

Chapter 2

Capillary phenomena

2.1 Thermodynamic stability

Dispersions are – more often than not – thermodynamically unstable, in other words the general tendency for a dispersion is to separate into the phases that it was originally composed of. This process is initiated by aggregation of the entities that form the dispersed phase. On these larger clusters or flocs of dispersed phase the dispersive effect of Brownian motion is much less than on the original entities and sedimentation or creaming initiates the process of phase separation.

The Gibbs energy G of a dispersion depends on temperature T , pressure p , mole numbers n_j of the various components, and surface area A . It reads

$$dG = -SdT + Vdp + \sum_j \mu_j n_j + \gamma dA \quad (2.1)$$

with V the volume of the dispersion, μ_j the chemical potential of component j , and γ the surface tension. The Gibbs energy mainly depends of two groups of contributions because pressure and temperature are usually kept constant. The term with the chemical potential accounts for solubility effects and in particular for the contributions of surface active components. The other term accounts for the larger Gibbs energy due to the larger surface area inside a dispersion. The fact that the total entropy of the system increases upon dispersion has no major effect here.

2.2 Surface free energy

From numerous experiments it is known, that the force F needed to pull a needle from a liquid surface – corrected for attaching liquid volume – is proportional to the length L of the needle, see figure 2.1, where the proportionality factor is a constant for a given liquid

$$F = 2\gamma L \quad (2.2)$$

The proportionality factor, apart from a factor 2, is called the *surface tension* γ of the liquid-air interface and its dimension is N/m.

By pulling the needle a distance dh from the liquid, the surface area A of the liquid increases by an amount of $dA = 2Ldh$, the factor 2 arises because on either side of the needle a surface area Ldh is created. The work needed to bring this surface increase about is given by

$$dW = Fdh = \gamma dA \quad (2.3)$$

From this latter expression one deduces the dimension of the surface tension to be J/m^2 which is indeed equivalent to N/m .

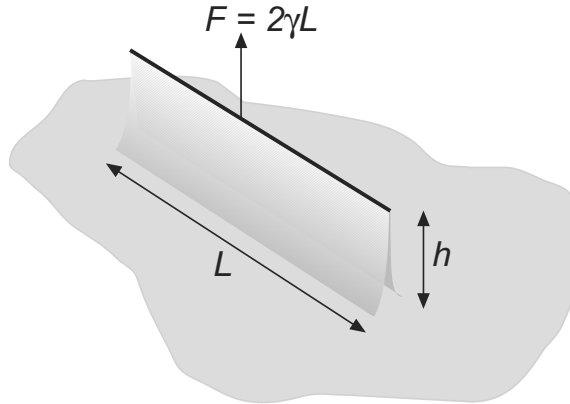


Figure 2.1 Pulling a needle from a liquid surface.

As an example, consider a needle of 5 cm at the air-water interface. The surface tension of water is equal to 73 mJ/m^2 and so the force that is required to pull the needle from the surface is equal to 7.3 mN.

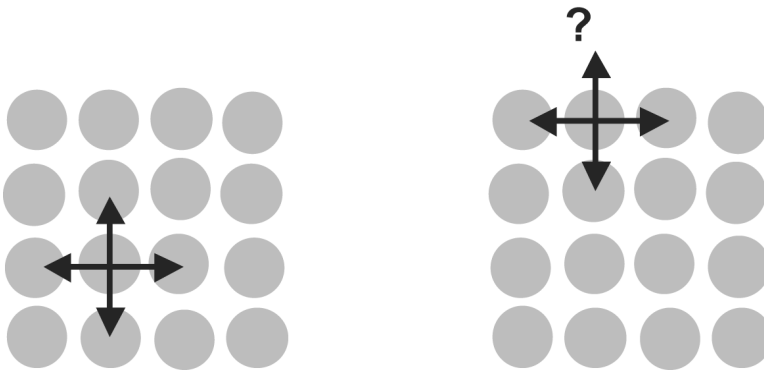


Figure 2.2 Left: molecule in the bulk, right: molecule at the surface.

The origin of surface tension lies in the frustration of the molecules that are located in the surface. Consider figure 2.2 where the situation of a molecule at the surface (right panel) is compared to that of a molecule in the bulk (left panel). The molecule in the bulk is typically surrounded by z neighboring molecules where z is the coordination number. The total (negative) interaction energy of this molecule is given by

$$u_{bulk} = \frac{z}{2} w_{AA} \quad (2.4)$$

where w_{AA} is the interaction energy, due to van der Waals interactions, between a pair of molecules. At the surface, there is at least one unsatisfied bond so that the surface

coordination number z_s is less than the bulk coordination number z . The interaction energy of a molecule at the surface is hence given by

$$u_{surf} = \frac{z_s}{2} w_{AA} \quad (2.5)$$

The surface excess energy is now readily calculated to be

$$\gamma = \frac{u_{excess}}{\sigma} = \frac{z_s - z}{2\sigma} w_{AA} \quad (2.6)$$

where σ is the area that a single surface molecule occupies.

As an example, consider carbontetrachloride for which the vaporization enthalpy is given by $\Delta_{vap}H^\ominus = 29.7$ kJ/mol. From this vaporization enthalpy the typical energy between neighboring molecules is estimated to be

$$w_{AA} = -\frac{\Delta_{vap}H^\ominus}{N_A z/2} = -\frac{29.7 \text{ kJ/mol}}{6.0 \cdot 10^{23} \times 6/2 \text{ mol}^{-1}} = -1.6 \cdot 10^{-20} \text{ J} \quad (2.7)$$

where it is assumed that the typical coordination number is 6 for carbontetrachloride. This appears to be a relatively small number, but it still amounts to about $-4 k_B T$. The typical surface area per surface molecule is estimated from the typical distance between the molecules, which is for a fluid of molecular mass 154 g/mol and density 1.6 kg/dm³ approximated by

$$d = \sqrt[3]{\frac{M}{\rho N_A}} = \sqrt[3]{\frac{154 \cdot 10^{-3}}{1.6 \cdot 10^3 \times 6.0 \cdot 10^{23}}} = 0.54 \text{ nm} \quad (2.8)$$

so that $\sigma = 0.3 \text{ nm}^2$. Assuming that the surface coordination number of carbontetrachloride is one less than the bulk coordination number we arrive at an estimate for the surface tension of

$$\gamma = \frac{z_s - z}{2\sigma} w_{AA} = \frac{5 - 6}{2 \times 0.3 \cdot 10^{-18}} \times (-1.644 \cdot 10^{-20}) \text{ J/m}^2 = 27.4 \text{ mJ/m}^2 \quad (2.9)$$

which is to be compared to the tabulated value of 26.4 mJ/m². The above example demonstrates two facts

- The vaporization enthalpy, which indeed essentially consists of breaking all the bonds that molecules have in the liquid phase, provides for a good estimate of the interaction energy between molecules and hence for the surface tension.
- The picture of the “frustrated molecule” is essentially correct.

The experiment described above is in essence the principle according to which many methods for surface tension measurement work. Examples are the Wilhelmy plate method that uses a platinum plate and the Du Noüy ring method.

2.3 The Five Laws of Interfacial Engineering

The energy cost involved in the increase in surface area manifests itself in five specific ways. Each of these ways can be manipulated specifically and offers the possibility to control the process at hand.

2.3.1 Hamaker's law

The work per unit area that is needed to separate two identical surfaces by a distance h , the cohesion energy as depicted in figure 2.3, is given by

$$\frac{W}{A} = -\frac{A_H}{12\pi h^2} \quad (2.10)$$

with A_H the so called Hamaker coefficient. At closest separation h_{min} , which is of molecu-

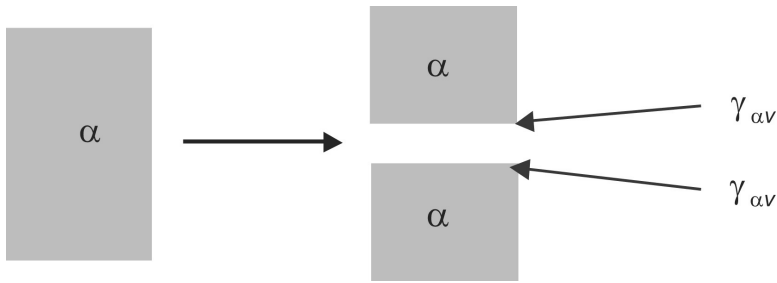


Figure 2.3 Work of cohesion.

lar size, this work is just twice the surface tension between the material and air (vacuum). Equating both results leads to a relatively easy way to estimate the Hamaker coefficient which can be summarized as

$$\frac{W}{A} = -\frac{2\gamma h_{min}^2}{h^2} \quad (2.11)$$

The above equation gives the (macroscopic) *van der Waals interaction* between two flat surfaces. For many geometries the van der Waals interaction has been calculated, for instance for two identical spheres of radius a and separation h it is given by¹

$$W = -\frac{A_H a}{12h} \quad (2.12)$$

2.3.2 Young's law

When a droplet of liquid is put on a solid surface there are three interfaces, one between solid and liquid, one between solid and air (vapor), and one between liquid and air. Each of these interfaces will try to minimize its surface area. At the contact line, this leads to opposing forces as depicted in figure 2.4. The projection of the forces in the plane of the solid surface gives rise to the force balance which is known as *Young's law*²

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \quad (2.13)$$

with θ the *contact angle*.

For a vanishing contact angle, the liquid spreads over the surface to completely wet it. In contrast, when the contact angle is 180° the droplet lies on the surface without any

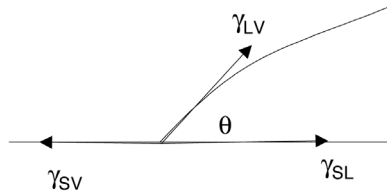


Figure 2.4 Contact angle of a drop on a surface.

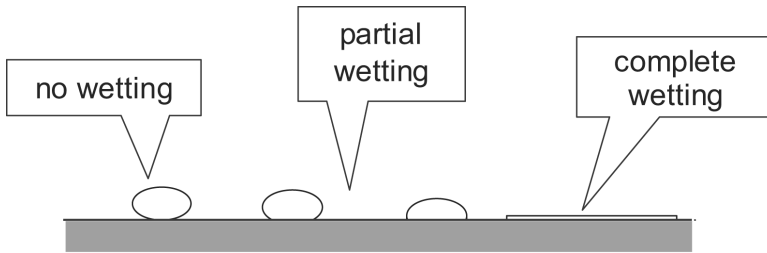


Figure 2.5 Various wetting situations.

flattened part except for the deformation due to gravity. For intermediate contact angles one passes from completely wetting, through partial wetting to non-wetting as the contact angle changes from 0° to 180° . Measurement of the contact angle is often used to compare surface tensions of solid surfaces.

2.3.3 Laplace's law

In many situations one encounters the case of droplets of one phase dispersed in another continuous phase, see figure 2.6. The consequence of the general tendency of the interfacial surface to become as small as possible has two consequences here. The one is that the droplet tries to acquire the minimal surface that is possible with the given volume of material, which results in the spherical form for liquid droplets in a fluid continuum. The other is, that a pressure difference $\Delta p = p_{in} - p_{out}$ between inside and outside develops that is commonly known as the *Laplace pressure*.

$$\Delta p = \frac{2\gamma}{a} \quad (2.14)$$

in which γ is the surface tension and a the radius of the droplet. A more elaborate form of Laplace's equation can be constructed using the local curvatures of a surface. A discussion of this more involved situation is deferred to a subsequent section. The Laplace pressure is significant for colloidal systems, for $1 \mu\text{m}$ droplets of water in air it amounts to 1.5 Bar.

¹See J. Israelachvili, *Intermolecular and Surface Forces*, Academic Press 1992, Chapter 11.

²For a solid or liquid drop on a liquid surface similar albeit more involved equations can be formulated.

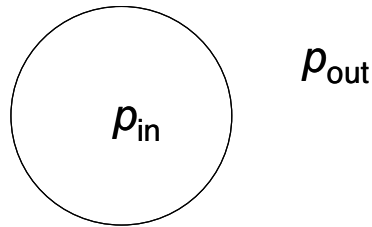


Figure 2.6 Droplet of one phase in another continuous phase.

The proof of the statement that the sphere is the shape that has the minimal surface for a given volume is an interesting topic in mathematics. A simpler proof can be constructed using spherical harmonics as perturbations around the spherical form.

In order to prove Laplace's law, we consider a sphere, as depicted in figure 2.6, with radius a . The surface area of a sphere is given by $A = 4\pi a^2$. A small change da in the radius of the sphere brings about a change in the surface area of $dA = 8\pi a da$ and the work that is involved in this change is given by $dW = \gamma dA = 8\pi \gamma a da$. The force, due to the surface tension, that opposes this change is therefore given by $F = -dW/da = 8\pi \gamma a$. In addition, there is the difference in pressure between the inside of the droplet and the exterior of the droplet that makes up the force balance

$$(p_{in} - p_{out})4\pi a^2 - 8\pi \gamma a = 0$$

from which one immediately derives equation 2.14.

Capillary rise

One frequently encountered example of Laplace' law is in connection with capillary rise, see figure 2.7 for a schematic sketch of the archetypal situation of a capillary of diameter $2a$ in which liquid has risen to a height h above the liquid surface in contact with ambient pressure. In actual fact, there are two phenomena that are acting simultaneously. The one is the curvature of the liquid surface enforced by the contact angle of the liquid in contact with the solid surface and the ambient gas (vapor) phase. This curvature forces the liquid interface to be larger and this induces a force that tries to flatten the interface. Instead, this is the second phenomenon, the liquid level rises until the forces balance on either side of the curved surface. Hence, the Laplace pressure is balanced by the pressure due to the column of liquid. This leads to the capillary rise formula

$$h = \frac{2\gamma \cos \theta}{\rho g a} \quad (2.15)$$

In many cases, such as water in glass tubes, the contact angle vanishes and in many other cases this is assumed to happen in the absence of sufficient knowledge of the situation. Important to realize is, that the shape of the capillary is immaterial, it is only the diameter of the opening where the meniscus is formed that counts in the calculation.

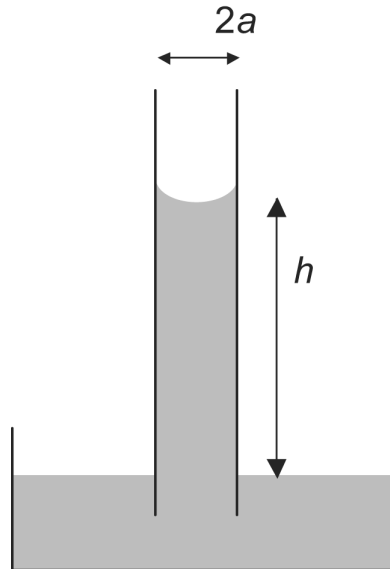


Figure 2.7 Capillary rise.

As an example, consider the vessels in trees that at the top, the pores in the leaves, have a diameter of about 100 nm. These vessels can transport water until the height of the tree exceeds 146 m, which is indeed the height achieved by sequoias. The situation is of course much more involved than the simple picture of water in vessels where the contact angle is almost zero.

Washburn equation

When the capillary in figure 2.7 is just put in the liquid, the liquid level will start to move: the difference between the Laplace pressure and the hydrostatic pressure is then driving the upward flow of the liquid. For the situation where the hydrostatic pressure is not present or can be neglected, the Washburn equation describes the time evolution of the height h of the liquid in the capillary

$$\frac{dh^2}{dt} = \frac{\gamma}{2\eta} a \cos \theta \quad (2.16)$$

in which η is the viscosity of the liquid.

For small capillaries this flow will be laminar and the Poiseuille equation may be used, which relates the volumetric flow to the pressure gradient as

$$\frac{dV}{dt} = \frac{\pi a^4}{8\eta} \frac{\Delta p}{h}$$

with a the radius of the capillary and h the length of the liquid column over which the pressure difference Δp acts. Substituting $V = \pi a^2 h$ as the volume transferred at time t

and the Laplace equation for the pressure across the capillary (neglecting hydrostatic pressure!) yields

$$\frac{dh}{dt} = \frac{\gamma}{4\eta} \frac{a}{h} \cos \theta$$

from which equation 2.16 follows after substituting $dh^2 = 2hdh$.

In porosimetry both the capillary rise equation and the Washburn equation are invoked to translate pressure versus transferred volume relations into a pore size distribution.

2.3.4 Kelvin's law

The formation Gibbs energy of a liquid droplet of radius a in a (supersaturated) vapor at pressure p is given by

$$\Delta G = -\frac{4\pi a^3}{3} \frac{RT}{V_L} \ln \left(\frac{p}{p^o} \right) + 4\pi a^2 \gamma \quad (2.17)$$

in which V_L is the molar volume of the liquid and p^o is the equilibrium vapor pressure at the given temperature. The pressure ratio is often termed the *degree of supersaturation*. It contains two terms, the first of which is associated with the pressure work (evaluated for a perfect gas) and the second with the work to create the interface. A graphical representation of this formation Gibbs energy is given in figure 2.8. For very small droplet sizes, the surface work dominates which leads to an initial increase of the formation Gibbs energy.

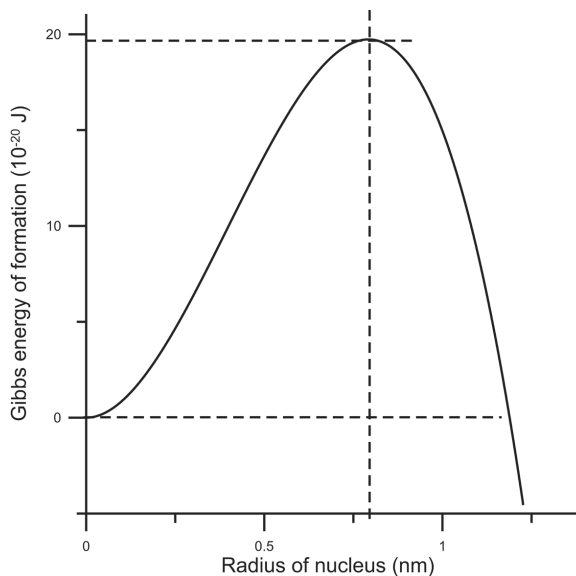


Figure 2.8 Formation Gibbs energy for a water drop in its vapor at 373 K and a supersaturation of 3.

For larger sizes the volume work dominates and leads to spontaneous droplet growth. The maximum that is thus achieved is an *unstable equilibrium* situation which is described by the Kelvin equation

$$RT \ln \left(\frac{p}{p^o} \right) = \frac{2\gamma V_L}{a} \quad (2.18)$$

where the radius a is the *critical droplet size*.

The above treatment holds equally well for the situation of the development of solid phase formation in supersaturated solutions.

Nucleation

In a supersaturated vapor or solution the density fluctuations sometimes overcome the critical droplet size predicted by the Kelvin equation which leads then to the formation of a nucleus that is viable to grow further. In this picture, the formation Gibbs energy describes the energy barrier that embryonic nuclei have to overcome in order to grow. Similar to the situation for chemical reactions, one invokes the Arrhenius equation to relate the formation rate of nuclei to this energy barrier by

$$r \propto p^2 \exp \left(-\frac{\Delta G}{RT} \right)$$

where the proportionality constant is of the order of 10^7 . In figure 2.9 the formation rate of water drops at 0 °C is plotted as a function of supersaturation. The prediction of the presented model using the formation Gibbs energy and the Arrhenius equation

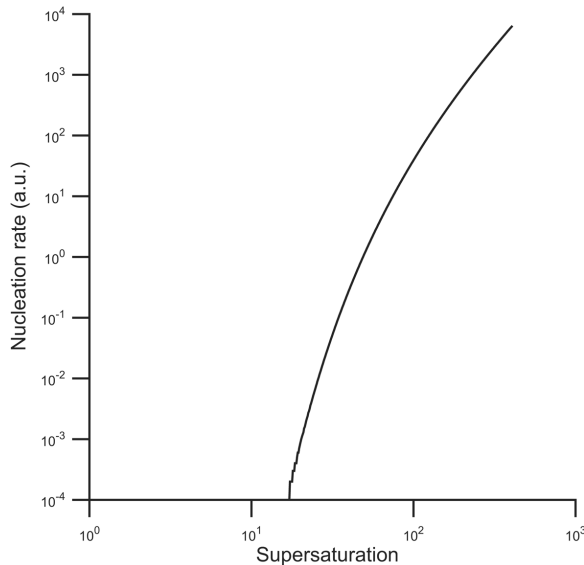


Figure 2.9 Formation rate of water drops at 0 °C as a function of supersaturation.

accounts for the general observation that homogeneous nucleation sets in rather abruptly with pressure variation.

When in a supersaturated vapor or solution there are particles of another material, the wetting behavior of these particles largely determines nucleation behavior which becomes heterogeneous. When the particles are fully wetting and larger than the critical radius, there is no energy barrier for nucleation left. The partial wetting situation is well described by the equation

$$\Delta G_{max,hetero} = \Delta G_{max,homo} \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} \quad (2.19)$$

where θ is the contact angle of the liquid with the particle material.

Droplet growth is described by the Rayleigh equation

$$a \frac{d^2 a}{dt^2} + \frac{3}{2} \left(\frac{da}{dt} \right)^2 = \frac{1}{\rho_L} \left(p_{in} - p^o - \frac{2\gamma}{a} - \frac{4\eta}{a} \frac{da}{dt} \right) \quad (2.20)$$

with p_{in} the pressure inside the bubble and ρ_L the mass density of the liquid. Care should be taken in using this equation in the case of solutions, as it assumes that the concentration outside the droplet remains constant whereas usually depletion sets in close to the growing droplets.

The mechanisms described above allow for the formation of droplets of all kinds of sizes. This is in practice limited by a phenomenon called *Ostwald ripening* which states that the larger droplets will grow at the expense of the smaller droplets.

The mechanism of Ostwald ripening is easily understood if one considers two droplets of different size, the smaller having a larger Laplace pressure than the other one. If a connection would be brought about between the droplets, a mass flux would establish that depletes the smaller droplet completely. If only vapor or solution exists between the two droplets, the rate of Ostwald ripening is controlled by the diffusion of material between the droplets. The diffusion will go faster at higher concentrations (or pressures).

2.3.5 Gibbs' law

A closer look at the interface between two fluid phases reveals that at the molecular scale the interface is not abrupt but rather extends over a certain distance. In figure 2.10 this is illustrated with x the height coordinate. At heights $x \ll x_0$ there is phase α and for $x \gg x_0$ there is phase β . Along the ordinate is plotted an arbitrary observable property P of the system such as the density. In phase α this property has the uniform value P_α and in phase β the uniform value is P_β . Around x_0 , within a region of width Δx this property smoothly changes from the one value into the other.

For ease of calculations, one introduces a *dividing surface* that in figure 2.10 is arbitrarily put at the height $x = x_0$. It is subsequently assumed that the phase α extends all the way up till this dividing surface where it abruptly changes over into the phase β . The hatched areas in figure 2.10 mark the regions where the actual value for the property

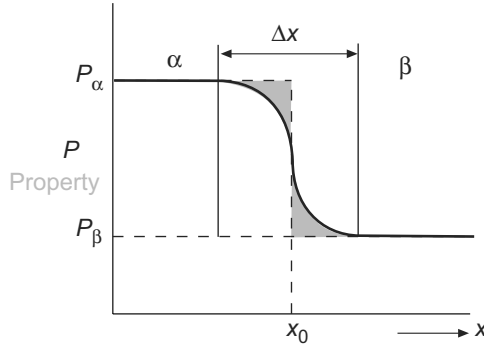


Figure 2.10 Illustration of the dividing surface and surface excess.

P deviates from the one that follows from the application of the dividing surface. The integral of this difference is the *surface excess* P^σ of the property across this interface

$$P^\sigma \equiv P - p_\alpha V_\alpha - p_\beta V_\beta \quad (2.21)$$

in which $p_i = P_i/V_i$. The value of the surface excess will depend on the choice of the location of the dividing surface. However, measurable quantities that are calculated using the concept of surface excess are independent of the location of the dividing surface. In addition, there is often a rationale for the choice of a particular dividing surface, such as the so called *equimolar surface* which is located in such a way that the molar concentration of one component, usually the solvent, vanishes.

It was Gibbs who for the first time declared the surface as an independent thermodynamic system, albeit with an extensivity less than that of the surrounding bulk phases. Just like for the bulk phases there is a thermodynamic relation for the Gibbs energy of this surface

$$dG^\sigma = -S^\sigma dT + \gamma dA + \sum_j \mu_j dn_j^\sigma \quad (2.22)$$

The intensive quantities, such as temperature and chemical potential, are considered to be uniform throughout the interface assuming of course equilibrium. From the above equation, Gibbs derived his famous adsorption equation that reads

$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d \ln(c/c^\ominus)} \quad (2.23)$$

for a single component mixed with a solvent where the dividing surface is chosen to be the equimolar surface for the solvent. In this equation, $\Gamma = n^\sigma/A$ is the surface excess of the solute.

To derive the above Gibbs' adsorption equation, consider equation 2.22 for two components, a solvent and a solute. The dividing surface is chosen to be equimolar such

that the surface excess of the solvent vanishes. The temperature is assumed to be constant, $dT = 0$. Under these conditions the equation 2.22 reduces to

$$dG^\sigma = \gamma dA + \mu dn^\sigma$$

Using Euler's equation for extensivity (not bulk but surface this time) yields

$$G^\sigma = \gamma A + \mu n^\sigma$$

and subsequent differentiation yields

$$dG^\sigma = \gamma dA + A d\gamma + \mu dn^\sigma + n^\sigma d\mu$$

Combined with the previous equation this yields the Gibbs Duhem equation for the surface

$$A d\gamma + n^\sigma d\mu = 0$$

One finds equation 2.23 using the definition of the surface adsorption $\Gamma = n^\sigma / A$ and

$$\mu = \mu^\ominus + RT \ln \left(\frac{c}{c^\ominus} \right)$$

with the standard chemical potential μ^\ominus given for the reference concentration c^\ominus .

In many cases, the specific area of a molecule at the interface is the more useful quantity. This specific area is defined as

$$\sigma = \frac{1}{\Gamma N_A} \tag{2.24}$$

where the division by Avogadro's number yields the result in area per molecule rather than per mole.

A special class of molecules are surfactants, who have the tendency to preferentially reside at the interface between a polar and a non-polar medium. This is due to their special structure of a lyophilic and a lyophobic part. In the following chapter it will be discussed how such molecules affect the surface tension of interfaces and how this can be analyzed using Gibbs' equation, see figure 3.3.