathrm{mN} \cdot \mathrm{m}^{-1}$$

*Example 5.3.* We have a liquid with surface tension of 70 mN  $\cdot$  m<sup>-1</sup>. To what height can we expect it to rise in a capillary with a diameter of D = 0.5 mm?



Figure 5.19. Schematic of spinning drop method. 1: heating jacket around rotating tube, 2: drop, 3: liquid in rotating tube

Ø 

Using equation (5.51) and assuming the contact angle to be zero then

3

mm

$$h = \frac{2 \cdot \sigma}{r_K \cdot \rho \cdot g}$$

so

$$h \approx \frac{4 \cdot 70 \cdot 10^{-3} \text{N} \cdot \text{m}^{-1}}{D/\text{m} \cdot 10^3 \text{ kg} \cdot \text{m}^{-3} \cdot 10 \text{ m} \cdot \text{s}^{-2}} = \frac{280 \cdot 10^{-4} \text{ m}}{D/\text{m}}$$
$$h \approx \frac{28 \text{mm}}{D/\text{mm}}$$

In this way, we can create a table listing the height to which a liquid will rise in capillaries of different diameter:

D / mm	<i>h /</i> mm
0.5	56
1	28
2	14
5	5.6
10	2.8

## 5.2.2 Measuring Contact Angle

Measuring the contact angle with use of YOUNG's equation (5.39) can provide information about interfacial tension and wetting ability, and can also give information about kinetics of interfacial effects. Contact angle measurement is normally performed by optical means. With the help of an optical instrument, along with appropriate image processing software, the shape of a single droplet can be analyzed and evaluated. This is called drop shape analysis (DSA).

The contact angle can also be approximated with the WILHELMY method. The interfacial force on the WILHELMY vertical plate depends on the contact angle,  $\varphi$ , and so it can be calculated. Sometimes, the WILHELMY plate is moved in and out of the liquid to measure the contact angles for "wetting" and "unwetting," which may be different. Then, the readings have to be corrected for buoyancy effects. This is called the dynamic WILHELMY technique [5].

When the contact angle between a liquid and a porous solid (or powder particles) has to be measured, it can be performed with the technique after WASHBURN. In this technique, the powder is placed in a glass tube with a filter at the bottom, all of which hangs from a balance. By dipping the filter bottom into the liquid of interest, the powder begins to become wetted. By recording the weight gain of the powder (moisture uptake), the wetting progress can be studied over time. The WASHBURN method also includes plotting the square of the weight gain versus time, which normally appears as a straight line. From the slope of this line, the contact angle can be calculated [14], as follows:

$$t = \frac{\eta}{C \cdot \rho^2 \cdot \sigma \cdot \cos \varphi} \cdot m^2 \tag{5.56}$$

where

ttime after contact in s $\sigma$ interfacial tension in N  $\cdot$  m<sup>-1</sup>Cconstant of solid sample $\eta$ viscosity in Pa  $\cdot$  s $\rho$ density of fluid in kg  $\cdot$  m<sup>-3</sup> $\varphi$ contact anglemmass of liquid adsorbed in kg

#### 5.2.3 Dynamic Measurement

In order to study the kinetics of interfacial effects, measurements have to be performed over time [6, 7]. Dynamic interfacial tension measurements are based on the principle of generating a "fresh" interface area, and observe how the surface tension changes over time on the way to reaching equilibrium. In order to study liquid–liquid interfaces, small droplets are formed through a narrow orifice at a given rate. When the gravitational force of a droplet exceeds the interfacial force, it detaches from the orifice. The time period between



Figure 5.20. Tension versus surface age (schematic)

"birth" of a droplet and its detachment (lifetime) is identical to the age of the interfacial area. The interfacial tension of a droplet with a given interfacial age can be calculated as shown in equation (5.55) for a stalagmometer. By increasing the droplet formation rate, different ages can be scanned, and interfacial tension can be plotted versus lifetime of the interface. This method can be used to study how fast an emulsifier or surfactant can act in decreasing the surface tension of a system. For fast processes like emulsification or homogenization, fast interfacial kinetics are desirable. If a surfactant or emulsifier is too slow, new droplets are not stabilized fast enough, and the desired quality of emulsion or dispersion cannot be achieved in spite of good equipment performance. Other techniques are the overflowing cylinder technique [6,18] and dynamic bubble pressure method [17,19] and the drop volume method [20] which allows for time resolved measurement of interfacial tensions [21,22].

Also, similar to surface tension, the contact angle (e.g. of a droplet on a surface) can be measured and recorded over time to study the kinetics of wetting processes.

#### 5.3 Applications

ice cream: foam stability and interface properties	[8-10]
chocolate: emulsifiers and physical properties of chocolate	[11]
whey protein: foam stability and interface properties	[12]
emulsions: adhesion on packaging materials and equipment surfaces	[13]
membrane emulsification: effects of interfacial tension	[7,15]
interfacial properties of water / water emulsions	[16]
wine tears: forming by interfacial tension gradient	[136]
liquid films: MARANGONI effect enhances film stability	[136]
foam stability: milk protein surfactant system	[23,26]
proteins adsorbed at O/W interfaces: dynamic measurement	[24]
galactomannans: emulsification activity	[25]

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