Lecture notes: Physical Chemistry of Interfaces and Colloids

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The script also contains background information. When preparing for the exam, also look at the questions from previous exams. Last updated: 11/29/2024

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1 General, literature

In the introduction to physical chemistry, "phases" play a prominent role (in addition to thermodynamic equilibrium). There is often talk of "almost all" molecules and "almost all" means: all molecules except those at the interfaces between the phases. The term "almost all" becomes problematic when the size of the phases becomes small and the surface-to-volume ratio becomes large. This is the case with colloids. The course does, however, not start with the colloids, but with the interfaces themselves. Interfaces may have some finite thickness the vertical, but they are not phases. Often they are sharp. Molecular details therefore are more important than in the bulk. Interfaces often carry function, not only in colloids. And of course they are technically important – always a good reason study them in depth.

Good books are:

- Butt, H.-J. et al. Physics and Chemistry of Interfaces [1]
- Goodwin, J., Colloids and Interfaces with Surfactants and Polymers [²].
- Morrison, I. D et al, *Colloidal Dispersions* [3].

These are lecture notes, this is not a textbook. Because lecture notes live and change, inaccuracies and errors occasionally creep in. If you find room for improvement, send an e-mail to johannsmann@pc.tu-clausthal.de.

One more disclaimer: I spent time to diligently formulate the German version of this text. The translation was done with DeepL and I spent limited time to catch errors. Equations are labeled as "Glg." (the abbreviation for German "Gleichung"). It would have been much work to change those labels into "Eq." because these are targets for cross-references. Some figures have German labels for the same reason.

2 The surface energy

2.1 General

Interfaces are characteristic of *phase coexistence*. A phase is a region in which the material parameters are either constant or vary slowly. The latter may be caused, for example, by gravitation (as in the atmosphere).⁴ At interfaces between phases, the physical parameters change (almost) discontinuously. Because the jump is sharp, the structure and the behavior of interfaces is influenced by details of the molecular organization. For example, most ions dissolved in water increase the surface energy. Some types of ions, however, decrease it.

At interfaces, the free energy per molecule is higher than in the bulk. If this increased energy (more precisely: the increased free enthalpy) is normalized to the surface area, one arrives at the surface energy, γ . As long as γ is positive, the system tries to minimize its surface. Drops and bubbles therefore tend toward spherical shape. Negative surface energy, which

Fig. 2.1

If a water surface is divided into two compartments with a thread and when a surfactant is spread onto one of the compartments, the surfactant exerts a force on the thread. The force is caused by the difference in the surface energies. It is proportional to the length of the filament. This illustrates that γ can also be viewed as a force per length.

F=LAY

¹ Butt, H.-J.; Graf, K.; Kappl, M., Physics and Chemistry of Interfaces. Wiley-VCH: 2006

² Goodwin, J., Colloids and Interfaces with Surfactants and Polymers. Wiley: 2004

³ Morrison, I. D.; Ross, S., Colloidal Dispersions. Wiley: 2002

⁴ For nematic liquid crystals, the preferred direction can vary slowly in space.

occurs in connection with electrocapillarity and which leads to an instability, will be discussed in Sect. 2.4.

The dimension of the surface energy is either J/m² or N/m. (Remember: 1 J = 1 Nm.) The second view is close to intuition. Fig. 2.1 shows a planar water surface, which is divided into two compartments by a thread. Let the surface on the left be covered by a molecular monolayer of a surfactant, which is insoluble in water. To be precise, let the solubility of the surfactant in the water phase be so low that the number of molecules on the surface can be considered constant. If the surfactant is largely insoluble, it cannot migrate through the bulk phase to the other side of the trough. The surfactant lowers the surface tension. The difference in surface tensions between left and



right results in a force on the filament, which is proportional to the length of the filament. γ is given as this force divided by the length of the filament. This force/length is the 2D analog to the pressure in 3D.⁵ This analogy will be discussed in more detail to in Sect. 7.2. The 2D pressure exerted by surfactants causes surfactants to spread spontaneously on a water surface. If a hydrophobic wire is bent into a horseshoe shape, if this horseshoe is placed on the water surface so that it does not sink, and if a surfactant is sprayed into the space between the two arms, the recoil of the surfactant flowing out propels the horseshoe forward.

Fig. 2.2 shows a second example, which is the Wilhelmy plate. The plate (it can also be a piece of filter paper) is immersed in the liquid. The meniscus exerts a force on the plate. This force is proportional to the surface tension and the length of the three-phase line.

Guided by intuition, one might be tempted to identify surface tension with capillary pressure (section 3). Surface tension and capillary pressure are related, but they are not the same. The units are different (N/m and N/m²).

A note on terminology: Surface tension is largely equivalent to surface energy. Keep track of the units: surface tension as units of N/m, whereas the conventional tension has units N/m^2 . Surface tension can be viewed as a tension in 2D, hence N/m instead of N/m².

It is common to report surface energies in units of mN/m (mN for milliNewton). The prefix "milli" achieves two separate things. First, the numerical values are the same as in the cgs system (in the centimeter/gram/second system instead of the meter/kilogram/second system, the latter also called the "SI" system⁶). In the cgs system, the unit for force is the dyne. The analog of the Joule is the erg. 1 erg = 10^{-7} J. The dyne (abbreviated as dyn) and the Newton are related by 1 dyn = 10^{-5} N. The quantity mN/m corresponds to one dyn/cm. Secondly, the unit mN/m makes it easy to express the

 $^{^5}$ The pressure in 3D has either the unit J/m^3 or the unit N/m^2 .

⁶ The cgs system is common in North America, the SI system in Europe. The cgs system has nothing to do with the inches, pounds, and miles-per-gallon that US-Americans use to celebrate their cultural roots. It is a "metric" system.

numerical values of γ for the ordinary liquids. For example, water has a surface energy 72 mN/m (or 0.072 N/m, but the latter is less easily pronounced).

Some values should be remembered. Among the different liquids, water has a relatively high surface energy $(\gamma = 72 \text{ mN/m})$ because the internal cohesion is high due to the H-bonds. Mercury has an even higher surface energy (486 mN/m). This is due to the metallic bonding. Solids also have surface energies. However, these are difficult to measure because solids do not form droplets. Still, the surface energy as such does exist and it actually is greater than the surface energy of most liquids.⁷ This is due to the high internal cohesion. Tungsten (one of the "refractory metals") has both a high surface energy and a high melting point.

Table 1.1 Values of the surface energyfor selected substances				
	γ [mN/m] (20°C)			
Helium (2–4 K)	0.12 - 0.35			
n-Pentan	16			
PTFE (Teflon)	18			
Silicone	20 - 25			
Benzene	29			
Water	73			
Mercury	486			
Aluminum	1100			
Tungsten	4400			

Low surface energies are of some practical importance. At room temperature, the surface

energies of ordinary liquids can hardly fall below about 10 mN/m, because the material would then have such low internal cohesion that it would evaporate.

Fig. 2.3 shows the surface energies of liquid noble gases, plotted against the atomic number. This is a homologous series, i.e. a series of substances that are similar to each other except for a single parameter (here: the atomic number). As can be seen, the surface energy is correlated with the vaporization enthalpy (Sect. 2.3), with the boiling temperature, with the refractive index and with the polarizability. This is an example for which the relationship between the properties of molecules (in this case, atoms) and the properties of the corresponding macroscopic substances is well understood. The larger the atom, the larger the number of electrons and the larger the electronic polarizability. In turn, the electronic polarizability⁸ is correlated with the refractive index (an optical property). One can convert electronic polarizability and refractive index into each other using the Lorentz-Lorenz equation. A high polarizability also entails large quantum mechanical fluctuations of the dipole moment. The correlated fluctuations of the dipole moment generate the London dispersion interaction (one of the three contributions to van-der-Waals attraction). Therefore, as the atomic number increases, so does the attraction between



Fig. 2.3

An example of the relationship between the properties of certain atoms on the one hand and the macroscopic properties of the phases concerned on the other. This relationship is also called "structureproperty relationship". The substances are a "homologous series".

⁷ Polymers are considered liquids in this context because the bonds exist only along the chain.

⁸ There also is a polarizability, which results from the displacement of whole atoms with respect to each other, and, furthermore, a polarization, which results from a preferential orientation of molecules with permanent dipole moments in an external field. These two effects lead to "atomic polarization" and "orientation polarization". Both mechanisms are too slow to follow the frequency of light ($\approx 10^{15}$ Hz) and therefore have no influence on the refractive index.

neighboring atoms. As a consequence, the evaporation enthalpy, the boiling point and the surface tension all increase.

Remember

- Interfaces usually carry a (free) energy. In liquid phases, the system therefore minimizes the size of the surfaces. This leads to the spherical shape of drops or bubbles.
- The surface energy is reported in units of mN/m (milliN/m). Typical numerical values are a few 10's of mN/m. Water at 25°C has a surface energy of $\gamma = 72$ mN/m.
- The surface energy is high for materials with high internal cohesion.
- 2.2 Thermodynamic treatment of the surface energy

The thermodynamic treatment of interfaces contains a few subtleties, which we avoid for now by making assumptions. To the extent that we drop these assumptions later, it will become clear how

complicated interfaces can be. Consider the surface shown at the top in Fig. 2.4. A liquid is in contact with a vapor phase. By moving the piston up, the area of the interface between the liquid and a vapor is increased. In the process, a surface work is done. The assumptions are:

- a) Liquid and vapor are in thermodynamic equilibrium.
- b) The interface is almost molecularly sharp.⁹ Because it is sharp, it is easy to see where it exactly lies. Even for strongly curved interfaces (such as the surfaces of nanodroplets), the size of the surface (given as $A = 4\pi r^2$ for spherical droplets) can be specified with good accuracy.¹⁰
- c) No work other than the work on the surface is done when the piston moves. The piston moves without friction. All other surface energies in the system are zero. Gravity is negligible. The



Fig. 2.4 When the piston is moved, the interface between the liquid and the vapor is changed by an amount d*A*. This change in area associated with a surface work $dG_{surf} = \gamma dA$.

⁹ The exceptions are worth a mentioning and considering.

⁻ Interfaces between liquid and vapor near the critical point are not molecularly sharp. In two-phase systems close to the critical point (the critical point of segregation or the critical point of vaporization), both phases have almost equal properties. Then the surface energy tends to zero; the surface width tends to infinity. Exactly at the critical point, the interface finally disappears completely.

⁻ Interfaces of electrolytes are still not molecularly sharp (keyword: diffuse double layer, section 10.7).

⁻ Interfaces between moderately incompatible polymers are still not molecularly sharp. Here, a molecularly sharp interface would force a refolding of chains at the interface and thus disturb the tangle statistics. The resulting small widening of the junction is of practical importance because it can lead to hooking between the different polymer materials ("polymer welding"). Entanglements are favorable for adhesion. Note that the debonding work per area is always greater than the equilibrium surface energy. In the favorable cases, it is greater by a factor of 1000 or more. Adhesives cause work to be done during delamination that far exceeds the equilibrium surface energy. This can include the unwinding of polymer chains. Most of this energy is dissipated as heat. It may also remain in the system as chemical energy (chain fracture). In the latter two cases, the mixed region is sometimes called "interphase" instead of "interface." This term is problematic because the interface – even if it is broad – is not a phase in the thermodynamic sense. An exception is the solid-electrolyte interphase (SEI) in lithium-ion batteries. This *is* a phase. It consists of decomposition products of the electrolyte. It may be thought of as a film.

¹⁰ Because interfaces are molecularly sharp, the molecular details matter for their description. This coin has two sides. On the one hand, it makes the description of interfaces more complicated. On the other hand, molecular interactions and molecular processes can be studied at interfaces with moderate experimental effort. Example: Ions like to stay in hydrophilic environments. This is due to the hydration shell and the counterion cloud. Therefore, ions are usually *depleted* at the water-air interface. As discussed in Sect. 5.25.2, this increases the surface tension. Using surface tension, one may quantify the degree of depletion (equating to the negative Γ_2). It now turns out that ions sometimes *lower* the surface tension. The argument "hydration shell and counter ion cloud \rightarrow repulsion away from hydrophobic surfaces" obviously does not apply in these cases. The reasons for these peculiar "ion-specific effects" are not quickly explained or even well understood. However, an enrichment of ions on hydrophobic surfaces is of outstanding importance for molecular biophysics. There, too, ion-specific effects are poorly understood. The water/air interface plays the role of a model system that can be used to study ion-specific effects.

pressure-volume work on the vapor phase is compensated by an equal pressure-volume work on the back of the piston. The piston and the tube are rigid bodies and therefore no elastic work is done.

- d) There are no impurities.
- e) The three-phase boundary between the tube, the liquid and the vapor is anchored at the outer edge of the tube. The meniscus is immobile ("pinned"). Only the area of interface between liquid and vapor changes.
- f) There is no evaporation or condensation while the piston moves.

For this situation and under these conditions, the surface energy γ is defined as

$$\gamma = \left(\frac{\mathrm{d}G}{\mathrm{d}A}\right)_{p,T,n}$$

G is the Gibbs Free Enthalpy of the entire system and *A* is the area of the liquid-vapor interface. When using the Gibbs Free Enthalpy, it is implied that all derivatives are to be carried out at constant pressure and temperature. Recall that the Gibbs Free Enthalpy is given as G = U + pV - TS and that systems under isothermal and isobaric boundary conditions tend towards minimum *G*. At constant temperature and pressure, minimal *G* defines thermodynamic equilibrium. *In assumption a) we restricted the scope to systems in thermodynamic equilibrium*. These are the liquids and gases (often collectively referred to as "fluids"). For fluids, *G* is usually is equal to $G_{eq} = G_{min}$. Note: This restriction is not strictly needed for a discussion of the surface energy. Solids (which are not usually in thermodynamic equilibrium) also have a surface energy, see sect. 2.5).

The local thermodynamic equilibrium is established at interfaces between fluids over a time of a few nanoseconds. That is the residence times of individual molecules at the interface. After this time, they are exchanged for other molecules from the bulk of the adjacent phases.

The area *A* is well-defined because phase boundaries are molecularly sharp (assumption *b*). If the time-averaged density is plotted versus *z* (*z* the normal coordinate at the interface, cf. Fig. 2.5), this density drops continuously at the interface, but the drop is steep.¹¹ The energetic conditions are more favorable in the bulk phases than in the transition region, and the system therefore keeps the transition region as narrow as possible. For the exceptions, see footnote 10.

In the formulation of Glg. 2.2.1 it was assumed that the punch only does work on the interface. No work is done on the bulk phases (assumption *c*). To be precise, in the experiment sketched Fig. 2.4 the work against gravity (which is nonzero) has to be subtracted from the total work to obtain γ . A

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¹¹ There is a complication here, which goes back to the existence of *thermal capillary waves*. Capillary waves (more generally: waves on the surfaces of liquids) are complicated and we will not go into details. At finite temperature, every fluid interface exhibits dynamic ripples, even without being externally excited. These are a form of Brownian motion. These ripples can be decomposed to Fourier components. The capillary waves contribute to the broadening of the density profile. This has two consequences:

⁻ When averaging over large areas to calculate the density profile, even very boring Fourier components contribute to the width of the transition; otherwise they do not. Thus, the shape of the profile $\rho(z)$ depends on the size of the area over which one averages. (A corresponding fact also applies to the specification of surface roughness. Here, too, the numerical value depends on how large the area of averaging is).

⁻ One might be tempted to ignore the capillary waves in some way and calculate a local, "intrinsic" interface width. But there is no clear prescription for this, because there are - at least in principle – also capillary waves with a wavelength of two molecular diameters. There is no clear prescription to distinguish between the motion of single molecules and short wavelength capillary waves. The intrinsic width of the interface depends on what is meant by "local". One must truncate the capillary wave spectrum at a certain (high) wavenumber and attribute all smaller-scale fluctuations to the intrinsic width.

similar problem arises (in a form not easily dealt with) when measuring the surface energy of solids (Sect. 2.5). One cannot change the interface of a solid without doing elastic work at the same time. This elastic work must be subtracted from the total work.¹² A related topic: When droplets rest on deformable bodies (e.g. on elastomers or on gels), the capillary pressure inside the drops deforms the substrate, which leads to "elastocapillarity". Elastocapillarity is of much importance when the capillary pressure is high. This is the case in many porous and granular media. Another form of non-surface work is pressure-volume work on air bubbles. This work is important for large air bubbles (with small capillary pressure, Sect. 3). It is insignificant for liquid drops because these are almost incompressible.

We avoided transport equilibria in the context of Glg. 2.2.1 by considering only one species (assumption d). Transport equilibria at interfaces are important in practice because interfaces are rarely clean. Note that adsorption equilibria often develop slowly because diffusion takes time because adsorbate layers often reorganize internally.

The anchored contact line (assumption e) is only necessary if one wants to write down simple relation between the movement of the punch and the change of A. The definition of the surface energy per se is independent of the anchoring the meniscus. Of course, one has to take the surface energy between solid substrate and fluid into account in case the contact line slides on the substrate (Sect. 6). An anchoring of the meniscus (as in Fig. 2.4) is quite realistic.

Evaporation and condensation must be excluded because work is associated with it (Sect. 4.1).

So much for the definition of surface energy. We now turn to a conceptual subtlety. One can assign a Gibbs free enthalpy to the interface according to

$$G_{\sigma} = G_{tot} - G_{\alpha} - G_{\beta}$$

The indices α and β denote the two bulk phases here. The index σ denotes the interface. One has

$$G_{\sigma} = A\gamma$$

with γ from Glg. 2.2.1. G_{σ} is an extensive quantity. *However, the Free Enthalpy associated with the interface does not imply that the interface itself was a "phase"*. This latter notion underlies the Guggenheim picture (blue area at the top of Fig. 2.5). According to Guggenheim, the interface would correspond to a certain spatial region of approximately the width of the transition in Fig. 2.5. However, the Guggenheim picture is misleading. This can be seen from the fact that it is not clear how wide the strip in question would have to be. But there is a more fundamental



¹² If interested in the details, google for the Shuttleworth equation.



problem: The Gibbs free enthalpy G has no well-defined zero. *Differences* in G drive spontaneous processes; G is not defined absolutely. The surface energy, however, can be defined and measured in absolute terms. It can also become negative (Sect. 2.4). This cannot be understood within the framework of the Guggenheim picture.

Differing from Guggenheim picture, G_{σ} is an *excess quantity*. For the definition of excess quantities, we consider only cases where there is a majority component. A majority component is either a pure substance or a solvent in which the solute is diluted. By convention, the majority component is given the index 1. Near the surface, the time-averaged density $\rho_1(z)$ decreases continuously. Again: This continuum picture neglects the molecular structure. Fluid-fluid interfaces are almost molecularly sharp and the molecular details do matter. Nevertheless, one can always determine a time-averaged density $\rho_1(z)$. This density will gradually decrease at the interface. In the next step, one compares the profile $\rho_1(z)$ with a hypothetical profile with an infinitely sharp interface (dashed vertical line in Fig. 2.5). This hypothetical interface is the "Gibbs-dividing-surface" (GDS). The exact position of this interface on the z-axis is fixed by the requirement that the integral over the difference between real density profile $\rho_1(z)$ and hypothetical density profile with a sharp edge is zero. The two dashed areas in Fig. 2.5 must be equal in size. The integral over this difference is also called the "interface excess". The interface excess of the density of the majority component (only of the majority component) is always zero according to the definition of Gibbs-dividing-surface.¹³

A surface excess can be calculated for any other density. For all densities except ρ_1 , the surface excess is non-zero in general. This includes the density of enthalpy, entropy, free energy, and the density of solutes. One always extrapolates the bulk values of the density on both sides to the GDS and subtracts this box profile from the real profile. This extrapolation procedure ensures that all excess quantities have a well-defined zero. If the density under consideration is the density of a substance in units of mol/L, it may be enriched at the interface (as is the case for many surfactants in water) or depleted (as is the case for many ions in water, Sect. 5).

By means of the surface excess, extensive quantities are defined for interfaces and one can apply the formalism of thermodynamics to interfaces. For example, one can write

 $dG_{\sigma} = \gamma dA = dU_{\sigma} + V_{\sigma} dp - S_{\sigma} dT$ Glg. 2.2.4

Two complications: From the equation above, we derive a "surface volume" and a "surface entropy". The "surface volume" is defined as

$$\frac{V_{\sigma}}{A} = \left(\frac{\mathrm{d}\gamma}{\mathrm{d}p}\right)_{T,n} = \left(\frac{\mathrm{d}^2 G}{\mathrm{d}A\mathrm{d}p}\right)_{T,n}$$
Glg. 2.2.5

If one naively defines a "volume density" (i.e. volume/volume), then this density is trivially equal to one everywhere and there can be no excess volume. But one can also define the volume density as the volume per particle. Then the formalism is consistent again.

¹³ If a majority component does not exist, the determination of the location of the GDS becomes more complicated. One must then use that the interface excess of the *G*-density is equal to γ according to Glg. 2.2.1. We do not prove that this is also the case for the definition of the GDS using the majority component.

The surface entropy is defined as

$$\frac{S_{\sigma}}{A} = -\left(\frac{\mathrm{d}\gamma}{\mathrm{d}T}\right)_{p} = -\left(\frac{\mathrm{d}^{2}G}{\mathrm{d}A\mathrm{d}T}\right)_{p}$$

A word of caution: It is problematic to define an "entropy density" as an average value over a volume corresponding to a molecular volume. Entropy is related to the number of microconformations of a "system". For systems where there are interactions on the one hand and steep density gradients on the other, it is not possible to define an entropy density as a function of *z* at the molecular volume level. The simplest way is to start again directly from the derivation of γ according to the temperature.¹⁴

As a rule, the surface energy decreases with temperature. From this, one concludes that the surface entropy (an excess entropy) is positive. This is not trivial, but nevertheless plausible. At the interface between two phases, it is easy to imagine that the number of possible microstates per volume is higher than in the homogeneous adjacent bulk phases. At this point, thermal capillary waves also play a role (footnote 11).

Note: If the two bulk values to the right and left of the interface are different, the value of the relevant excess size depends on the location of the GDS. In Fig. 2.5, we had placed the GDS in such a way that the interface excess of the majority component is zero. Of course, this procedure is viable only if there is such a majority component. The general rule is: the GDS must be such *that* the excess quantity in question (call it B^{σ}) corresponds to the derivative of the quantity in question with respect to the surface ($B^{\sigma} = dB/dA$). This is the way to proceed; the concept is consistent.

One last remark: Be careful not to assign a chemical potential to the molecules at interfaces in one-component systems. To do this, one would have to write

Glg. 2.2.7

 $\mathrm{d}G_{\sigma} = \gamma \mathrm{d}A + \mu_1 \mathrm{d}n_{\sigma,1}$

However, this notation is misleading because the area *A* and the amount of substance at the interface $n_{\sigma,1}$ cannot be varied independently. This is another consequence of the fact that the interface is not a phase. For multicomponent systems, one can define chemical potentials at interfaces (Sect. 5) but the number of these well-defined chemical potentials is always 1 less than the number of chemical components.

One may question the practical benefit obtained from the Gibbs formalism, if it is so complicated. For the practice it is in fact mostly more purposeful to start directly from the derivation of the quantity in question according to the area (as in Glg. 2.2.5). The notion of an excess quantity is a conceptual bridge by means of which one can see that the same thermodynamic principles apply at interfaces and in the bulk. The Gibbs formalism primarily is applied the context of the Gibbs adsorption isotherm (Sect. 5.2). There, the excess refers to a quantity of substance.

Remember

- The surface energy is defined as $\gamma = (dG/dA)_{p,T}$.

 $^{^{14}}$ In aqueous systems, the analysis of the temperature dependence of γ has its limitations because many bulk properties of electrolytes are also temperature-dependent.

- The interface is not a phase of its own.

2.3 The surface energy as a consequence of the missing neighbors

The processes and conditions at surfaces can be extraordinarily complicated. This includes the surface energy. In particular, there may be *interface anomalies*. A material can behave differently at an interface than it does in the bulk. An important example is water, which often orders at interfaces.¹⁵ However, that is not to say the surface energy is always and without exception linked to an anomaly. One might suspect some kind of skin at interfaces which forces the droplet into a spherical shape, just as a balloon forces the gas volume inside into an almost spherical shape. However, the surface energy can be explained without recourse to a skin. It can be caused by missing neighbors alone (Fig. 2.6).

Let ε be the interaction energy between two molecules, let *z* be the average number of neighbors of a molecule (the "coordination number"), and let A_m be the area per molecule. The surface energy can then be estimated as

$$\gamma \approx \frac{1}{A_m} \frac{z}{2} \frac{\varepsilon}{2}$$

The factor 1/2 at *z* occurs because about half of the neighbors are missing. The factor 1/2 at ε occurs because the interaction always links two partners and must not be counted twice. This simple equation has a number of implications:

- The surface energy should be correlated with the evaporation energy. We follow an elementary argument of Young from 1815. Young derives an estimate for size of the molecules d_M from the ratio of $\Delta_{vap} \bar{U}$ and γ . Young glosses over complications arising from the coordination number. He argued with the dimensions: The size

 $\Delta_{vap}\bar{U}/\bar{V}$ is an energy per volume γ is an energy per area. Then the ratio/ $(\Delta_{vap}\bar{U}/\bar{V})$ has the dimension of a length. This length should be approximately the molecule diameter. We use the values for water ($\gamma = 72 \cdot 10^{-3} \text{ J/m}^2$, $\Delta_{vap}\bar{H} = 44 \text{ kJ/mol}$, $\Delta_{vap}\bar{U} = \Delta_{vap}\bar{H} - RT$, $\bar{V} = 18 \times 10^{-6} \text{ m}^3$) and obtain

$$d_M \approx \frac{\gamma \overline{V}}{\Delta_{vap} \overline{H} - RT} = 0.03 \text{ nm}$$

This is about a factor of 10 below the experimental value. The agreement can be improved by various refinements (e.g., a consideration of the coordination number), but we leave the argument as it is.



Fig. 2.6 In simple models, the surface energy arises from the fact that molecules at the surface have fewer neighbors than molecules in the bulk.

Glg. 2.3.2

¹⁵ Sometimes one speaks of "ice-like" structures. This term is problematic in that although the order at the interface of liquid water is high, the structure is not the same as the structure of ice.

The surface energy is correlated with the internal cohesion of the material. Mercury, for example, has a high surface energy (486 mN/m) due to the metallic bonds. Water also has a fairly high surface energy (72 mN/m) because of the H-bonds. The surface energy of benzene – typical van der Waals fluid – is 30 mN/m. The surface energy of fluoropolymers (e.g. Teflon) is particularly low because fluorine is poorly polarizable.¹⁶

- A final remark on the missing-neighbor model concerns not its consequences, but the assumptions

entering it. The model assumes that a given molecule interacts primarily with its *neighbors* – possibly also with the second shell of neighbors. The model presupposes a *short-range* interaction. The van der Waals attraction ($\propto r^{-6}$) is a short-range interaction in this sense.¹⁷

On the subject of short-range interaction, there is an interesting historical note from nuclear physics. In the early days of nuclear physics, it was shown that there is a contribution to the energy of the nucleus that scales like $N^{2/3}$, where N is the number of nucleons (protons and neutrons).¹⁸ For nuclei with spherical shape, the surface area also scales like $N^{2/3}$ (like $V^{2/3}$ with V the volume, the latter proportional to N) and it is natural to interpret the $N^{2/3}$ -term as a surface energy. This led to the "droplet model" of the nucleus. This model makes only makes sense if the interaction between the nucleons (the nuclear force, also: the "strong interaction") is indeed short-ranged. It is; as was confirmed by scattering experiments.¹⁹ The surface term in the nuclear energy explains the energy gain in nuclear fusion. The energy gain in nuclear fission has a different cause. It results from the competition between short-range attraction (caused by the nuclear force) and long-range repulsion (caused by the electric repulsion between the protons). We will come back to such a competition in Sect. 7.1.

There are aggregates which are held together by long-range



Fig. 2.7

47 Tucanae, the second brightest globular cluster in the Milky Way.

Globular clusters consist of several 100 000 stars, which are loosely bound to each other by gravity. Since gravity is a long-range interaction, there is no sharp interface between the interior of the cluster and the surrounding galactic space. Such a sharp interface would require a short-range interaction. *en.wikipedia.org/wiki/Bullet Cluster*

attractive interactions, but which do not have a sharp interface because of the long range attraction. These are the globular clusters. Fig. 2.7 shows a picture. Globular clusters contain some 100 000 stars, which move (on the time scale of many millions of years) randomly. A statistical analysis is

¹⁸ This binding energy is determined – starting from the relation $E = mc^2$ – by mass spectroscopy. Because of the finite binding energy, the mass of a nucleus is not exactly equal to the sum of the masses of the nucleons (the protons and the neutrons). The difference is called the "mass defect". One can determine the sum formula of a molecule with high resolution mass spectrometers. (For example, one can distinguish 12 H atoms from one C atom). In principle, this procedure might also be applied to the energy of chemical bonds. However, this would require to determine the molecular mass to within 10 decimal places, since 1 eV is roughly equivalent to 10⁻⁹ atomic mass units. The current accuracy of mass spectrometers is 4 – 5 decimal places. This suffices to determine the binding energies in the nucleus (on the order of mega-electronvolts, MeV), but not the binding energies from chemistry (a few eV).

¹⁶ Teflon is rather expensive. If cost is an issue, silicones are an option. Why silicones have low surface energy is not easily understood. Silicones contain segments of the form -O-(SiR₁R₂)- in the main chain

¹⁷ "Short-range" in this context means that the interaction between two spheres of the materials in question decays to zero for large *D* in the limiting case $D \ll a$ (*D* the distance between the surfaces, *a* the radius of the sphere). This is the case for all exponentially decaying force laws. It is further the case for all power laws r^n with an exponent $n \leq -6$. The vdW interaction is thus short-range in this sense (albeit marginally).

¹⁹ When two particles with short-range interaction almost collide, they do not change direction because they do not see each other. For the Coulomb interaction, there is a small change in direction even if the particles do not come close.

appropriate and successful. For stars, interaction with distant partners is essential. While the interaction potential scales like r^{-1} , the number of stars in a shell of radius *r* scales like $r^{2,20}$ A star does not interact with its neighbors only. The density profile $\rho(r)$ (ρ the number density of stars) therefore decreases continuously at the edge of the cluster; there is no sharp edge.

Because molecules interact primarily with their nearest neighbors, liquid/liquid interfaces and liquid/vapor interfaces are almost atomically sharp. The fact that interfaces are sharp implies that there is a clear difference between "surface" and "bulk" in nanoparticles. Extremely small aggregates, where one can no longer make this distinction, are called "clusters".



When you charge a conductive droplet, the charge accumulates on the surface. Then the surface tension decreases in proportion to the square of the charge. The decreased surface tension is caused by to the repulsion between charges of the same sign.

Remember

- Although there are many types of surface anomalies, the surface tension is not necessarily associated with a "skin". The missing neighbors alone also create a surface energy.
- The missing-neighbor model requires short-range interactions (interactions with the neighbors only).
- The missing-neighbor model explains why surface energy is correlated with internal cohesion.

2.4 Electrocapillarity and negative surface energies

A negative surface energy cannot be a property of an equilibrium state, because such an interface will always strive to increase in size. At the end of such a process, the bulk phase in question will dissolve completely.²¹

Consider a conductive liquid (e.g. mercury or any electrolyte), which is electrically charged by means of an inserted electrode. Since all electric fields inside the drop are dissipated by corresponding electric currents, and since, according to Maxwell's 1st



²⁰ Assuming constant density, which is questionable.

²¹ The lamellar phases, that sometimes result from self-assembly of surfactants, can be viewed as the result of such a process. We will come back to self-organization in Sect. 7.

law, the charge density is equal to the divergence of the field ($\rho = \nabla \cdot E$), the relation $\rho = 0$ follows from

E = 0. The entire charge is therefore located at the surface. Since charges of the same sign repel each other, the charge at the surface *lowers the* surface energy. The Lippmann equation states that:

$$\sigma_{M} = -\frac{d\gamma}{d\Delta \omega}$$
 Glg. 2.4.1

 σ_M is the surface charge density, $\Delta \phi$ is the potential jump at the interface. (Glg. 2.4.1 can be made plausible by the relation $\delta \gamma = -\sigma_M d\Delta \phi$). If $\sigma_M = C$ $\Delta \phi$ with *C* the capacitance, integration leads to

$$\gamma \approx \gamma_0 - \frac{1}{2}C(\Delta \varphi - \Delta \varphi_0)^2$$
 Glg.
2.4.2



This relation is shown in Fig. 2.8. Using this relation, one can find the "potential of zero charge" (PZC) for liquid electrodes (like the mercury electrode). At the PZC, the surface energy attains a maximum, so the drop comes closest to a spherical shape.

If the charge is sufficiently high, γ becomes negative and the surface area increases spontaneously. The result of this process is sometimes called a "Coulomb explosion." Applications of the Coulomb explosion include electro-spray ionization (ESI, Fig. 2.10) and electrospinning (Fig. 2.11). The process of electrowetting is related to this. In electrowetting, however, one stays below the threshold for the Coulomb explosion with the voltage and manipulates only surface energy and contact angle via the charge. Conductive

droplets can be moved back and forth in an oil phase by a clever arrangement of electrodes and potential sequences on the surface ("droplet-based microfluidics"). One can also change the droplet radius and create switchable optical lenses.

Remember

 Charges migrate to the interface in conductive bodies. They lower the interfaces energy.



- When the surface energy becomes negative, a Coulomb explosion occurs. Applications are electrospray-ionization, electrospinning and electrowetting (the latter without Coulomb explosion).

2.5 Surface energies of solids

Solids also have a surface energy. This is difficult to measure because solids do not form droplets. One can change the surface of a solid, but in doing so, one always also does elastic work. To subtract this elastic work from the total work in a quantitatively correct way and thus to calculate the surface work is difficult.

Solids usually have *high* surface energies. Tungsten, for example, has γ = 4400 mN/m. This is not surprising, because tungsten has an enormously high internal cohesion. Therefore, it has a very high melting point (3422°C). A side note: Most polymers have surface energies similar to those of liquids, although from a mechanical point of view they appear to be solids. This is due to the chain topology. The cohesive forces *between chains in* polymers are similar to the cohesive forces in liquids.

Changes in the surface energy of solids upon adsorption can be tracked quite easily by bending thin bars ("cantilevers"). One can construct sensors based on this bending. Fig. 2.12 shows a micromechanically fabricated beam.²²

Solids can have heterogeneous surfaces. Then also the surface energy is not laterally constant. This can be seen very simply from the fact that the meniscus does not remain smooth when it is immersed in water. It adheres to the defects. This is a simple test for cleanliness (also in industrial practice).

Remember

- Solids also have a surface energy. It is often high (> 1000 mN/m) because the internal cohesion is high.
- Measuring the surface energy of solids absolutely is difficult because elastic work is done when the interface area changes. *Changes of the surface energy* (e.g. caused by adsorption) can be measured by the bending of thin beams.
- Solid-state interfaces are often laterally heterogeneous.



Fig. 2.12 Measuring surface energies of solids absolutely is difficult. The differential measurement of a *change of* γ can be done via beam bending at adsorption. *www.cs.unc.edu/~nanowork/tam s.html*

²² Also "cantilever" (German: "Blattfeder"). Typical thicknesses of cantilevers are in the range of a few micrometers. Cantilevers are products of microsystems technology. They belong to the MEMS-devices (MEMS for "microelectromechanical systems") and have become cheap. In the academic field, bending is often read out with the "optical lever technique" (i.e. with a reflected laser beam). In engineering, this is considered too complicated. Mostly, piezoresistive elements are used on one side of the cantilever.

3 The capillary pressure

3.1 Motivation

We begin the discussion of capillary pressure with an argument, which will prove to be false, but which illustrates the usefulness of capillary pressure for calculations of all kinds. Consider the figure shown in Fig. 3.1. As is well known, such bridges give rise to attractive capillary forces. One might be tempted to calculate the force as

$$F_{cap} \stackrel{?}{=} \gamma S$$

S is the circumference of the fluid bridge at the narrowest point. Once again, this formula is *wrong*. It also contradicts experience. Insert the values S = 1 cm and $\gamma = 72 \text{ mN/m}$. With these values, the force results as 0.7 mN, corresponding to a weight $M = F_{cap}/g = F_{cap}/(9.81 \text{ m/s}^2) \approx 70 \text{ mg}$. Thus, a capillary force of this magnitude would never be sufficient to support the weight of a microscope slide. The opposite is true. Two wet microscope slides adhering to each other can only be separated by shearing motion. Pulling along the normal leads to nothing.

To correct the error in Glg. 3.1.1 we calculate the force as the derivative of work with respect to displacement:



Glg. 3.1.1





$$F_{cap} = \left(\frac{\mathrm{d}W_{cap}}{\mathrm{d}z}\right)_{Vlid}$$

At this point the old wisdom comes into play that when taking derivates of this kind it must always be specified which quantities are held constant. (Recall the difference between the specific heats at constant pressure and constant volume, c_p and c_V .) Glg. 3.1.1 would be correct if the circumference of the water droplet at the narrowest point remained constant during the process of expansion. *On the*

*contrary, the volume of the drop remains constant.*²³ Therefore, the bridge constricts at the narrowest point (Fig. 3.2). The circumference decreases and the surface area A increases more rapidly than would be the case if the circumference remained constant.

For the geometry from Fig. 3.2, the calculation of the surface area and its change when the distance between the two bodies is changed is tedious. It is easier to reason about the capillary pressure. The correct result is

$$F_{cap} = \gamma S - \Delta p \ A_{waist}$$
Glg. 3.1.3

 Δp is the capillary pressure (see below) and A_{waist} is area of the bridge, where it narrowest.



Fig. 3.2 If you pull on the solid bodies in Fig. 3.1 the liquid bridge constricts. This effect must be taken into account when calculating the surface work.

²³ Evaporation or condensation are left aside.

Remember

The force exerted by a capillary bridge is *not* given as surface tension× circumference. The capillary pressure comes into play, as well.

3.2 The Laplace equation

Curved fluid-fluid interfaces result in a pressure difference between the two fluids. This is the *capillary pressure*, Δp . To calculate Δp , we consider a fluid sphere (a drop or a bubble) and use the fact that the free enthalpy *G* is minimal at equilibrium (Fig. 3.3). Let the radius of the sphere be such that *G* is minimal. Change the radius of the sphere from the minimum position by the small value *dr*. Two different forms of work are done, namely a pressure-volume work, given as $-\Delta p dV_{drop}$ (Δp the difference of pressures, defined as $p_{in} - p_{out}$ and V_{drop} the volume of the droplet, not





Glg. 3.2.1

Glg. 3.2.3

Glg. 3.2.4

to be confused with the volume of the whole system) and further the surface work, given as γdA_{drop} (with A_{drop} the surface area of the droplet). Since both V_{drop} and A_{drop} depend on r, we must post-differentiate. because G_{tot} is minimal, $dG_{tot}/dr = 0$. The sum of both works must be zero:

$$\frac{\mathrm{d}G_{_{tot}}}{\mathrm{d}r} = -\Delta p \, \frac{\mathrm{d}V_{_{drop}}}{\mathrm{d}r} + \gamma \, \frac{\mathrm{d}A_{_{drop}}}{\mathrm{d}r} = 0$$

We use the equations for the volume and the surface area of a sphere:

$$-\Delta p \frac{\mathrm{d}}{\mathrm{d}r} \left(\frac{4}{3}\pi r^{3}\right) + \gamma \frac{\mathrm{d}}{\mathrm{d}r} \left(4\pi r^{2}\right) = 0$$
Glg. 3.2.2

The differentiation results in

$$-\Delta p \ 4\pi r^2 + 8\pi \gamma r = 0$$

and

$$\Delta p = \frac{2\gamma}{r}$$

This is the Laplace-equation. Δp is the *capillary pressure* (also: "Laplace-pressure"²⁴).

²⁴ An opinion to the terminology: If there is a choice for naming something, the name based on the discoverer (here: Laplace pressure) is the second best choice. The speaking terms (here: capillary pressure), are the better terms.

The calculation that lead to Glg. 3.2.4 was performed for a sphere. For a long cylinder ($L >> r_{cyl}$), one has $V_{cyl} = \pi r_{cyl}^2 L$ and $A_{cyl} = 2\pi r_{cyl} L$. The capillary pressure then is $\Delta p = \gamma/r_{cyl}$.

Glg. 3.2.1 can be rearranged as

$$\Delta p = \gamma \frac{\mathrm{d}A_{drop}}{\mathrm{d}V_{drop}}$$

For arbitrarily shaped interfaces, this leads to

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

 $1/R_1$ and $1/R_2$ are the "principal curvatures". For the explanation of the principal curvatures we borrow from differential geometry.²⁵ On curved surfaces one can always find lines locally which have no curvature in the plane. They only have a curvature perpendicular to the surface. These lines are the geodesics. The geodesics are at the same time always the shortest connections between two points. At any point on the surface there is always a set of geodesics running through this point. At the north pole these are the longitudes. Among the geodesics, there is always one with a maximum curvature out of the plane and one with a minimum curvature out of the plane. Of course, this is not the case if all curvatures are equal. It is not the case at the north pole. It is the case at the equator because the earth is slightly oblate. The two geodesics are the equator (with the smaller curvature, that is, the larger radius of curvature) and the longitude (with the larger curvature). The two geodesics with maximum and with minimum curvature are perpendicular to each other. $1/R_1$ and $1/R_2$ (the "principal curvatures") are the maximum and minimum curvatures. To the Laplace pressure: If the curved surface is not a segment of a sphere, the Laplace equation must one contain the term $(1/R_1 + 1/R_2)$ rather than the term 2/r.

Fig. 3.4 A minimal surface www.soapbubble.dk/english/scie nce/the-geometry-of-soap-filmsand-soap-bubbles/

Without proof: The surface of a body (a drop, a soap bubble, ...), which has its surface minimized under given boundary conditions (attachment to a solid surface, fixed volume....), has the same mean curvature everywhere $(1/R_1 + 1/R_2 = \text{const.})$.

Glg. 3.2.6 has the interesting consequence that the capillary pressure can vanish even if the surface is not planar. For these particular surfaces, the two principal curvatures point in opposite directions. Fig. 3.5 shows an example. One can create such *minimal surfaces* oneself by dipping a loop of a wettable wire into a vessel filled with water and soap and then pulling it the loop out in such a way that a soap lamella remains attached. The capillary pressure is zero because there is

Glg. 3.2.5

²⁵ Differential geometry is the geometry on curved surfaces or - more generally - the geometry in curved spaces. Einstein catapulted differential geometry from a niche of mathematics to the center of our understanding of nature when he postulated a curved space. In general relativity, inertial systems always move on geodesics in curved four-dimensional space-time.

atmospheric pressure on both sides of the lamella. The surfaces with vanishing mean curvature are the smallest possible surfaces bounded by the edge in question (hence the name "minimal surface"). That the minimal surfaces have vanishing mean curvature everywhere $(1/R_1 + 1/R_2 \equiv 0)$ is proven in

differential geometry with some effort. If the Laplace equation is expressed in the form of Glg. 3.2.6 this result is plausible without mathematics.

We estimate the magnitude of capillary pressure for nanodroplets and nanobubbles. Assume $\gamma = 50$ mN/m and r = 10 nm. Inserting these values into Glg. 3.2.4 leads to $\Delta p \approx 10^7$ Pa = 100 bar. The capillary pressure inside nanosized drops is substantial. It is so substantial that nanobubbles are not easily stabilize mechanically. If no special measures are taken (a metallic matrix or surface tension close to zero) they collapse. Nanofoams with spherical bubbles are somewhat challenging from a materials engineering perspective.²⁶ However, such large pressures only occur when the droplets or bubbles are indeed of nanoscopic dimension. The capillary pressure of a drop of water on a car's windshield (let the radius be 1 mm), is only 10⁻³ bar. There is a *scale dependence*. Capillary pressure is only significant on small scales. Another example: an air bubble in a vein ($r \approx 10 \ \mu$ m) is equivalent to a plug (which is dangerous). Macroscopic bubbles are much less rigid. $h \approx r \approx \lambda_{cap}$

Fig. 3.6

If the characteristic length of a problem (e.g. the radius of a droplet) is equal to the capillary length, gravitational forces and capillary forces roughly balance each other. On smaller length scales capillarity predominates, on larger ones gravitational forces.

If the capillary pressure competes with a pressure of some other origin, the size dependence of the capillary pressure and the competing pressure results in a characteristic length, the *capillary length*. Consider a droplet sitting on a plate (Fig. 3.6). It could also be hanging (Fig. 3.7) or stick laterally to a vertical surface (like the raindrops outside a window). At what drop size will gravity noticeably affect the drop's shape? From the drops outside the window we know that this size is about 1 mm. This can be understood by demanding that the capillary pressure and the gravitational pressure are similar:

Glg. 3.2.7

Glg. 3.2.8

$$\frac{2\gamma}{r} \approx \rho g h$$

 $G = 9.81 \text{ m/s}^2$ is the acceleration constant due to gravity and *h* is the size of the drop. Assume $h \approx r$ and call this length λ_c (the capillary length). Solving for λ_c results in

$$\lambda_c \approx \sqrt{\frac{\gamma}{\rho g}}$$

A factor of 2 has been omitted. For water, $\lambda_c \approx 2$ mm. (Sometimes the factor 2 is not omitted. The capillary length then has a slightly different value).

If the drop size is fixed, the ratio of gravitational energy to the surface energy is sometimes called "Bond number".²⁷ Drops which are larger than the capillary length have a Bond number larger than 1.

²⁶ There are also foams in which the bubbles are separated only by lamellae.

²⁷ There are other, slightly different definitions of bond number.

The capillary length underlies a rather accurate method for determining the surface energy. This is the *pendant-drop method* (Fig. 3.7). The contour of a pendant drop is captured by a camera and analyzed by a computer. If the drop size is comparable to the capillary length, the surface tension can be derived from the contour. The lower the drop hangs, the smaller the surface tension.

Characteristic lengths similar to the capillary length (and often also called "capillary length") are also used in other contexts. In these situations, the capillary pressure always is in competition with another pressure. An example is the splitting up of emulsion droplets in a shear flow.²⁸ Here the capillarity competes with the stress exerted by viscous medium. We leave details away. The smaller the droplet, the more difficult it is to break it up in the flow field. A practical lower limit is in the range of $r \approx 50 \,\mu\text{m}.^{29}$

Sometimes such competition is also quantified by a *capillary number* (*Ca*). Consider again the fragmentation of droplets in the shear field. The capillary number is defined as

$$Ca = \frac{\eta v}{\gamma} = \frac{\eta v}{r} \frac{r}{\gamma}$$

 η is the viscosity³⁰ and v is a characteristic velocity. After the second equal sign *r* was added. The parameter $\eta v/r$ is a stress, which is a consequence of the viscosity. γ/r is (up to a factor of 2) the capillary pressure. Glg. 3.2.9 does not show that *Ca* depends on the drop size. The size dependence arises because the "characteristic velocity", v, for this case is the product of shear rate and droplet size. If the capillary number is large, the droplet can be split in the shear field.

There are other definitions of capillary number for other situations. The surface tension is always in the denominator. If the capillary number is large, the capillary force is small compared to the competing forces.

Capillary pressure can cause the local hydrostatic pressure to be negative in condensed matter. (This is impossible in a vacuum or in gases.) Consider the situation shown in Fig. 3.8. A notch in the surface of a solid

contains a liquid. The solid is wetted by the liquid. If the (negative) capillary pressure is larger than the ambient pressure (1 bar), the absolute pressure is negative in the liquid. This is a consequence of the cohesive forces and the rigid wall.

Negative capillary pressure often occurs at the surface of wet porous media. This include drying latex films. The negative pressure deforms the latex particles (Sect. 11.2). Negative capillary pressure







²⁸ An emulsion is a mixture of two liquids that are not "molecularly dispersed".

²⁹ In this area, one must always keep a careful eye on whether the radius or the diameter is used to indicate the drop size.

³⁰ For accurate treatment, one must take into account that the droplet and the surrounding fluid generally have different viscosities.

also explains why hydrogels often swell less in 100% saturated air than in water. The latter phenomenon also carries the name "Schröder paradox".

A word of caution: If there is a transport equilibrium between liquid and vapor in porous media, the capillary pressure depends on the relative humidity, because capillary condensation (instead of geometry and a fixed amount of liquid, section 4) determines the radius of curvature.

Remember

- For spheres, the capillary pressure is given as $p = 2\gamma/r$.
- Capillary pressure is significant when local radii of curvature are small.
- 3.3 *Consequences of capillary pressure*



The consequences of capillary pressure are numerous. We discuss a few examples:

- The surface tension of liquids can be determined by the bubble pressure method (Fig. 3.9). The end face of the capillary must be designed such that the three-phase boundary line adheres to the outer edge. If one starts from the situation in Fig. 3.9 on the left, and air is forced through the capillary, the radius of curvature initially *decreases*. This situation is stable because the pressure increases with increasing bubble volume. This changes when the radius of curvature becomes larger than the radius of the face. Then the pressure decreases with increasing bubble volume and *instability* occurs . The bubble ruptures. The maximum pressure is given as $p_{max} = 2\gamma/r_s$ with r_s the radius of the opening of the tube. From p_{max} , one calculates the surface tension.
- Capillary bridges in conjunction with negative capillary pressure lead to capillary adhesion. This is known, for example, from sand piles. Some animals secrete a fluid when walking on smooth surfaces, which induces adhesion ("wet adhesion").

At this point, we remind ourselves of the force exerted by a capillary bridge (Sect. 3.1). The capillary force is *not* given as γS with S the circumference. The capillary force is given as $-\Delta pA + \gamma S$. A and S are to be evaluated at the narrowest point. (For other locations or geometries, there are extensions of this equation.) Note that $\Delta p < 0$ for capillary bridges (most of the time). For macroscopic situations, capillary pressure dominates. However, capillary adhesion is also very relevant at the microscopic level.

Exercise: Calculate the capillary force exerted by a hemispherical drop on its support. (The result should be zero.)

- Attractive capillary forces create tensile stress when porous media dry. This can lead to cracking. Structures with high porosity (> 90%) often collapse during drying. (That can be avoided with supercritical fluids).
- In hydrophilic tubes, *capillary rise* occurs (Fig. 3.11). Equating capillary pressure and gravity pressure $(2\gamma/r = \rho gh)$ leads

$$h = \frac{2\gamma}{r \rho g}$$
 GIg. 3.3.1

Here it was assumed that the contact angle is zero. If the contact angle is finite, the radius *r* must be replaced by the quantity $r/\cos \theta$ (right in Fig. 3.10).

Note that the height of the capillary rise does not depend on the thickness of the wall. This was first observed in 1808 by Clairaut. Clairaut concluded that the underlying forces are of short range. Using the numerical values of water ($\rho = 10^3 \text{ kg/m}^3$, $g = 9.81 \text{ m/s}^2$, $\gamma = 72 \times 10^{-3} \text{ J/m}^2$), a contact angle of 0°, and a radius of the capillary of 1 µm, a height of h = 7 m is obtained. This corresponds approximately to the height of trees. Trees use the capillary force as a pump fluids to the top. Note that the capillary radius only needs to be small at the end. In the trunk, the capillaries can be larger. This is favorable for flow resistance.

Capillary pressure drives the transport of liquids in porous media. This is important, for example, in printing on paper ("imbibition"), in candles ("wicking"), or in agriculture and ecology (spreading liquids on a soil). These processes are also known from the up-take of coffee by a piece of sugar dipped into the coffee mug. Capillary forces also drive transport in the "lateral flow device" (an "assay", the best-known example previously being the pregnancy test strip, no replaced by the Covid19 tests). The simplest equation to describe the imbibition is the Lucas-Washburn equation

$$z(t) = \sqrt{\frac{\gamma r \cos \theta}{2n}t}$$
 Glg. 3.3.2

To prove this, equate capillary pressure to flow pressure. These are given as:

I:
$$\Delta p_{stream} = \frac{8}{r^2} \eta z(t) \frac{dz}{dt}$$
 II: $\Delta p_{cap} = \frac{2\gamma \cos \theta}{r}$

Equation I is the Hagen-Poisseuille law. *z* is the length to which the capillary in question is filled. dz/dt is the flow velocity. Use $\Delta p_{stream} = \Delta p_{cap}$, separate the variables, and integrate:



Fig. 3.11 The rise height depends on the radius of the capillary. Hydrophobic surfaces lead to capillary depression for water.

Glg. 3.3.3

$$\int_{0}^{z} \tilde{z}(\tilde{t}) d\tilde{z} = \int_{0}^{t} \frac{\gamma r \cos \theta}{4\eta} d\tilde{t}$$

The tildes were introduced so that the integration variables are named differently from the integration limits. One finds

$$\frac{1}{2}z^2 = \frac{\gamma r \cos \theta}{4\eta}t$$

Solving for *z* proves the Lucas-Washburn equation (Glg. 3.3.2). Glg. 3.3.2 describes transport in a capillary. For systems of pores there is a large set of extensions and complications. A side note: *z* scales here like $t^{1/2}$, similar to the root-mean-square displacement in diffusion. However, this is *not* diffusion in the sense of Brownian motion.



Glg.

When two soap bubbles of unequal size are in contact with each other, the material flows to the larger bubble. This can be explained by the capillary pressure (Glg. 5.2.6). It can also be explained by the decrease in total surface area.

A subtlety: According to the Lucas-Washburn equation, the large pores fill first. Later, the liquid is redistributed towards the small pores, because the negative capillary pressure is larger there.

Remember

- The pendant-drop method takes advantage of a competition between capillary pressure and gravity to determine surface tension.
- Capillary pressure can lead to capillary adhesion.
- Capillary pressure leads to capillary rise. This drives the liquid transport to the tops of trees.
- Capillary pressure often drives fluid transport in porous media.

3.4 Capillary instabilities

Consider a tube with a valve on which soap bubbles are sitting on both sides (Fig. 3.12). Let the radius of the bubble on the left (r_L) be smaller than the radius of the bubble on the right (r_R) . If you open the valve, the small bubble will become smaller and the large bubble will become larger. The situation is *unstable*.

At this point, capillary pressure is often used as an argument. Because the capillary pressure is larger on the left than on the right, the left bubble shrinks. The instability can also be understood from the change of the total surface area. For the bubbles shown in Fig. 3.12, the sum of the surface areas of both spheres decreases if the sum of the volumes remains constant and the smaller sphere gives up its material to the larger one. Take advantage of the constant volume:

Glg. 3.4.1

$$\frac{4\pi}{3}\left(r_A^3+r_B^3\right)=const \implies r_A^2 dr_A=-r_B^2 dr_B$$



Fig. 3.13 The Rayleigh instability en.wikipedia.org/wiki/Surface_tension en.wikipedia.org/wiki/Urination

Calculate the change of the surface as

$$dA = 4\pi \left(d\left(r_A^2\right) + d\left(r_B^2\right) \right) = 8\pi \left(r_A dr_A + r_B dr_B\right)$$
$$= 8\pi r_A dr_A \left(1 - \frac{r_B^3}{r_A^3}\right) < 0 \text{ falls } r_B > r_A$$

A similar situation is known for liquid cylinders (Fig. 3.13). If – for some reason (a thermal fluctuation?) – the cylinder is slighter thinner somewhere, the capillary pressure is increased there and the surface tension displaces the liquid from this area until the cylinder has split into drops. This is the *Rayleigh instability*. An implicit assumption in this argument is that the curvature of the surface along the axis is less than across the axis. Thus, the unstable perturbations must have a certain minimum length. On the other hand, very long wavelength perturbations require material transport over long distances to turn the jet into a chain of droplets. From these two competing requirements, one calculates a characteristic droplet size. The details are even more complicated. High-speed videos show that a droplet in the process of pinching off breaks into more smaller droplets. The dynamics is complicated but reasonably well understood. That there is more than a



Glg. 3.4.2



single characteristic drop size can also be seen in the spider webs, on which dew has formed drops overnight. One sees drops of different sizes. These drops are also a consequence of the fact that a uniformly thick liquid film on a thin fiber is unstable.

Note: Two menisci in hydrostatic equilibrium are stable if the concave (Fig. 3.14).

Remember

- When two soap bubbles of different sizes are in contact with each other, the larger one grows at the expense of the smaller one.
- A related instability (the Rayleigh instability) causes liquid cylinders to decay into droplets.
- These instabilities can be understood based on either capillary pressure or the lowered total surface area.

3.5 Ostwald ripening

Another important capillary instability is Ostwald ripening. Replace the flow through the tube in Fig. 3.12 by a transport through the vapor phase. ³¹ There then is an evaporation-recondensation equilibrium at the surfaces of the droplets. (The local vapor pressure is larger over the small droplets than over the large ones, Sect. 4.1.) Diffusion through the continuous phase causes the large droplets to grow at the expense of the small droplets.

Ostwald ripening is a widespread phenomenon. It turns fog drops into rain drops. It also occurs in emulsions. Emulsions must be stabilized against a) sedimentation, b) coalescence and c) Ostwald

³¹ The same argument applies to oil droplets in water, if there is some residual solubility of the oil in the water. It also applies to air bubbles in a liquid. We formulate the facts for droplets in steam; the transfer to the other cases is simple.

ripening. Without stabilization, the oil phase will separate from the water phase (as is known from milk).

For emulsions, there is a remedy for Ostwald ripening. A substance is added to the droplets (the "disperse phase") that is virtually insoluble in the continuous phase. When the droplets become smaller, this substance builds up an osmotic pressure and thus brings Ostwald ripening to a halt. In the context of *miniemulsions*, this substance carries the name " hydrophobe". (These are oil-in-water emulsions.) A typical hydrophobe is hexadecane. "Miniemulsions" are not characterized by a certain size range (e.g., to be distinguished from microemulsions³²). Miniemulsions³³ are characterized by this particular mechanism of stabilization. The same mechanism can also stabilize water droplet I mist. This is the famous "smog". In smog, certain molecules coming out the cars' exhaust pipes stabilize the fog droplets and prevent them from becoming raindrops via Ostwald ripening. (Dust can play a similar role).

Ostwald ripening also occurs in polycrystalline materials. In these, at high temperatures (just *below* the melting point), the large crystallites grow at the expense of the small ones. Controlling the "grain ripening" is part of the "thermomechanical treatment" of steel. We recall at this point that capillary instabilities are ultimately driven by surface-to-volume, not capillary pressure (see the discussion before Glg. 3.4.2). Polycrystalline materials can lower the energy of the inner surface by undergoing Ostwald ripening.

Remember

 In Ostwald ripening, large droplets (bubbles, particles) grow at the expense of small ones, which is caused by the capillary instability,

³² Microemulsions contain surfactant mixtures that cause spontaneous curvature. Microemulsions are thermodynamically stable. They form spontaneously. Other emulsions are metastable at best. Microemulsions typically have droplet radii in the range of a few nm. They are technically problematic in that they require large amounts of surfactant.

³³ The term "miniemulsion" is mainly used in the context of miniemulsion polymerization. Stabilization of emulsions against Ostwald ripening by addition of long-chain non-polar molecules is also found in the food sector, in crop protection and in cosmetics.

4 Vapor pressure above curved surfaces, nucleation

4.1 The Kelvin equation

When the surface tension was defined as $(dG/dA)_{p,T,n}$ (Glg. 2.2.1), evaporation and condensation were excluded from the discussion. This is not problematic at the macroscopic scale, because evaporation and recondensation always shift in partial pressure near the surface, slowing further evaporation/recondensation. This is different on the nanoscale, because all paths are short and transport is correspondingly faster.

We start the discussion with a digression on steam distillation. A distribution equilibrium of a substance between a liquid and a vapor phase can be influenced by the hydrostatic pressure . This is favorable if one does not want to heat (e.g. because the substance to be distilled would then decompose). Compare situations I and II in Fig. 4.1. On the step from I to II, an inert gas was added to the gas phase, which dissolves poorly in the liquid. This gas increases the hydrostatic pressure. Do not confuse the hydrostatic pressure with the partial pressure of the substance of interest . Hydrostatic pressure is primarily a mechanical quantity, although in gases it is closely related to concentration. (The partial pressure mostly denotes a concentration).



vapor pressure of a liquid.

There are two separate equilibria between liquid and vapor: the hydrostatic and the material. Because we assume that the inert gas does not dissolve in the liquid, it affects the chemical potential of the component of interest only through pressure. (Otherwise, the mixing entropy and the

mixing enthalpy would affect the chemical potential). The chemical potentials are the same in both phases:

Ia:
$$\mu_{liq} = \mu_{vap}$$
 IIa: $\mu_{liq}' = \mu_{vap}'$ 4.1.1
Ib: $\mu_{liq, \Delta p_{hyd}=0} = \mu_{vap}^{\varnothing} + RT \ln \frac{p_{sat}}{p^{\varnothing}}$ IIb: $\mu_{liq, \Delta p_{hyd}=0} + \overline{V}_{liq} \Delta p_{hyd} = \mu_{vap}^{\varnothing} + RT \ln \frac{p_{sat}}{p^{\circlearrowright}}$

Primed parameters refer to the situation on the right in Fig. 4.1. In equation Ib, ideal behavior was assumed for the chemical potential in the gas phase. In equation IIb ,it was used that the liquid is pure. Then $\mu = \frac{dG}{n} = d\overline{G} = \overline{V}_{liq} dp$. (The bar represents a molar quantity.) Calculate the difference IIb – Ib:

$$\overline{V}_{liq}\Delta p_{hyd} = RT \left(\ln \frac{p_{sat}}{p^{\varnothing}} - \ln \frac{p_{sat}}{p^{\varnothing}} \right)$$
Glg. 4.1.2

which leads to

$$\ln \frac{p'_{sat}}{p_{sat}} = \frac{\overline{V}_{liq} \Delta p_{hyd}}{RT}$$
Glg. 4.1.3

The hydrostatic pressure thus causes the vapor pressure to increase. Figuratively speaking, the increased hydrostatic pressure drives the molecules out of the liquid into the vapor.

The path from vapor distillation to vapor pressure over curved surfaces is short. One uses the capillary pressure for the hydrostatic pressure and obtains

$$\ln \frac{p'_{sat}}{p_{sat}} = \frac{V_{liq} 2\gamma}{RTr}$$

 p_{sat} and p_{sat}' are the equilibrium vapor pressure over a planar surface and over a curved surface, respectively. The subscript "*sat*" stands for saturation. Glg. 4.1.4 is the *Kelvin equation*. *Increasing capillary pressure causes the vapor pressure to increase*.

4.2 Homogeneous nucleation

The Kelvin equation is closely related to the phenomenon of *homogeneous nucleation*. When the saturation vapor pressure is exceeded in a vapor phase (as often occurs during cooling, including summer evenings in humid weather), this often leads to a



metastable situation because nanoscopic droplets decay shortly after having been formed. The equilibrium vapor pressure above a nanoscopic droplet is substantially higher than the equilibrium vapor pressure above a planar surface. Only when a certain critical droplet size is exceeded, do the droplets grow. One can calculate the critical drop size from the Kelvin equation by rearrangement:

$$r_{crit} = \frac{\overline{V}_{liq} 2\gamma}{RT \ln(p'_{sat}/p_{sat})} = \frac{\overline{V}_{liq} 2\gamma}{RT \ln(rH)}$$

rH stands here for relative humidity. (The last transformation only makes sense for water.) The larger the supersaturation, the smaller the critical radius.

In the following, we discuss nucleation not on the basis of the Kelvin equation, but on the basis of volume energy and surface energy. This description is equivalent to the reasoning with the Kelvin equation. However, we do not prove this equivalence.

Fig. 4.2 has the radius of a droplet on the x-axis. The total energy of the particle has two contributions: a surface energy and a volume energy. The surface energy is quadratic in magnitude ($4\pi r^2$ for spheres). The coefficient is the surface energy γ . The volume energy is cubic in magnitude



 $(4\pi/3 r^3 \text{ for spheres}).^{34}$ The coefficient is the difference of the chemical potentials in the outer space and in the particle, normalized to molar volume $\Delta \mu/\bar{V}$. $\Delta \mu$ increases with increasing supersaturation. When subtracting a cubic function from a parabola, one finds a maximum at small *r*, because the quadratic term in the limit of $r \rightarrow 0$ is always larger than the cubic term (even if both approach zero, individually). In consequence, there always is a nucleation barrier. The critical radius (the radius at the barrier) is the same as the critical radius as derived from Glg. 4.2.1. (The proof is a bit tedious.) The derivation via the energies also allows to estimate the height of the nucleation barrier.

An alternative to homogeneous nucleation is always heterogeneous nucleation, i.e. nucleation at surfaces. There is an important difference between liquids and crystals. For liquids, the advantage of heterogeneous nucleation is simply the lower curvature of the surface for the same volume (Fig. 4.3). (This occurs only when the liquid wets the interface, i.e., when the energetic conditions at the solid/liquid interface are favorable). In crystals, *epitaxial growth* is a second requirement.³⁵ Heterogeneous nucleation of crystals requires a surface of the same crystal or at least a surface with similar structure (similar spacing between the lattice plains, in particular).

4.3 Capillary condensation

If the surface is concave, the radius in the Kelvin equation (Glg. 5.2.4) is formally negative. Into a notch (as in Fig. 3.8), condensation takes place even at *undersaturation*. This is called *capillary condensation*. For this reason, porous media and also rough surfaces are almost always moist. One can use porous media (if they are initially dry) as drying agents. A well-known example is silica gel.

At contacts, capillary condensation leads to *capillary adhesion*. A number of examples of this are known:

- Sand piles are stabilized by capillary bridges. (Attention: In the case of the sand piles at the sea, the salt acts as an adhesive. This has nothing to do with capillary condensation).
- Capillary forces also play a major role in atomic force microscopy. One must work in very dry air to exclude capillary forces.
- Capillary condensation is one reason why the static friction coefficient (sec. 9.2) increases in the course of time. The phenomenon as such was already reported by Leonardo da Vinci. It was long thought that the main cause of this increase was plastic deformation of roughness in the contact zone ("asperity creep"). Capillary aging also plays a role.

As shown in Fig. 4.4, capillary condensation is often hysteretic because a capillary bridge, once formed, does not break again. There is an interplay be capillarity and elasticity. This interplay of capillary forces and other forces is of much importance in soil mechanics.

A side note on capillary forces. At the beginning of section 3.1 it was reported that the capillary force can be calculated from the virtual work and, further, that the virtual work must be calculated at constant fluid volume (instead of constant circumference of the capillary bridge). At the nanoscale, local curvatures are large and transport in the vapor phase is fast. Therefore, for all liquids having



rH = 0.9 h₀ > 2r_{crit}

rH = 0.99

Kapillarbrücke

 $h_0 < 2_{rcrit}$

³⁴ This argument would apply in exactly the same way if *r* were the edge length of a cube. In this case, the surface area would be proportional to $6r^2$ and the volume would be proportional to r^3 . The surface-to-volume ratio scales like the inverse size regardless of shape. (An exception are the "fractal" objects.)

³⁵ Energy and favorable packing at the interface are linked. The packing aspect is less important liquids than in crystals.

substantial vapor pressure (all liquids except ionic liquids and silicone oils), the boundary condition at virtual work is given as *constant chemical potential* (i.e.; constant mean curvature of the surface and constant Laplace pressure) instead of constant volume. One might think that this circumstance would have an influence on the capillary force. In calorimetry, c_p is different from c_V ; constant volume or constant pressure make a difference. But the capillary force does *not depend* on whether the volume or the chemical potential is constant. This is because there are evaporation or condensation processes when drawing under conditions of constant chemical potential. There is a work associated with these processes (of size $\Delta V \Delta p$). This work just compensates for the difference between the surface work at constant volume or constant chemical potential.

Remember

- Above convexly curved surfaces, the vapor pressure is higher than above planar surfaces.
- The vapor pressure follows the Kelvin equation: $\ln(p_{sat'}/p_{sat}) = (2\gamma/r)/(RT/V_{mol})$.
- There is a critical minimum droplet size for droplet growth in supersaturated vapor. Once this is
 reached, homogeneous nucleation has occurred. For droplets on wettable surfaces, the radius of
 curvature can be larger than in the bulk for the same volume. This circumstance leads to
 heterogeneous nucleation.
- The mechanisms of homogeneous and heterogeneous nucleation can also be understood in terms of the sum of surface and bulk energies.
- Homogeneous and heterogeneous nucleation also exists for crystals, although these do not have a spherical shape and therefore no capillary pressure can be calculated. The surface-to-volume ratio is decisive. Heterogeneous nucleation in crystals implies epitaxial growth of the crystal phase on the surface in question (requires a "seed").
- Over *concave* curved surfaces the vapor pressure is lower than over planar surfaces. This leads to capillary condensation even in undersaturated vapor. Capillary condensation is of great practical importance because it entails capillary adhesion.

5 Adsorption

5.1 General remarks

Adsorption of molecules at interfaces is important first because it is ubiquitous. Whenever adsorption lowers the surface energy, it takes place. (It is the *free* energy of the interface. Entropy can also drive adsorption, although these effects are usually rather small.³⁶) The relationship between energy and adsorption is, at its core, the content of the Gibbs adsorption isotherm.

Important applications of adsorption are

- Surface modification
- Adhesion
- Adhesion of coatings to their substrate
- Corrosion protection
- Compatibilization
- Flotation
- Adsorption on activated carbon: purification of air
- Chromatography and inverse chromatography
- Surface-based sensing

The prevention of adsorption is as important in technology as adsorption itself. The *cleaning of* surfaces cannot be overestimated in its importance. Because of ubiquitous adsorption, it is virtually impossible to keep metal surfaces clean.³⁷ This includes electrodes. The key advantage of the mercury drop electrode in electrochemistry is that it is constantly regenerating.³⁸ Silicones are good biomaterials in part because they have low surface energy.³⁹

In adsorption, one must always distinguish between the adsorption *kinetics* and the adsorption *isotherm*. The former is the adsorbed amount as a function of time, the latter is the adsorbed amount at equilibrium as a function of the concentration (more precisely, of the activity) in the adjacent bulk phase. A practical problem: The adsorption equilibrium requires time. That is particularly important for strong adsorption to solid surfaces, because the adsorbate molecules often reorganize slowly. When an adsorption equilibrium is out of reach, one sometimes resorts kinetic measurements and evaluates the rate constants of adsorption and desorption, k_{on} and k_{off} . One may also



Fig. 5.1

An adsorption isotherm shows the equilibrium values of the adsorbed amount versus the concentration in the bulk. These values are the final results of many measurements of adsorption kinetics at different bulk concentrations. Depending on how quickly equilibrium is reached, one can also ramp the bulk concentration as a slow ramp and hope to be close to adsorption equilibrium at all times.

have a model for adsorption kinetics, from which one can derive the adsorbed amount at equilibrium, based on this this kinetic model. Fig. 5.2 shows an example.

³⁶ When entropy dominates, large molecules (including proteins or polymers, for example) displace small molecules at an interface because the many small molecules lose less entropy during adsorption than the few large molecules. Small molecules in this context are often solvent molecules

³⁷ Clean metal surfaces have a high surface energy (but they are - as said - almost never clean).

³⁸The surface of a jet of a liquid directly behind the outlet nozzle is also relatively clean.

³⁹ "Low-fouling" surfaces are also efficient if they bind water well. In liquids, adsorption is always *competitive adsorption*.

The measurement of rate constants is a problem when the adsorption kinetics is transport-limited. Remember the unstirred layer of the thickness of the Nernst length (a few $100 \,\mu$ m), inside which all

transport must be diffusive. From diffusive transport follows a time constant $\tau_{diff} = L^2/D$ with *L* the thickness of the Nernst layer (a few 100 µm) and *D* the diffusivity ($D \approx 10^{-5}$ cm²/s = 10^{-9} m²/s for small molecules in water). Inserting numerical values gives characteristic times on the order of seconds. This is often long compared to the molecular processes immediately at the interface. In this respect, colloidal spheres (rather than planar substrates) are more favorable. The transport problem is an important consideration for sensor design.

In biology, adsorption is often kinetically dominated in the sense that the molecules that reach a surface first irreversibly adsorb there, preventing adsorption of the molecules that arrive later. This is referred to as a "race for the surface." The fast molecules are usually the small molecules, because these can diffuse most quickly through the unstirred boundary layer (the Nernst layer, a fraction of a millimeter thick).

5.2 The Gibbs adsorption isotherm and its consequences



General SPR Sensorgram – The target (pictured in blue - an antibody) is immobilized on the surface of a sensor chip. Then, the <u>analyte</u> (pictured in red - an antigen) is flowed over the surface and binding (Association or red curve) is seen. Once <u>analyte</u> is no longer supplied to the surface, the Dissociation of the <u>analyte</u> from the target is seen (blue curve). At the end of the dissociation, any remaining bound <u>analyte</u> is removed completely using a regeneration solution (green line). For simple 1:1 binding, the equilibrium dissociation constant (K₀), is defined as the dissociation rate constant (K_d).

Fig. 5.2

In the context of biointeraction analysis (BIA), one monitors the adsorption of an analyte as a function of time. In this process, equilibrium is reached rather rarely. The kinetics are analyzed, with the relevant fit containing the equilibrium constant as a parameter. One usually concludes with a "rinse". First, a desorption constant is determined. Furthermore, "unspecifically" adsorbed material is removed. www.rdmag.com/article/2015/12/biggest-challenges-

www.rdmag.com/article/2015/12/biggest-challengesencountered-when-doing-spr-experiments also: Reichert Technologies , 11/6/18

Although the exact experimental determination of an adsorption isotherm is tedious, the isotherm (i.e., the adsorption equilibrium) is central to the discussion. We discuss three different adsorption isotherms, namely the Gibbs adsorption isotherm, the Langmuir isotherm, and the BET isotherm. The Gibbs adsorption isotherm has a certain special position here because it makes *no* assumptions about the interactions. It simply establishes a relationship between the amount adsorbed and the surface energy. It is also special in that on the right-hand side is not the activity of the adsorbed species in the bulk, but the derivative of the surface energy by the logarithm of that activity, $\delta\gamma/\delta(lna_2)$. The relationship between adsorbed quantity (more precisely, surface excess) on the one hand and this differential ratio on the other is rigorously correct and universal. The derivation of the Gibbs adsorption isotherm is instructive. The relationship between $\delta\gamma/\delta(lna_2)$ and a_2 depends on the molecular details. The Gibbs adsorption isotherm makes no statement about the latter relationship.

The Gibbs adsorption isotherm is based on a treatment of the interface within the framework of thermodynamics. Thereby, all extensive quantities are to be understood as excess quantities (Fig. 2.5). Excess quantities have already been introduced in the context of surface energy (Sect. 2.2). We recall

a difficulty: the definition of the "Gibbs dividing surface" requires the existence of a majority component (a solvent).

When discussing the thermodynamics behind the surface energy, it was stated that:

$$\mathrm{d}G_{\sigma} = \gamma \mathrm{d}A = \mathrm{d}H_{\sigma} - T\mathrm{d}S_{\sigma}$$

The subscript σ stands for the product of an area and an excess quantity in the Gibbs sense. In analogy to the fundamental theorem of thermodynamics we extend this equation to

$$dG_{\sigma} = dH_{\sigma} - TdS_{\sigma} + \sum_{Species} \mu_{J} dn_{J,\sigma}$$

= $\gamma dA + \sum_{Species} \mu_{J} dn_{J,\sigma}$
Glg. 5.2.2

 $n_{J,\sigma}$ is given here as $A\Gamma_J$ with *J* the index for the species. Note again the $\Gamma_1 = 0$. "1" denotes the majority component. The excess of the majority component is always zero according to the definition of Gibbs-dividing-surface. For a binary mixture we can write

$$dG_{\sigma} = dH_{\sigma} - TdS_{\sigma} + \sum_{Species} \mu_J dn_{J,\sigma}$$
$$= \gamma dA + \mu_2 dn_{2,\sigma}$$

At this point we use *homogeneity*. A function is "homogeneous"⁴⁰ in its arguments, if for each factor α applies

$$f(\alpha x, \alpha y, ...) = \alpha f(x, y, ...)$$

The size G_{σ} is homogeneous in $n_{1,\sigma}$, $n_{2,\sigma}$ and A:

$$G_{\sigma}\left(\alpha A, \alpha n_{1,\sigma}, \alpha n_{2,\sigma}\right) = \alpha G_{\sigma}\left(A, n_{1,\sigma}, n_{2,\sigma}\right)$$

In prose terms, if you double an interface in size and all quantities of matter (while keeping the composition the same), the Gibbs Free Enthalpy of that system doubles. We derive Glg. 5.2.5 according to α :

$$\frac{\partial G_{\sigma}}{\partial (\alpha A)}A + \frac{\partial G_{\sigma}}{\partial (\alpha n_{1,\sigma})}n_{1,\sigma} + \frac{\partial G_{\sigma}}{\partial (\alpha n_{2,\sigma})}n_{2,\sigma} = G_{\sigma}(A, n_{1,\sigma}, n_{2,\sigma})$$



Glg. 5.2.6

 $^{^{40}}$ It is also called "homogeneous of degree 1" because α occurs everywhere in the first power.

This relation is valid for all values of α , which includes $\alpha = 1$:

$$\frac{\partial G_{\sigma}}{\partial A}A + \frac{\partial G_{\sigma}}{\partial n_{1,\sigma}}n_{1,\sigma} + \frac{\partial G_{\sigma}}{\partial n_{2,\sigma}}n_{2,\sigma} = \gamma A + \mu_1 n_{1,\sigma} + \mu_2 n_{2,\sigma} = G_{\sigma}$$
Glg. 5.2.7

We form starting from Glg. 5.2.7 the total differential dG_{σ} :

$$dG_{\sigma} = \gamma dA + Ad\gamma + \mu_1 dn_{1,\sigma} + n_{1,\sigma} d\mu_1 + \mu_2 dn_{2,\sigma} + n_{2,\sigma} d\mu_2$$
Glg. 5.2.8

We use again that the surface excess of component 1 is zero and draw Glg. 5.2.3 from Glg. 5.2.8 subtract

$$0 = Ad\gamma + n_{2,\sigma}d\mu_2 = Ad\gamma + A\Gamma_2d\mu_2$$

= $Ad\gamma + A\Gamma_2d(\mu_2^{\varnothing} + RT\ln a_2)$
= $Ad\gamma + RTA\Gamma_2d(\ln a_2)$

Glg. 5.2.9 is a variant of the *Gibbs-Duhem equation*. In step 2, it was used that $n_{2,\sigma} = A\Gamma_2$. In step 3, we used the definition of activity in terms of chemical potential. We truncate by *A* and rearrange:

Glg. 5.2.9

$$\Gamma_2 = -\frac{1}{RT} \left(\frac{\mathrm{d}\gamma}{\mathrm{d}\ln a_2} \right)_T \approx -\frac{1}{RT} \left(\frac{\mathrm{d}\gamma}{\mathrm{d}\ln \left(c_2 / c_2^{\varnothing} \right)} \right)_T$$

This is the *Gibbs adsorption* isotherm. In the second step, the activity coefficient was assumed to be 1.⁴¹ Note: The Gibbs adsorption isotherm is only valid in thermodynamic equilibrium.

Before discussing the Gibbs adsorption isotherm further, we briefly address the question of what happens when a majority component does not exist. (A majority component was required in the definition of the Gibbs dividing surface, GDS). Basically, one then falls back to the situation that we also found in the context of thermodynamic principles. Then the GDS has to be placed in such a way *that* the Gibbs adsorption isotherm holds. One wonders, of course, what then is the statement of the Gibbs adsorption isotherm. It is then a definition of the surface excess. If there is the majority component, one can measure Γ_2 in principle. The emphasis here is on in principle, because such measurements are complicated at interfaces between two fluids. (The fact that the position of the GDS as postulated by Gibbs indeed produces the correct surface excess has not been proved here, by the way).

If there is no majority component, the Gibbs adsorption isotherm must be reformulated in two other places. First, there is then a surface excess of component 1. Second, the chemical potentials μ_1 and μ_2 are not independent. For binary mixtures, the Gibbs-Duhem relation applied to the bulk leads to the relation

⁴¹ Remember: $a = \gamma c/c \Theta$ with γ the activity coefficient (not the surface energy) and $c\Theta$ the standard concentration.

Glg. 5.2.12

Glg. 5.2.13

 $0 = n_1 \mathrm{d}\mu_1 + n_2 \mathrm{d}\mu_2$

The extension of Glg. 5.2.9 to systems without high dilution is therefore.

$$0 = Ad\gamma + n_{1,\sigma}d\mu_1 + n_{2,\sigma}d\mu_2$$

= $Ad\gamma + A\Gamma_1d\mu_1 + A\Gamma_2d\mu_2$
= $A\left(d\gamma + \left(-\Gamma_1\frac{n_2}{n_1} + \Gamma_2\right)d\mu_2\right)$

It follows that

$$\Gamma_2 - \frac{n_2}{n_1} \Gamma_1 = -\frac{1}{RT} \left(\frac{\mathrm{d}\gamma}{\mathrm{d}\ln a_2} \right)_T$$

At high dilution, the second term on the left-hand side can be neglected.

To apply the Gibbs isotherm, we discuss two examples. Fig. 5.4 shows the surface tension of water versus the logarithm of the concentration of the surfactant CTAB (cetyl trimethylammonium bromide) in the water phase (the latter often called "subphase" in this context). Note the logarithmic x-scale. If we approximate the activity coefficient to be 1, the concentration is proportional to the

activity. Because the *x*-axis in this graph was chosen to be logarithmic, the slope is equal to $-RT\Gamma_2$.

The kink in Fig. 5.4 is of minor interest here. The kink occurs at the critical micelle concentration (CMC). We will return to micelles in Sect. 7. At concentrations larger than the CMC, the chemical potential of the CTAB molecules in the water phase does not increase further because the excess molecules are trapped in the micelles (Fig. 5.6).

At $c < c_{CMC}$ the curve $\gamma(\ln c_2)$ shows downward curvature, meaning that Γ_2 increases with increasing concentration, as one would expect. Remarkably, there is a broad region below the CMC (about half a decade), in which the slope is nearly constant, meaning that Γ_2 is almost independent of the concentration in the subphase. c_2 . In this range, the surfactants must be in a particularly stable conformation, which causes the packing density to deviate only slightly from its most favorable value, even when the chemical potential of CTAB in the subphase varies. This favorable packing is sketched in Fig. 5.5. The alkyl chains are largely stretched. There is an attractive interaction between the stretched chains that requires the stretched chains to be





The surface tension of an electrolyte solution decreases when a surfactant is added to the subphase. Note the logarithmic scale on the *x*-axis. From the slope, calculate the surface excess of the surfactant. The kink occurs at the critical micelle formation concentration (CMC). Adapted from . Goodwin, J., Colloids and Interfaces with Surfactants and Polymers.

close to each other. This requirement brings about the wide range with $\Gamma_2 \approx const$. This brings us to the important fact that surfactants are distinguished by *two* separate characteristics. The first is amphiphilicity. Surfactants are hydrophilic at one end and hydrophobic at the other. (One also says "lipophilic" instead of hydrophobic.) Ethanol is also amphiphilic, but is not considered a surfactant. The second key property of surfactants is lateral interactions and the ability to self-assemble (Sect. 7). Amphiphilicity is only one of two prerequisites for the formation of micelles, organized layers at the water/air interface, and lamellae.

The surface excess can also be *negative*. Molecules can be *depleted* at the interfaces. Many salts are interfaces at the airwater interface, which has a simple explanation. According to the Debye-Hückel theory, each ion is surrounded by a counter ion cloud. Note: The counterion cloud does not contain many counter ions. That would violate electroneutrality. The

counterion cloud is a in increased probability density. On time average, it contains one counterion, because charge neutrality must be maintained. Because the counterion cloud is cut off from the interface, many ions avoid the interface. $\Gamma_2 = -RT \partial \gamma / \partial (\ln a_2)$ is negative and the surface energy *increases* with increasing salt concentration (Fig. 5.6).

As for most results of the Debye-Hückel theory, there are experimental counterexamples to this prediction. Regardless of the counter-ion cloud (that loss of half of it), ions sometimes are enriched at the air-water interfaces. This is one of the "ion-specific effects" (ISEs), related to the Hofmeister series (Sect. 10.8). One knows the consequences of this enrichment from thunderstorms. Prior to lightning, , heavy hailstones (descending) strike light hailstones (ascending). Triboelectricity transfers charge between those. (Triboelectricity sometimes occurs between shoes and carpets.) The triboelectricity occurs because there are ions on the surface of the grains. The details are complicated

and variable: not all thunderstorms are the same.

5.3 The Langmuir isotherm and the BET isotherm

Unlike the Gibbs adsorption isotherm, the Langmuir isotherm makes specific assumptions about the interactions between the surface and the adsorbate. These are:

- There is a fixed number of adsorption sites.
 These can either be empty or occupied once.
 Multi-layer adsorption is not permitted.
- All adsorption sites are equivalent.
- Apart from double occupation not being allowed, there are no interactions between the adsorbed molecules.
- The particles do not change their properties upon adsorption. (This is often not true for proteins.



By adding methanol, NaCl, or CaCl₂, one can control the surface tension of aqueous solutions within certain limits. Addition of salt can increase the surface energy, because salts are often deposited at the interface. *Source: R&D, Sartorius AG*



increasing the surfactant concentration _____

Fig. 5.5

Arrangement of surfactant molecules in aqueous solutions: (i) at low concentrations – some surfactant molecules adsorb at the air-water interface; (ii) at higher concentration a monolayer is formed at the air-water interface; (iii) an increase of surfactant concentration does not change the state of this monolayer. Surface. All additional surfactant molecules aggregate as micelles.

www.tau.ac.il/~phchlab/experiments_new/surface_tenstion/th
eory.html

These often "denature" upon adsorption and then are no longer biologically active.)

For this situation, one might, in principle, calculate a free energy of the adsorbate per unit area (equivalent to γ), take the derivative to $\ln(a_2)$, and obtain Langmuir isotherm from the Gibbs

adsorption isotherm. However, another argument turns out to be easier. Let θ be the fraction of occupied sites (the "coverage)". At equilibrium, θ is constant in time. The desorption rate is proportional to θ . Name the rate constant k_{des} . The adsorption rate is proportional to the fraction of vacant sites (to $1 - \theta$) and to the pressure of the gas (or the concentration of the species of interest in the bulk). In the following, we use the pressure *p*. Name the kinetic coefficient k_{ads} . In equilibrium both rate are equal and opposite

$$0 = \dot{\theta} = -k_{des}\theta + k_{ads}(1-\theta)p$$

Solving for θ leads to

 $\theta = \frac{k_{ads} p}{k_{des} + k_{ads} p} = \frac{p}{K^{-1} + p} = \frac{Kp}{1 + Kp}$ Glg. 5.3.2



In the second step, the ratio k_{des}/k_{ads} was renamed as K^{-1} . One might have called this ratio *K*. It is called K^{-1} because *K* as defined

this way can be viewed as binding constant, also known from chemical reactions ([AB] = K [A][B] with AB a complex of A and B and [] the concentration in units of mol/L⁴²). The binding constant is given as k_{assoc}/k_{diss} with k_{assoc} and k_{diss} the kinetic coefficients for association and dissociation.

Note: In liquids adsorption is *competitive adsorption*. The adsorption of a solute molecules involves the displacement of solvent molecules. The same applies to the effective van der Waals forces between molecules in liquids. These are always competing interactions. This is sometimes called and "Archimedes' principle".

Usually, the coverage itself is not experimentally accessible, but only the adsorbed amount n_{ads} . We write $\theta = n_{ads}/n_{sat}$ with n_{sat} the adsorbed amount at saturation. We us Glg. 5.3.2 and write

Glg. 5.3.3

$$n_{ads} = \frac{Kp}{1 + Kp} n_{sa}$$

⁴² Note the similarity in the shape of the Langmuir isotherm and the Michaelis-Menten kinetics. This similarity has its roots in saturation.
The right-hand side of this equation has three free parameters. All these parameters are subject to measurement in different situations. Before we come to these situations, some further remarks:

- In solution, the pressure *p* is replaced by the concentration *c*.
- As always, one should in principle replace pressure and concentration with fugacity and activity because there may be interactions between the molecules in the bulk phase, which will affect the adsorption equilibrium.
- The central characteristic of the Langmuir isotherm is *saturation* (Fig. 5.8). Saturation occurs frequently. If a particular species of molecules were to attach to a surface consisting of the *same* molecules, then those molecules would also cluster in the bulk or form condensed phases. Those molecules, which are well soluble, at the same do not form multilayers at surfaces.⁴³

From this last observation, a strategy for the preparation of low-fouling surfaces in biotechnology and medical technology is derived. The primary process in biofilm formation is the adsorption of proteins. If a particular species of proteins dominates, a dense, smooth packing of proteins of this same species can prevent further adsorption of proteins.

Sometimes the saturation in the sense of the Langmuir isotherm is not perfect in the sense that multilayer formation occurs at high bulk concentrations. This possibility is accounted for by the *BET isotherm* ("BET" for to Brunauer, Emmet, and Teller). A BET isotherm is shown in Fig. 5.8. Note:

The BET isotherm also shows a plateau caused by (incomplete) saturation.

The algebraic form proposed by Brunauer, Emmet and Teller is

Glg. 5.3.4

$$\theta = \frac{n}{n_{sat}} = \frac{K - \frac{1}{p_{sat}}}{\left(1 - \frac{p}{p_{sat}}\right) \cdot \left(1 + \frac{(\tilde{K} - 1)p}{p_{sat}}\right)}$$

p

The BET isotherm has a microscopic justification, but it may also be viewed as heuristic.⁴⁴ Note: \tilde{K} is dimensionless in this formula. In the limiting case of $p_{ads} \rightarrow 0$, θ is proportional to $\tilde{K}p/p_{sat}$, not to Kp, as in the Langmuir isotherm. One could, of course, replace \tilde{K} by K/p_{sat} , but we stick to the usual form.



Fig. 5.9

A data set as it appears in BET porosimetry. The plateau corresponds to the saturation. From the amount of substance taken up by the porous medium on the plateau, the integral surface area of the pore system is inferred www-

omcs.materials.ox.ac.uk/facilities/surfaceanalysis/bet-surface-area-analysis.html.

⁴³ When gases adsorb from the vapor phase, the tendency to wetting increases as the critical point is approached (the tendency to divergent film thickness at $p \rightarrow p_{sat}$ and at the same time to the spreading of droplets at $T \rightarrow T_{crit}$). This is due to the fact that the tendency to form clusters increases at $T \rightarrow T_{crit}$. There is the phenomenon of "critical wetting", i.e. a wetting transition near the critical point. Critical wetting would be technically interesting if it were robust. Unfortunately, it is not.

⁴⁴ The term "heuristic" is commonly used in the sense that the argument in question is formulated in limited time and with limited effort, even though a deeper understanding may be lacking. Many empirical equations are heuristic in this sense. From a methodological point of view, the term can be sharpened somewhat. Heuristic is the process of knowing. (Archimedes exclaimed "Eureka" as he grasped the principle of buoyancy while sitting in the tub). A heuristic equation is a step along the path of recognition. It describes experimental facts without the equation being grounded in fundamental scientific principles. An anchoring in the fundamental principles can follow. The Planck formula for the black body radiation was heuristic in this sense. It was guessed. Subsequently it was anchored in the fundamental principles of physics in the sense of quantization. In the process, it changed these principles. The Planck formula was guessed, but it was nevertheless a step towards knowledge.

Fig. 5.9 shows data obtained with *BET porosimetry*. Essential for BET porosimetry is also the saturation. One can see from the data at what absorbed amounts saturation occurred. With an assumption for the area per molecule, one can calculate the internal surface area of a porous medium from this. One writes

$$A_{pore} = \overline{A}_{ads} n_{ads} = N_A A_{Molekil} n_{ads}$$

 A_{pore} is the inner surface of the porous medium (i.e. the surface accessible to the adsorbate). \bar{A}_{ads} is area per mole of the adsorbate, n_{ads} is the adsorbed amount. At this point it is easier to calculate with area per molecule (${}^{A}_{Molecule} \approx 10 \text{ Å}^2$). Either way, the Avogadro constant N_A , shows up somewhere.

Talking of porous media: Capillary condensation can occur in nanoporous media. Capillary condensation can explain the rise on the right side of the BET isotherm without the need to postulate multilayers.

5.4 Adsorption energies

The Gibbs adsorption expresses in algebraic form what is intuitive, as well. Adsorption is driven by a decrease of the surface energy. Furthermore, the Gibbs isotherm can be used to convert from Γ_2 (adsorbed amount) to $\partial \gamma / \partial (\ln(a_2))$ and vice versa. To obtain $\gamma(a_2)$, one would have to integrate $\partial \gamma / \partial (\ln(a_2))$ over a_2 , which of course requires accurate measurements. The advantage: This method also works on solids or powders. Nevertheless, procedure it is not widely used. In more general terms, an adsorption isotherm may have structures (see e.g. Fig. 5.10) and these structures can be attributed to a dependence of the adsorption energy on the degree of coverage.

There is also a direct access to the energy of adsorption with calorimetry. Since the adsorbed amount is only a few μ mol/cm², such measurements require good calorimetric sensitivity. Using thin membranes as the substrates helps. These have a low heat capacity, which is why even small amounts of heat case as measurable increase in temperature. One can also increase the surface area by replacing the substrate with a large number of colloidal spheres. In both cases, it helps if the adsorption is fast because there are instrumental drifts. Fast adsorption requires fast exchange between the surface and the bulk and/or fast mixing.

Related to calorimetry is thermal desorption spectroscopy (TDS). A sample is heated in vacuum and the desorbed molecules are fed to a mass spectrometer (Fig. 5.11)

5.5 Structure and dynamics of adsorbates

In addition to the energetics, one is always interested in the structure of the adsorbate, possibly also in its microscopic dynamics. For adsorbates on single crystal surfaces in high vacuum, there have been spectacular successes in this regard in recent decades (2007: Nobel Prize to Gerhard Ertl, Berlin). An important application is heterogeneous catalysis in gases. A molecularly detailed understanding - for model systems - has also been achieved in an electrochemical context. Methods of investigation

Glg. 5.3.5

are the tools of electrochemistry (especially current-voltage relations) and the scanning tunneling microscope.

For many technical adsorbates, ab-initio modeling is out of reach. This is especially true for

structured surfaces. Catalyst grains (often metallic nanoparticles, themselves heterogeneous with cocatalyst) are ceramic-supported, so not even the structure is well known. Research on heterogeneous catalysis is quite largely empirical. (The same is true for the use of surfactant mixtures for colloid stabilization).

Linear alkane chains with thiol end groups on gold form a special case. These molecules are laterally mobile. They reorganize *after* adsorption and form an ordered structure (Fig. 5.12). This is referred to as a "self-assembled monolayer" (SAM). The structure is particularly well ordered on the Au111 surface. The structures are robust in the sense that they are preserved when a few molecules do not consist of alkane chains. The alkane chains then form a matrix. Quite often, a subgroup of molecules contains groups at the end



Fig. 5.10

An adsorption isotherm may have a non-trivial structure. The second stage is the result of reorganization of the adsorbate at high coverage. The surfactant CTAB was adsorbed. The substrate consists of kaolin particles (a clay mineral also used in porcelain production). Adapted from . Goodwin, J., Colloids and Interfaces with

Surfactants and Polymers.

which can undergo chemical reactions (amines, carboxyl groups, ...) or which are specifically recognized (biotin, recognized by streptavidin). SAMs are called a "platform" for surface functionalization.

5.6 Inverse Gas Chromatography

iGC also gives access to the surface energies. The longer the retention time, the stronger the adsorption.

Remember

- Adsorption occurs to the extent that it lowers the surface energy.
- On solid surfaces, adsorption equilibrium is often not achieved.
- The Gibbs adsorption isotherm states that the surface excess Γ_2 follows the relation $\Gamma_2 = -RT \partial \gamma / \partial \ln(a_2).$



About Thermal Desorption Spectroscopy (TDS) wiki.ornl.gov/sites/cnms_imaging/website/nanotransport/stabilityo fsrru03.html.

- The Langmuir isotherm and the BET isotherm are characterized by *saturation*.
- Surfactants are amphiphilic and they self-organize due to interactions between the hydrophobic alkyl chains.
- The energy of adsorption can also be determined calorimetrically.
- The structure and dynamics of adsorbates are the subject of current research.
- Alkane thiols on gold form selfassembled monolayers (SAMs).



Fig. 5.12

On the formation of a "self-assembled monolayer" on a gold substrate by thiolation. *www.ifm.liu.se/applphys/molphys/research/self/*



Wetting and contact angle 6

6.1 General

According to the BET isotherm (Sect. 5.3), the thickness of an adsorbate layer continuously approaches infinity as the vapor pressure approaches the saturation vapor pressure. This is realistic for porous media because of capillary condensation. For planar surfaces it is rather the exception. Such continuous divergence leads to complete wetting, and complete wetting of a surface by a liquid is not often found. As shown in Fig. 6.1 illustrated, at the edge of a droplet the vapor pressure is always close to the saturation vapor pressure. Then liquid would have to condense onto the surface in such a way that macroscopic thicknesses are reached. This amounts to spreading of the droplet.

Even though this complete wetting is not often observed, there is always a microscopically thin, "prewetting film" in the vicinity of a droplet. Fig. 6.2 shows a scanning electron micrograph of a cooled glass drop. (Such images cannot be obtained in liquid form because most liquids evaporate in vacuum). This prewetting film is not usually seen by eye. Nevertheless, one must always keep in mind the possibility of its existence. This is especially true for contamination of clean-



When the thickness of an adsorbate in the limit of $p_{vap} \rightarrow p_{sat}$ tends toward ∞ , droplets spread out because $p_{vap} \approx p_{sat}$ at the edge of the drop.

apparent slides that one has touched with bare fingers. The contamination with a molecular monolayer of fats spreads over the slide after touching it, without being seen. One may be able to visualize the contamination by wetting it with water and then blowing it off with nitrogen. (More generally, the latter procedure is a simple test for cleanliness).

The thickness of the prewetting film is of the order of the range of the intermolecular forces. This range is only a few molecular diameters. Within the prewetting film, all molecules feel both interfaces. It is not a bulk phase. The fact is also sometimes expressed to mean that there is an attractive interaction between the two interfaces substrate/film and film/vapor. This attractive interaction prevents the film thickness from becoming infinite.

Of particular importance are prewetting films of air in a water phase, which form on hydrophobic surfaces. One can see these films ("nanobubbles", "nanopancakes") with the scanning force microscope. IR spectroscopy was used to prove that they were indeed gaseous media. A rotational vibrational spectrum was seen.⁴⁵ These thin layers of air facilitate the slip of the water on the surface in question (section 9.1).

As a rule, droplets do not spread completely, but form a finite contact angle with the surface. Consider the droplets sketched in Fig. 6.3. The



Fig. X-15. SEM picture of a drop of cooled gl same coefficient of thermal expansion), ×130.

Fig. 6.2

A prewetting film In this case, it is a solidified glass, imaged with a scanning electron microscope. Adamson, A. W.; Gast, A. P., Physical Chemistry of Surfaces, John Wiley: 1997.

⁴⁵ Zhang, X. H.; Quinn, A.; Ducker, W. A., Nanobubbles at the interface between water and a hydrophobic solid. *Langmuir* 2008, 24, (9), 4756.

contact angle is calculated from an equilibrium of forces. A surface tension is a force per length. This length is perpendicular to the plane of the paper. The substrate is planar and solid. The meniscus can therefore only move in the substrate plane. This is a constraint condition. The force exerted by the liquid-vapor interface acts obliquely to the substrate plane. Only the part of this force that acts parallel to the interface is included in the force balance. The force equilibrium is

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

This is the *Young equation*. The indices *S*, *L* and *V* denote "solid", "liquid" and "vapor". Solving for $\cos \theta$ results is

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

Thus, wetting occurs when the sum of the surface energies $\gamma_{SL} + \gamma_{LV}$ is less than the surface energy γ_{SV} . ⁴⁶ By the way, it is difficult to test the Young equation experimentally because it contains the surface energies of *solids*.

Note: The contact angle is independent of what the conditions are at the molecular level at the three-phase boundary.

Unfortunately, it is not possible to calculate the two surface energies γ_{SV} and γ_{SL} separately from the contact angle, because on the right side of Glg. 6.1.2 there are three unknowns; but we have with θ and γ_{LV} only two measurands. Nevertheless, the rule holds: the higher the surface energy of a solid, the smaller the contact angles with liquids. Zisman has made this argument a bit more quantitative. To make a Zisman plot, one determines the contact angle for a series of homologous liquids. These are, for example, alkane chains or alcohols with different chain lengths. It is found that as γ_{LV} decreases, the contact angle decreases, so $\cos\theta$ increases. This behavior can be explained by the Young equation (Glg. 6.1.1) is plausible. Zisman



Zisman plot for a polyethylene surface with a series of liquid. www.biolinscientific.com/zafepress.php_pdf_Attension_Theor y_Note_FAT_TN_4_sfe.pdf

plots $\cos\theta$ versus γ_{LV} , extrapolates to $\cos\theta = 1$, and calls the value on the x-axis γ_c . γ_c is a measure for the surface energy of the body. Fig. 6.4 shows an example. Polyethylene is wetted by nonpolar fluids with low surface energy, but not by fluids with higher surface energy. Plotting $\chi_{0\sigma}\theta$ against γ_{LV} indeed leads to a straight line.

⁴⁶ One might expect that the sum of two surface energies would often be larger than a single third. The opposite is predicted by simple models for nonpolar substances. In this picture, the surface energy between substances A and B can be written as $\gamma_{AB} \approx \alpha (\delta_A - \delta_B)^2$ with α a prefactor that brings about the correct dimension in particular, and δ a dimensionless measure of internal cohesion. Calculate with $\delta_{solid} = 2$, $\delta_{liq} = 1$ and $\delta_{vap} = 0$. Then $(\delta_{solid} - \delta_{vap})^2$ becomes 4, while the sum $(\delta_{solid} - \delta_{liq})^2 + (\delta_{liq} - \delta_{vap})^2$ becomes 2. According to this argument, complete wetting should be quite frequent. In practice, however, it is rather rare. Dirt plays a major role, because solid surfaces with high energy are rarely clean.

The considerations leading to the Zisman plot are complicated. In all cases, there is an underlying - more or less realistic - assumption as to how the surface energy γ_{SL} depends on the surface energies γ_{SV} and γ_{LV} . With such a relation one reduces the number of unknowns in the Young equation (Glg. 6.1.1) by one and then one can invert this equation. One can understand such a relation as a combining rule.⁴⁷ The combining rules make assumptions about how the interactions between two media (here: solid and liquid) can be described simply, if the interactions of the molecules concerned with the same molecules are known (the latter here inferred from the surface energies with the vapor phase). The mixing rules are manifold and all of them are of limited viability.

Since the assumptions underlying the Zisman plot are quite broad, it is not surprising that homologous series of polar or nonpolar fluids do not lead to the same value of γ_c . One then speaks of γ_p and γ_d . ("*p*" for polar and "*d*" for dispersive, i.e. nonpolar). Sometimes other homologous series and other parameters are introduced. The procedure is semiempirical and oriented to practical requirements.

In deriving Young's equation, it was assumed that the meniscus was free to move on the surface. Because it usually is not, there is a difference between the advancing contact angle and the receding contact angle. The difference between the two angles ($\Delta \theta$, a measure of contact angle hysteresis) provides information about the roughness of the surface and about chemical heterogeneities (dirt).

When determining the contact angle hysteresis, make sure that the menisci have come to a

standstill before the measurement. The contact angles during movement are part of the dynamic wetting. Dynamic wetting and dewetting are complicated and at the same time technically important. The difficulties stem from the fact that molecular scale processes at the three-phase boundary line play a role. (In equilibrium one does not need to consider them. One can consider the forces in Fig. 6.3 far away from the contact line).

For wetting on rough surfaces (Fig. 6.6), a distinction is made between two limiting cases, named after Wenzel and after Cassie and Baxter. In the former case, the liquid penetrates into the troughs. One calculates an apparent macroscopic surface energy between solid and liquid. This increases with increasing roughness because the true surface area increases. Therefore, in this limiting case, the contact angle

decreases with increasing roughness. In the limiting case named after Cassie and Baxter, the liquid wets only the tips. The apparent macroscopic contact angle increases. These two limiting cases also

play a role in the context of pressure sensitive adhesives (PSAs, an example being Tesa film). If the adhesive fully wets a rough surface (i.e., it is soft enough to penetrate the indentations), roughness improves adhesion. Otherwise, it counteracts adhesion.

The Cassie-Baxter case is the basis of ultrahydrophobic surfaces and the lotus effect. Ultrahydrophobic surfaces are both hydrophobic and rough. Often, "fractal" roughness is required, i.e., a surface that is rough at all scales. Ultrahydrophobic surfaces are technically attractive because all droplets roll off, taking dirt with them. These

Fig. 6.5 On contact angle hysteresis www.pocketgoniometer.com/main.php?co nt=hysteresis&lang=en



Fig. 6.6 Wetting on rough surfaces www.tau.ac.il/~phchlab/experiments_new/su rface_tenstion/theory.html

Tilt Angle 45° 98° 75°

⁴⁷ en.wikipedia.org/wiki/Combining_rules. An example for a combining rule is $\gamma_{SL} \approx (\gamma_{SV} \gamma_{LV})^{1/2}$

surfaces have therefore been called "self-cleaning." The technical breakthrough has failed to materialize. For one thing, these surfaces are often mechanically fragile. Another problem is dirt, which - firstly - settles in the valleys (thus reducing the roughness) and which - secondly - turns the hydrophobic surface into a surface with a contact angle in the middle range.

Today, the industry speaks of "easy-to-clean" rather than "self-cleaning". Among other things, "easy-to-clean" means scratch-resistant and in the sense that graffiti colors can be tackled "with a root brush" without destroying the paint.

"Superhydrophilic" surfaces lead to droplet spreading. This would be attractive for anti-fog applications. However, very hydrophilic surfaces are unsuitable for this purpose because contamination quickly reduces the hydrophilicity. One uses swellable coatings. The water penetrates a hydrophilic matrix, spreads there, and reappears on the surface next to the droplet, causing the

spreading. With this mechanism, contamination is less of a problem because the contaminants must penetrate the interior of the film to reduce the antifog effect (Fig. 6.7).

The wetting of a surface by an electrolyte can be switched electrically ("electrowetting", section 2.4).

Wettability plays a major role in offset printing.

Wetting and dewetting processes in porous media are extraordinarily complicated. Soil hydrology deals with this question. Mechanics, chemistry, capillarity and biology are mixed here.

Remember

- Complete wetting and complete dewetting are rare. This has to do with saturation in the context of adsorption.
- At the microscopic level, there is often a prewetting film.
- The three-phase boundary line is often anchored (roughness, chemical heterogeneities). The contact angle hysteresis provides information about such heterogeneities.
- If the three-phase boundary line is not anchored, there is an equilibrium of forces. The Young equation applies: $\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta$.
- Using the Zisman plot, one can infer the surface energy of solids from contact angles. However, the concept makes assumptions.
- Ultrahydrophobic surfaces are rough surfaces.



Fig. 6.7 Mechanisms of droplet spreading. a) Spreading on the surface b) Transport inside the film. An antifog layer based on spreading in the film is less susceptible to dirt and thus more durable than an antifog layer based on a hydrophilic surface.

7 Surfactants and self-organization

7.1 Mechanisms of self-organization

Self-organization has already been briefly discussed in Sect. 5.2 in connection with the formation of micelles. What is "special" about surfactants is their ability to self-organize. In the following, selforganization or self-assembly means the formation of spatially limited structures. The structures in question should be equilibrium structures. Robust structures are in view. This means that the structure formation principles do not depend critically on molecular details. Self-organization in this sense is central to the emergence of complex systems, including life.

The following objects do not count as self-organized structures:

a) Crystals

Crystals are not limited in size.

b) Pairs of molecules that recognize each other.

Self-organization has a certain similarity to supramolecular chemistry, but - if defined as above - is not the same. Specific recognition according to the lock and key principle can play a role in self-organization, but is not per se a form of self-organization. Specific recognition initially links two molecules (e.g., an antibody and an antigen). If the molecules have multiple binding sites, extensive aggregation may occur, but in this latter case, self-limitation of the aggregation process is not automatic.





Various membranes produced by precipitation of a polymer phase from a solvent. The sizes are 100 µm (left) and 40 µm (right). Provided by Dr. Volkmar Thom, Sartorius AG, Goettingen, Germany

c) Structures generated by a stopping a growth process.

Two examples may be mentioned. Gold nanoparticles (AuNPs) are formed from gold acid $(H^+(AuCl_4)^-)$ in the presence of citrate, where the citrate acts as a reducing agent. In a second step, the citrate adsorbs to the surfaces of the growing particles and passivates them against further growth. After citrate is loaded, it stabilizes the AuNPs against aggregation. A size of about 10 nm is easily predictable.

Filter paper (Fig. 7.1) is usually prepared by spinodal segregation of a polymer and a solvent in a precipitation bath. The structures are initially filigree and then coarsen. The process comes to an end by solidification of the polymer phase. The timing of the solidification determines the pore size.

d) Dissipative structures

Away from thermal equilibrium, spatiotemporal patterns sometimes form that are similarly important to self-organization in the formation of complex systems. Examples are the convection rolls in Rayleigh-Benard convection, the concentration gradients (or waves) that arise as solutions of nonlinear, autocatalytic reaction-diffusion equations (Belousov-Zhabotinsky reaction), the heartbeat, embryogenesis, and brain activity.

The following, then, is about equilibrium structures. Essential mechanisms are

- a) The frustrated incompatibility
- b) Topological constraints and in particular a high energetic price for edges of lamellas.
- c) Spontaneous curvature of lamellae
- d) Helicity

Box 7.1

Block copolymers

Block copolymers contain different monomers in each chain, but these are not randomly distributed but form blocks. Fehler! Verweisquelle konnte nicht gefunden werden. and Fehler! Verweisquelle konnte nicht gefunden werden. deal with linear di-block copolymers. The synthesis of such blocks requires controlled polymerization.

If the two monomers are incompatible, microphase separation occurs. The degree of incompatibility is proportional to the chain length. One uses the parameter χN with χ quantifying how incompatible the two materials are and *N* the chain length.





Fig. 7.3

Depending on block length ratio, incompatibility, degree of branching, and other properties, block copolymers form different morphologies.

www.chemie.unihamburg.de/pc/sfoerster/bilder/forschung/phasen.gif

Fig. 7.2

For linear block copolymers, the phase diagram is known to be a function of block length ratio and incompatibility.

- e) Short-range attraction combined with long-range repulsion (SALR)
- a) Frustrated incompatibility

When large molecules (such as polymers or surfactants) have domains that would segregate from each other but cannot because of a tight bond (usually covalent), the domains in question form at the microscopic level. Examples of such systems, in addition to surfactants, are block copolymers. Block copolymers are larger and more inert than typical surfactants. The self-assembled structures are often more stable than structures made from comparable surfactants.

Amphiphilic block copolymers play a certain role in controlled drug delivery. The polymersomes form nanocapsules that transport the active ingredient. They are referred to as "polymersomes" in reference to the structurally related liposomes. Polymersomes are often slightly larger than liposomes. The viscosity of the lamella is higher than the viscosity of the lipid lamella.

In the bulk, block copolymers produce what is known as microphase separation. This refers to "superstructures" from the different phases. Box 7.1 discusses microphase separation.

b) Topological constraints

Topology is a branch of mathematics that deals with the connectivity of objects. An often cited example is the difference between a torus and a pretzel. These two objects cannot be deformed into

each other without cutting either the torus or the pretzel somewhere. A ring is topologically different from a thread with two ends. A membrane with edges is topologically different from a spherically closed membrane.

Lipid membranes rarely have edges because alkyl chains would come into contact with water at the edges. They are closed in one way or another. They often form spherical vesicles and thus divide the space into an inside and an outside.

When two vesicles fuse, this changes their topology. The process of "vesicle fusion" is carefully controlled by nature.

c) Spontaneous curvature

A spontaneous curvature of a lamella has similar consequences as the prohibition of an edge. The spontaneous curvature leads to spherical or cylindrical structures. The shape parameter of surfactants (Fig. 7.4) quantifies their tendency to take up a packing with curvature.

In the case of vesicles, both spontaneous curvature and the surface-to-volume ratio come into play (Fig. 7.5). The surface of a vesicle is largely solid. The volume is mainly fixed by the salt content (by the osmotic pressure).

d) Helicity

Helicity is self-limiting in two different ways. First, there can be attractive interactions inwardly, but not outwardly. This is

the case with DNA. A second effect is somewhat more difficult. The inner fibers of a wire rope are barely bent ("bend") but twisted ("twist"). The reverse is true for the outer fibers. Nano-fibrils with a strong tendency to twist will form slender, twisted fibers instead of attaching to an existing thick fiber. This mechanism plays some role in cellulose fibers.

Due to their shape, cylindrical objects have a relatively low tendency to crystallize. More planar objects are easier to pack. This is why amylose (a component of starch) is readily soluble, whereas cellulose is not. The two polymers differ only at a single, seemingly insignificant site (α - and β -glycosidic bond, respectively). The consequences of this small difference for packing are farreaching.

e) Short-range attraction combined with long-range repulsion.

If an atom (more generally, a particle) interacts attractively only with its neighbors (let their number be z), but repulsively with all members of an aggregate (Fig. 7.7), the total energy of the aggregate E_{tot} can be written as:

$$E_{tot} = N(-Az + BN) = -AzN + BN^2$$

N is the number of members of the aggregate. A and B quantify attractive and repulsive interactions. In formula Glg. 7.1.1 the first term will predominate for small N, but the second term will predominate for large N.





The "shape parameter" is given as aL_c/V_c with a the area of the head group, L_c the length of the molecule, and V_c its volume. The larger the shape parameter, the larger the spontaneous curvature. *en.wikipedia.org/wiki/Thermodynamics_o* $f_micellization$

Glg. 7.1.1



The long-range interaction in nature is often the electrostatic repulsion. Short-range in this context is the hydrophobic interaction and hydrogen bonding. This mechanism helps in the packing of globular proteins. Proteins are held together internally by the hydrophobic interaction and H-bonds, among other mechanisms. However, the charge on the proteins prevents the neighboring protein molecules from attaching to each other and precipitating. (For ordinary polymers, it is quite exceptionally difficult to obtain collapsed globules consisting of single chains). The same mechanism also causes *atomic nuclei* to contain no more than about 100 protons. The short-range interaction here is the nuclear force, the long-range interaction is the electric repulsion between protons (Fig. 7.7). Thus, the principles of self-organization are also at work in nuclear physics.

Some side notes:

- The examples above referred to aggregates in the bulk phase. "Self-assembled monolayers" (SAMs) usually refers to layers of thiol-terminated alkanes on gold. Here, a substrate stabilizes a structure that nevertheless still exhibits self-assembly (Fig. 5.12).
- In the above cases, equilibrium is always reached. This is remarkable in protein folding and is often accomplished only by enzyme activity (through chaperones). Base pairing of DNA also succeeds only with oligonucleotides or when a new strand is polymerized in situ. The DNA origami process (Fig. 7.6) illustrates this. Here, a self-assembled system is formed by base pairing, but the linking elements ("staples") are oligonucleotides. They find their target because they are small and well mobile.
- If you like, molecules are also finite aggregates (like the atomic nuclei). Central for the formation
 of molecules is on the one hand the covalent bond and on the other hand the octet rule. The latter

states that a molecule is in a stable, closed state as soon as all atoms are surrounded by a total of 8 electrons. This interaction may also be considered a "principle of self-organization" because it leads to aggregates of finite size. The interactions within a molecule (the chemical bonds) are stronger than the interactions with the environment.

Aggregates of finite size are favorable for the emergence of complex structures. Therefore, the
evolution on a higher level generates again discrete objects with a certain internal organization and
with internal interactions, which are stronger than the interactions to the outside. One of the
characteristics of living beings is the demarcation to the outside.

Remember

- Self-organization means the spontaneous formation of finite aggregates at equilibrium. Self-organization is central to the spontaneous emergence of function.
- Limited aggregates in this sense are also the atomic nuclei and the molecules.
- Self-organization can also occur at interfaces.
- Principles of self-organization include frustrated incompatibility, helicity, short-range attraction combined with long-range repulsion, topological constraints, and spontaneous curvature of membranes.
- Limited aggregates can also form due to kinetic inhibition. This mechanism underlies many nanoparticles and nanorods.
- Examples of self-assembly include atomic nuclei, DNA, micelles, vesicles, the biomembrane, and self-assembled monolayers (SAMs) of alkane thiols on gold.

7.2 Excursus: Langmuir layers

We return briefly to Fig. 5.4 In this figure, on the right, the surface tension was largely constant because micelles form in the subphase at high surfactant concentration. This argument assumes that there is indeed a transport equilibrium between the surfactant layer at the surface, the dissolved surfactants and the micellar surfactants. For long-chain surfactants, this is often no longer the case because they are not sufficiently soluble. Such molecules can be "spread" on the surface and in this way the amount of substance can be fixed. One usually dissolves the molecules in an organic solvent (e.g. chloroform) and applies a drop of the solution to the surface so carefully that the drop does not sink to the bottom. The drop spreads out quickly, the solvent evaporates, and the surfactant layer (the "Langmuir layer") remains.

In this way, one can create a two-dimensional substance system and investigate its thermodynamics. The "concentration" is varied simply by changing the surface by means of a



movable barrier. One dips a sheet of paper (a Wilhelmy plate, Fig. 2.1) into the liquid and measures the surface tension. This experimental arrangement is called the Langmuir trough (Fig. 7.8). In this context, the difference between the surface tension and the surface tension of pure water is understood as a 2D pressure and is called π . The π A diagram (bottom in Fig. 7.8 below) is analogous to the pV-diagram in 3D.

Langmuir films are of interest for basic research because it is possible to experimentally investigate whether there are fundamental differences between 2D and 3D systems with regard to their phase behavior. Furthermore, Langmuir films can be transferred to solid substrates by carefully dipping them vertically in and out. It is also possible to create multilayers. These are called "Langmuir-Blodgett layers". The physics of Langmuir films is still of much relevance for wet foams (Section 8). Foam lamellae can be understood as an arrangement of two Langmuir layers with an

intermediate water phase. Finally, one wonders whether the peculiarities revealed by these studies are relevant to the physics of the biomembrane. Critics deny this and call this line of research "biomimetic" to be distinguished from "biological".

Some further comments on Langmuir films:

If the πA diagram shows a horizontal line, one suspects phase coexistence (compare to the horizontal line in the pV diagram of the van der Waals gas). This phase coexistence can be visualized with the Brewster angle microscope (Fig. 7.9). One can also





visualize it by staining with dyes. The horizontal lines in the πA diagrams are often not strictly horizontal because the dispersed domains have a vertical dipole and repel each other.

- The region at high area and low pressure would be thought to be a gas phase. However, a gas
 phase is very difficult to observe because of the strong interactions between the alkyl chains. It is
 an "expanded" liquid phase.
- One can visualize the nature of the different phases with X-ray diffraction. To do this, one must use synchrotron radiation under grazing incidence, because the sample is quite extraordinarily thin.
- X-ray diffraction on Langmuir films reveals a wide variety of phases (Fig. 7.10). There is a deeper reason for this. In 3D, a favorable packing has to be achieved with about 12 neighbors in all three dimensions, in 2D only with about 6 neighbors in two dimensions. The latter is easier because "frustration" occurs less often. Therefore, there is a greater variety of phases.
- The different phases can form complex superstructures of all kinds. These are aesthetically pleasing, but the technical relevance is not always obvious.
- In addition to structure, one can also study dynamics on Langmuir films. "Dynamic measurements" here means 2D rheology. 2D rheology is important for foams. But it could also mean at least in principle dielectric spectroscopy. (NMR is impossible, because the sensitivity of NMR is not sufficient for monolayers).

Remember

- Water-insoluble surfactants form two-dimensional systems at the water/air interface, the "Langmuir films". These can be transferred to solid substrates (Langmuir-Blodgett films).
- The πA diagram is the 2D analog of the pV diagram. The horizontal areas indicate phase coexistence.
- The phases can be visualized with Brewster-angle-microscope.
- X-ray diffraction allows to characterize the phases. There are more different phases than in 3D.
- A similar diversity of phases is suspected for the biomembrane (keyword: "rafts").

8 Air bubbles and foams

A distinction must be made between aqueous foams and foams with a solid (possibly also soft, but elastic) continuous phase. In foams with an elastic matrix, the outstanding feature is the low density. In semiconductor electronics, the low dielectric constant is an additional feature. In polymer foams, the volume compressibility (dominated by the high compressibility of the gas phase) is added. Foams are also used for thermal insulation.

First, some remarks on isolated bubbles (to be distinguished from air spaces bounded by lamellae):

- Bubbles are subject to Ostwald ripening. Nanobubbles are normally unstable. Reminder: For emulsions, Ostwald ripening can be prevented by adding a "hydrophobe" (keyword: "miniemulsions"). Such a mechanism does not exist for bubbles.
- Bubbles are subject to *cavitation*. This is a collapse driven by Laplace pressure. It leads locally to
 extremely high temperatures and pressures. In technical contexts (e.g. ships), cavitation must often
 be prevented. Ultrasound often develops its effect through cavitation.
- Nanobubbles could be stabilized by certain surfactants. Then they are good contrast agents for ultrasound due to their compressibility. Air pockets are sometimes also advantageous for adhesives and sealants (e.g. on window panes) due to their compressibility.
- Adsorption of bubbles onto mineral particles is significant in the context of *flotation*. Special surfactants are used there which promote the selective adsorption of bubbles onto specific particles and thus enable the separation of ground materials according to chemical constitution.
- The van der Waals interaction between bubbles is attractive. The effective Hamaker constant is positive.
- The surfaces of bubbles are often charged due to preferential adsorption of ions. Therefore, bubbles usually repel each other (despite the attractive vdW interaction).
- The van der Waals interaction between bubbles and solids is often repulsive. This occurs when the Hamaker constant of the liquid is less than the Hamaker constant of the solid. One then calculates an "effective Hamaker constant"⁴⁸ for the interaction between bubble and solid, which is negative. (This is a problem for flotation).
- When stabilization of bubbles is achieved with lipids, the high viscosity of the lipids is important in addition to the lowered surface tension.

Among *aqueous foams*, an economically very important example (and therefore quite well studied) is foam on beer. Foam is also found in washing processes, e.g. in car washes. Another application example is fire protection. Otherwise, foam formation in working fluids is rather

⁴⁸ Write $A_{123} = (A_{11}^{1/2} - A_{22}^{1/2})(A_{33}^{1/2} - A_{22}^{1/2})$ with "1" the solid, "2" the liquid, and "3" the air.

undesirable. Foams consume space. There are additives for foaming as well as for defoaming, the second application being basically the more important.

Other comments on foams include:

- The soap lamellae separating the air spaces usually contain a water layer in the center. The thickness of this layer is variable. It can, for example, be of the order of the Debye length. It can also be even thicker if polyelectrolytes are added. The physics of the soap lamellae is very different from the physics of the biomembrane.
- Foams are destabilized via drying, Ostwald ripening, and coalescence.
- To stabilize foams, one stabilizes the lamellae. Polymers, large molecules (e.g. proteins) and also particles are often used. This is where 2D rheology comes into play.
- Foams are destabilized with *defoamers*. *Defoamers* are usually amphiphilic substances that form lamellae poorly



On the structure of soap films. If there are repulsive interactions between the two surfactant layers, this lowers the negative energy of the lamella. Then the capillary pressure of the soap bubble is slightly smaller than $4\gamma/r$. *pubs.sciepub.com/wjce/4/2/2/*

(i.e., do not tend to self-organize). These initially adsorb to the water-air interface, but then tend to form droplets themselves. On the way, the lamella collapses.

Remember

- A distinction is made between wet and dry foams (the latter often made of polymers).
- Foams have low density, high compressibility, and low dielectric constant.
- Stabilizing nanobubbles is difficult because of the high Laplace pressure.
- Wet foams are compartmentalized by lamellae. The boundaries between the lamellae are the plateau borders. The lamellae are a few nanometers thick. In the water layer, forces between charges play a major role.
- Foams are destabilized by drainage, coarsening and coalescence.
- Defoamers attach to the lamella, but are themselves unstable (do not tend to self-organize).

9 Tribology remarks

Tribology is about *friction* and *wear*. Friction can be desirable (adhesion) or not (reduction of energy consumption). Wear may be desirable (machining) or not. Where wear is unavoidable, it should be gradual and controlled (tires). Sometimes, in addition to friction and wear, noise generation also plays a role (whispering asphalt, freight car brakes).

Tribology is a cross-cutting issue across engineering with huge financial implications (almost like corrosion). Tribology is addressed in an interdisciplinary manner. Phenomena from many different spatial and temporal scales contribute. There is a wide variety of material combinations and problems in detail.

Examples of tribosystems are:

- Rolling bearings
 - e.g. ball bearings or bearings with rollers

Rolling bearings are favorable in frictional resistance. However, there are high stress concentrations at the contact points. The modeling is done in the framework of the *lubricant film theory*. Wind turbines are currently operated with rolling bearings.

- Plain bearing lubricated
 - e.g. piston in engine
- Plain bearings without lubrication (Teflon, PEEK)

In this case, a "transfer film" is formed from the abrasion of polymers, which facilitates sliding.

- Wheel-rail contact, tire-road contact
 Contacts under rolling friction, non-lubricated.
- Read head above the hard disk

Here, the air takes over the role of the lubricant. Intermittent contacts occur. For this reason, the hard disk is coated with a thin layer of perfluoroethers (e.g. "ZDOL").

- Biolubrication

Here, there is never concentricity; the relative motion always comes to a halt.

The tribo-surfaces are formed by the extracellular matrix. Hyaluranic acid plays a major role. Hyaluranic acid may be thought of as a polymer brush (a polyelectrolyte brush). Such brushes are locally fluid structures, but they are not washed away due to terminal attachment to the substrate. The interaction *between* brushes is always repulsive for entropic reasons. This is favorable for friction.

- MEMS devices

MEMS stands for microelectomechanical systems. MEMS devices are often made of silicon. One uses the "CMOS technology", which is well known from the semiconductor industry. The motion is often induced and read out piezoelectrically. Examples of MEMS are the AFM tip, acceleration sensors for airbags, and systems of small mirrors for projection systems.

In principle, MEMS devices can also be used to construct rotor-shaft systems (micromotors). However, these have so far had a problem with tribology. A related problem sometimes occurs with irreversible adhesion (e.g. promoted by capillary forces).

This concludes the list of examples. We turn to the basics. *One must fundamentally distinguish between friction in liquids and friction between solids.*

9.1 For friction in liquids

In liquids, the frictional force is proportional to the velocity if the velocity is not too high.⁴⁹ The force-velocity relation is *linear*. We treat three geometries: the sphere in the fluid, the sphere in the fluid near a surface, and the flow in a pipe.

The friction law for spheres in Newtonian fluids is Stokes' law (Fig. 9.1):

Glg. 9.1.1
$$F_{fric} = 6\pi r$$
ην

The friction force is therefore proportional to the radius. Also for other objects, the friction force is proportional to a characteristic *length* (not to an area, as also follows from dimensional considerations). One likes to write also for other objects $F_{fric} = 6\pi\eta r_h \text{ v and calls the length defined in such a way the$ *hydrodynamic radius*.

The friction force should be compared with other forces. A typical such force would be gravity, given as

$$F_{grav} = \left(\rho_p - \rho_{liq}\right) g\left(\frac{4\pi}{3}r^3\right)$$

Putting gravity and the frictional force in equilibrium, we calculate a sedimentation velocity, given as

$$v = \frac{2r^2g(\rho_p - \rho_{liq})}{9n}$$

Thus, the sedimentation velocity becomes small on small scales. More generally, the influence of friction often becomes large on small scales.

When the same sphere approaches a surface, the frictional force increases sharply (Fig. 9.2). According to a law named after Reynolds, in the limiting case $D \ll r$:

Glg. 9.1.4

$$F \approx 6\pi\eta r v \frac{r}{D}$$

D is the distance between the surface of the sphere and the wall. Since the frictional force tends towards infinity shortly before the impact, the impact never occurs - within the framework of this theory. This is favorable for ball bearings. Again, the smaller the dimension (the smaller the distance D), the stronger the frictional force.



^{8984/25/18/184003} Maali, A.; Bhushan, B., J. Physics-Condensed Matter **2013**, 25, (18).



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Glg. 9.1.2

⁴⁹ At very high speeds, it is no longer the viscosity that is constant, but the stress. This is referred to as "limiting shear stress". The conditions are then similar to the friction of solids on solids according to Amonton's law. The viscosity then scales like v^{-1} .

For the flow in a pipe with radius r and length L the Hagen-Poisseuille law applies:

$$v = \frac{r^2}{8\eta L} \Delta p$$

 Δp is the pressure difference. The smaller the radius, the larger the influence of friction. A side note: Capillary forces also increase on small scales. If there is an equilibrium of forces between friction force and capillary force, it is not clear a priori which one is stronger on small scales.

For all these geometries, a "no-slip" condition was postulated at the surface. This is often, but not always, the case. For gas bubbles it is different. For gas bubbles, the factor of 6 in Stokes' law is replaced by a factor of 4. Slip is even more significant in the case of flow through a capillary than in Stokes' law. In the presence of slip, there is a "slip length" (usually called *b*, cf. Fig. 9.2). One can then define an effective capillary diameter as r + b. Slip sometimes results on hydrophobic surfaces from "nanobubbles" and "nanopancakes" of air. There are small animals that lower their hydrodynamic resistance in water by thin layers of air on their surfaces.

The slip length can be several 10 nm, especially for water on hydrophobic surfaces. The roughness of the surface, the density of the water near the surface (which has to do with the interactions with the wall) and whether there are ice-like structures at the surface are important. One naturally thinks of an engineering application in terms of reducing hydrodynamic drag in fine capillaries. However, consider this: this large slip length occurs on hydrophobic surfaces. If at the same time capillary force is supposed to drive transport, you have a trade-off. In porous media, slip lowers friction, but you still have the viscous dissipation that results from the complex structure. This issue can be illustrated by looking at the drag of an air bubble. (At the surface of the bubble, the slip length is infinite.) This is given as $F/v = 4\pi\eta r$, to be compared with the value $F/v = 6\pi\eta r$, which results according to Stokes' law for a sphere with a no-slip condition. "slip" or "no-slip" accounts for only a factor of 2/3 here. This is different for the flow in nanotubes. Very low flow resistances were found for the flow of water through carbon nanotubes.

Do not confuse this form of slip with the sliding of a polymer melt against the wall in an extruder. The latter is a consequence of shear thinning. Viscosity can drop in polymers when the shear rate is high. This happens mainly at the edge of the tube. Then a positive feedback occurs (η decreases,

shear rate increases, η decreases further, shear rate increases further) until plug flow occurs. We know plug flow from toothpaste.

Further, do not confuse this form of slip with what the sharkskin does. The sharkskin is rough and thus lowers the diameter of the rolls, which result from turbulence. (Such structures are also used in airplanes.) Turbulence was left out here. (Turbulence takes place on large scales).

A side remark: Elastohydrodynamic friction (EHD friction) is friction in fluids. Nevertheless, the friction force is proportional to the normal force and largely independent of the velocity (see below). The



journals.org/bjnano/single/articleFullText.htm?public Id=2190-4286-2-9 "lubricating film theory" applies here. Of some importance in this context is the fact that the viscosity of normal oils increases sharply under pressure. High pressure occurs locally before the surfaces come into contact. The high viscosity causes dynamic stabilization of the fluid film and thus reduces wear. Water is a poor lubricant because this viscosity increase with increasing pressure is virtually non-existent in water.

Of further importance for the lubricating film theory is that at high shear rates the viscosity of most fluids decreases. High shear rates are present in EHD friction in the gap. In the limiting case, the viscosity is inversely proportional to the shear rate. The shear stress (viscosity \times shear rate) then becomes independent of the shear rate. As soon as this occurs, it makes sense to speak of a coefficient of friction for lubricated friction as well.

9.2 Friction between solid surfaces

Friction between the surfaces of solids is often described by a remarkably simple law whose justification is anything but trivial. It is Amonton's law^{50} :

$$Glg. 9.2.1$$
$$F_{\parallel} = \mu F_{\perp}$$

 F_{\parallel} and F_{\perp} are the tangential and normal force. μ (a number of the order of 1) is the *coefficient of friction*. Here, the "static" coefficient of friction (at the onset of sliding) is slightly higher than the dynamic coefficient of friction ($\mu_S > \mu_D$). Remarkably, the friction force is independent of the velocity and the apparent contact area in the Amontons scenario. The behavior is nonlinear. People got used to these laws. Some surprise would be appropriate. The Amontons laws are only are approximate. More precise measurements reveal a small velocity dependence of the friction force.

The Amontons laws were explained by Bowden and Tabor with roughness. There are "loadbearing asperities". Their area is just large enough that the local normal stress corresponds to the yield stress (σ_y). The true contact area is therefore proportional to the normal stress. During sliding, these local contacts constantly break. They do so at a critical tangential stress, σ_c . Bowden and Tabor write $\sigma_c = \mu \sigma_y$ and arrive at

Glg. 9.2.2

$$F_{\parallel} = A\sigma_c = A\mu \ \sigma_{\perp} = A\mu \ \frac{F_{\perp}}{A} = \mu \ F_{\perp}$$

Note the relationship between friction and fracture mechanics. Dry friction is basically more closely coupled to wear than lubricated friction.

When the friction coefficient becomes very small, "superlubricity" is present. Superlubricity requires atomically smooth incommensurable crystal surfaces.

A coefficient of friction also exists for lubricated friction, i.e. friction in the presence of fluids. The Stribeck curve (Fig. 9.4) shows the coefficient of friction for lubricated friction as a function of a (suitably normalized) sliding velocity. At low velocities, Amonton's law generally applies. At high speeds, a lubricating film keeps the two surfaces at a distance. The tangential force is proportional to the normal force because the gap width increases with speed. This feedback mechanism makes the

 $^{^{50}}$ Amontons (with s) is the proper noun. The s is not a genitive s.

system non-linear. The region in question goes by the name elastohydrodynamic friction (EHD friction). The main problem in EHD friction is wear in intermittent contact.

The area of "mixed lubrication" is particularly problematic for wear. The service life of car

engines therefore depends to a large extent on the number of starts.

9.3 Comments on practical tribo systems and lubricants

The following are some remarks on practical tribology:

 Hard surfaces are of great importance for lubricated surfaces (ball bearings). The surfaces are often specially hardened (e.g. by nitriding).



 In engines, there is "runningin" in the sense that carbon

from the lubricating oil is deposited in the areas of the steel near the surface.

- If there is abrasion, it is important that it is controlled and gradual.
- Zinc dialkyl dithiophosphate (ZDDP) is often added to lubricating oils. This creates "anti-wear layers" at the areas in danger of damage.
- Polymers, that swell at high temperature, are often added to lubricating oils, causing the temperature-viscosity profile to be flat.

Remember

- Tribology is a cross-disciplinary topic.
- Tribology is complex because many space and time scales are intertwined.
- Frictional forces become large on small scales.
- Friction in fluids is linear in velocity at sufficiently low velocities ($F \propto v$, Stokes' law applies).
- Layers of can lead to slip as solid surfaces in liquids.
- Friction on solid surfaces is nonlinear $(F_{\parallel} \approx \mu F_{\perp})$.

10 Colloids

The word "colloidal" comes from the Greek and can be translated as "glue-like". Colloids sometimes are sticky. At the time, the distinction between colloids and polymers had not been well established.⁵¹ Polymers are a bit more sticky than colloids. Stickiness of a material is closely related to its flow properties (to rheology). Colloids have interesting flow properties. Colloids - as well as polymers and liquids - are considered to be "complex fluids." The field is sometimes called "soft matter".

According to the IUPAC definition, "colloidal" means an "object, which at least in one of the dimensions lies between 1 nm and 1 μ m". This definition is broad and therefore unfortunately not very meaningful with respect to the phenomena studied. In the following, we restrict ourselves to solid, dispersed, colloidal objects in a liquid environment. These, of course, constitute only a subset of colloids. We exclude foams, aerosols, lamellar structures, and solid/solid colloids from the discussion.

With this restriction a somewhat more speaking definition becomes possible. Colloidal objects in this sense are on the one hand larger than molecules, but on the other hand are so small that the thermal motion (also: *Brownian motion*) brings about a *thermodynamic equilibrium*. This definition also leads to a maximum size in the order of 1 μ m.

The thermodynamic equilibrium is endangered by

- Fast processes (e.g. fast shear flow)
- Instability against Ostwald ripening (only with liquid/liquid emulsions) is prevented by using a "hydrophobe".
- Instability against sedimentation
- Instability against aggregation

Thermodynamic equilibrium occurs on the time scale of diffusion, the latter given as

Glg. 9.3.1

$$\tau_{diff} = \frac{L^2}{D} \approx \frac{a^2}{k_B T / (6\pi \eta a)}$$

D is the diffusion constant. In the second step, the Stokes-Einstein relation was used. Furthermore, the particle radius *a* was used for the characteristic length L^{52} Strictly speaking, one would probably have to use about four particle radii. Inserting (e.g.) the numerical values $k_BT = 4 \cdot 10^{-21}$ J, $\eta = 10^{-3}$ Pa s and a = 100 nm leads to $\tau_{diff} \approx 5 \cdot 10^{-3}$ s. This time scale can be compared, for example, with a shear rate, $\dot{\gamma}$. The shear rate has the dimension 1/s. The product $\dot{\gamma} \tau_{diff}$ also carries the name "Deborah number" *De* (a characteristic number from rheology, into which other characteristic times are sometimes inserted). For *De* > 1, a non-trivial rheological behavior can be expected. One such non-trivial behavior is (among others) shear thickening. If a dispersion holds a high solids content, this dispersion can usually flow only slowly. If one tries to shear it quickly, "jamming" occurs. There is transient solidification.

⁵¹ Polymers contain linear chains, which is reflected in rubbery elasticity and the sluggish flow caused by entanglements. Colloids do not exhibit rubber elasticity.

⁵² In colloid science, the sphere radius is commonly called *a* (instead of *r* or *R*). We adapt.

Regarding stability against sedimentation: the interaction of sedimentation and diffusion leads to a Boltzmann distribution of particles along the vertical coordinate z:

$$c(z) = c_0 \exp\left(-\frac{mgz}{k_BT}\right) = c_0 \exp\left(-\frac{z}{\xi}\right)$$

 ξ is the characteristic height. $M = \Delta \rho 4\pi/3 a^3$ and g are the mass and the acceleration constant due to gravity. One finds

$$\xi = \frac{k_B T}{\frac{4\pi}{3} a^3 \Delta \rho g}$$
Glg. 9.3.3

With $\xi = 1$ m and $\Delta \rho = 0.1$ g/cm³ one arrives at a critical particle radius of about 10 nm. In concrete terms, the ratios are generally somewhat more favorable than those given by Glg. 9.3.3 because there is almost always some degree of convection.

As a digression, we prove the Stokes-Einstein relation from the fact that the interaction of sedimentation and diffusion must lead to the Boltzmann distribution. The sedimentation flux J_{sed} is

$$J_{sed} = c \mathbf{v}_{sed} = c \frac{F_{grav}}{\xi_{fric}} = \frac{mg}{6\pi\eta a}$$

 v_{sed} is the velocity, F_{grav} is the gravitational force. The concentration distribution c(z) is subject to the Boltzmann law (Glg. 9.3.2). The diffusion flux is

$$J_{diff} = -D\frac{\mathrm{d}c}{\mathrm{d}z}$$

We set the fluxes equal and use the Boltzmann law for c(z):

Glg. 9.3.6

Glg. 9.3.5

$$J_{sed} = \frac{mg}{6\pi\eta a} J_{diff} = -D \frac{\mathrm{d}c(z)}{\mathrm{d}z} = -D \frac{\mathrm{d}}{\mathrm{d}z} \left(c_0 \exp\left(-\frac{mgz}{k_B T}\right) \right) = D \frac{mg}{k_B T} c_0$$

Solving for *D* leads to $D = k_B T / (6\pi \eta a)$.

For aggregation: the vdW potential in the limiting case of $D_{surf} \ll a$ is given as $-Aa/(12D_{surf})$ with *A* the Hamaker constant, *a* the particle radius and D_{surf} the distance between the surfaces. For fixed D_{surf} (e.g. 5 nm, corresponding to about two Debye lengths), the vdW potential increases with increasing *a* until one can no longer compensate it by another repulsive interaction.

Particles and aggregates of particles with sizes far above 1 μ m carry the name "granular matter". Granular matter plays a major role in industry in the form of powders, granulates and bulk materials. For granular matter, one chooses a particle size > 1 mm. One can then rely on gravitation and

sedimentation (even in air, keyword: dust formation). Also, one can always bring about disaggregation by shaking. (Here inertial forces and adhesion forces are in competition. On large scales, the inertial forces win).

A side note: Most colloidal spheres are too small for optical microscopy. People have developed special spheres, which

- are so large that you they can be resolved with an optical microscope
- have the same density as the liquid (\rightarrow no sedimentation)
- have the same Hamaker constant as the liquid (\rightarrow no aggregation)
- have the same refractive index as the liquid (\rightarrow no turbidity)

These spheres are made to be fluorescent, so that they can be imaged with a confocal microscope. The liquid is made viscous enough to slow down Brownian motion, so that it can be followed with the laser scanning confocal microscope (LSCM). This provides for a detailed picture of structure and dynamics. The vitrification and crystallization of colloids, for example, have been studied in this way.

Some numbers are interesting. Consider a total volume of 2 L. Let the solid fraction be 50% (so the polymer phase has a volume of L). Let the volume of a particle be about $100 \text{ nm} \times 100 \text{ nm} \times 100 \text{ nm}$. If the particle consists of polymer chains with 1000 segments each and if the volume of a segment is 0.1 nm³, the sample contains 10^{18} particles, each particle contains 10^3 chains and each chain contains (according to assumption) 10^3 segments. Large numbers – strictly speaking, not so large numbers – thus come into play three times. These numbers have different implications:

- The number 10^{18} may seem high, but it is only 1 µmol/L. (For comparison: water has a concentration of 50 mol/L.) The osmotic pressure that polymer dispersions build up is correspondingly small. We neglect the interactions (which is actually not allowed at a solids content of 50%) and apply the van't Hoff equation ($\Pi = RTn/V$). Inserting the values (RT = 2.48 kJ/mol, n = 1 µmol, $V = 10^{-3}$ m³) leads to a pressure of 2.4 Pa, corresponding to 0.024 mbar. For comparison: seawater (with a salt content of 3.5 wt%) generates an osmotic pressure of 30 bar.
- From the small number-density of particles it follows that latex blends (mixtures of different latex particles) have a strong tendency to segregation. If there are very weak favorable interactions between similar particles,⁵³ the small negative contribution of the mixture entropy to the free energy of the latex blend is overcompensated by the (positive) mixture enthalpy.
- The number 10¹⁸ shows in particular that it is virtually impossible to produce significant amounts of material from particles that are created as drops at the end of a capillary ("droplet-based microfluidics"). A nozzle can produce about 10⁶ particles per second. Such quantities are at best interesting for medical applications.
- After a particle contains 10³ polymer chains, the interior of the particle may be considered as a normal bulk polymer phase. Anomalies that would result from the geometric constraints (English: "confinement") are not to be expected. The same conclusion is reached if one remembers that the surfaces between condensed phases are molecularly sharp. With a particle radius of 50 nm and a surface width of a few nm, most chain segments do not "see" the surface.

⁵³ Then the interactions between unequal particles are less favorable than those between equal particles.

Remember

- According to IUPAC, colloidal systems have a size between a few nm (just above the molecular size) and about 1 µm. We restrict the considered area to dispersed particles in a continuous phase, where the particles should be smaller than 1 µm. This upper limit results from the requirement that Brownian motion should prevent sedimentation. ("Diffusion beats sedimentation.")
- For much larger particles (> 1 mm), firstly rapid sedimentation is assured and secondly deagglomeration by shaking is always possible. These are the "granular media".
- In polymer dispersions, a sphere may well contain a large number of molecules. One may call the interior a "bulk".
- Colloidal dispersions do not usually build up significant osmotic pressure because the number of particles - and thus mixing entropy - is small.

10.1 Examples of colloidal systems

 Fine regrinds can have colloidal properties. The manufacturing process is described by the words "top-down" (to be distinguished from "bottom-up").⁵⁴ Grinding is expensive and rarely results in particles smaller than 50 nm due to reaggregation.





Fig. 10.2 Due to the different charge on edges and surfaces, clay minerals form the house-of-cards structure. www.uni-kiel.de/anorg/ lagaly/ECGA/Fluorhectorite.gif



Fig. 10.3 Micelles are often erroneously depicted as spheres www.uni-essen.de/~cua040/ research.html

 Globular proteins (and antibodies⁵⁵, as well) are molecules, basically, but certain properties can be understood within the framework of the theory of colloids. Proteins mostly are charged. There are

⁵⁴ Talking of "top-down": In semiconductor technology, photolithography is a top-down process. Attempts to support photolithography with self-organization processes have not yet been put into practice. In photolithography, structure widths of a few nm can be achieved.

Top-down structuring down to the nanometer range is possible with the "focused ion beam" (FIB). It is possible to cut parts out of a crystal (in vacuum) and to investigate these parts (mechanically, optically, magnetically) with respect to the influence of the size on the physical properties. This is a rich field, especially in mechanics, because the effects of defects (e.g., dislocation lines and their migration) are undermined.

⁵⁵ But not the membrane-bound proteins and the proteins that form fibrils.

free counterions. Unlike ordinary polymer dispersions, the charge varies on the surface and there are hydrophobic regions on the surface. Proteins are called "patchy colloids".



Clay minerals ("layer silicates", "alumino-silicates", "nano-clays", Fig. 10.1) often form fine platelets. Examples are kaolinite and montmorrillonite. Mica is also a layered silicate, but is usually larger in diameter than a few 100 nm. The formation of these finite aggregates can be thought of as a process of self-organization (albeit away from thermodynamic equilibrium). The layered silicates consist of corner-linked tetrahedra (based on SiO₂) and octahedra (based on Al₂O₃). When a corner of a tetrahedron is unlinked, a net negative charge remains, which is compensated by cations. Why the tetrahedra and octahedra so often form layers is not obvious. (At times they form other structures, e.g., the zeolites.) But the mechanism is robust in the sense that there are quite a few related structures and that small deviations in stoichiometry from ideal conditions are tolerated.

In dry conditions, the various layers are ionically bonded by the cations. In water, this bond dissolves. The individual layers are "exfoliated". The size is in the range of a few nanometers. The edges are often positively charged, while the surfaces are negatively charged. If the charges are not screened, the house of cards structure is formed when the concentration in water is high enough, (Fig. 10.2). The house of cards structure is a weak gel. The charge at the edges is sometimes screened with phosphates. Then the gel turns into a fluid. Therefore, clay minerals can be used as rheology modifiers.

Clay minerals bind cations on the surfaces. They are important for soil hydrology. Clay minerals are also important for ceramics.⁵⁶ However, do not confuse clay minerals with cement.

- Polymer dispersions consist of polymer particles with a diameter of about 100 nm. They are used as binders, coatings and adhesives. Emulsion polymerization is a mature and flexible production process.
- Association colloids consist of surfactants aggregated into superstructures. The most important example is the micelles (Fig. 10.3). However, lamellae and cylindrical structures also form. Closed lamellae form vesicles (if formed from lipids: "liposomes"). These vesicles are "nanocontainers".
- Gold nanoparticles (AuNPs, Fig. 10.4) can be prepared relatively easily from gold acid (see also point c in Sect. 7.1). The citrate creates a surface charge that stabilizes the particles against aggregation. A typical size is 10 nm. Gold nanoparticles when isolated have a bright red color due to the "plasmon resonance". Plasmon resonance is a collective excitation of quasi-free electron gas. Gold nanoparticles have already been used in church windows. Due to their color and easy surface functionalization, AuNPs are popular markers in bioanalytics.
- Semiconductor nanoparticles (Fig. 10.5) are formed similarly to gold nanoparticles by a chemical reaction, which breaks down in an associating solvent (possibly also under the effect of additives) after a certain time. For the semiconductor nanoparticles, the band gap may depend on the particle size. This can be explained quantum mechanically with the particle in the box. So one can adjust the color via the particle size.
- There is a large variety of other inorganic nanoparticles, including rods (nanorods).
- The "Stöber particles" are formed by hydrolysis and subsequent recondensation of alkoxy silanes (Fig. 10.6). The process is triggered by basic pH. (In acidic environments, open networks form.) This class of reactions goes by the name "sol-gel synthesis." The process is robust and flexible (replacing silane with titanium, zirconium, etc. additives ...).
- Small particles in a gas phase can be produced cheaply by flame pyrolysis. For example, if SiCl₄ is blown through a flame in the presence of oxygen, SiO₂ particles are formed. However, these immediately aggregate (i.w. irreversibly) into larger clusters. A common product is called aerosil. It is also called "fumed silica".

Attention: Small particles in a gas phase are called aerosol. Aerosol physics is very different from the physics of colloids.

⁵⁶ Kaolinite (discovered by Johann Friedrich Böttger when he was actually commissioned by Augustus the Strong to make gold from urine) is an essential component of porcelain. Today, it is mainly used for the production of high gloss paper. Kaolinite induces blood clotting and is used in this capacity in dressing materials. Kaolinite is widely used and has many other applications, including as a filler in all types of polymers....





10.2 Surfactants

Surfactants have already been discussed in the context of Gibbs adsorption isotherm, selfassembly, and association colloids. Here we bring together some properties of surfactants from the point of view of chemistry and applications.

- The English word is "surfactant" is derived from "surface active".
- Surfactants are not only amphiphilic, they also have strong lateral interaction between the alkyl chains. This is the hydrophobic interaction. Surfactants tend to self-assemble.
 A side note on amphiphilicity: alkyl alcohols, for example, are also amphiphilic. However, these do not form micelles. Many proteins are also slightly amphiphilic. Many nanoparticles are slightly heterogeneous at the surface and therefore also slightly amphiphilic. Because the surface area per particle is large, nanoparticles often adsorb at the water/air and water/oil interfaces. Nanoparticles on the surfaces of oil droplets can stabilize the emulsions concerned against aggregation in a purely geometric way ("pickering emulsions").
- Functions of surfactants are
 - lowering of the surface tension
 - emulsifying
 - wetting aid
 - foaming (or also defoaming)
 - stabilization of colloids.

These functions can be combined with other functions. Polymerizable surfactants are called "*surfmers*" (composed of *surfactant* and *monomer*).

- For the representation one usually chooses the "head-tail-shape" (Fig. 10.7).

The head group can be

- anionic, e.g. sulfates, sulfonates, carboxylates, phosphates.

Sulfates are pH-stable. In the case of carboxylates, protonation occurs at low pH and the molecules

become neutral.

- cationic, e.g. quaternary amines ("quats"). These are pH stable, but expensive. Cationic surfactants are used a lot for hair care because hair (keratin) is often negatively charged. - zwitterionic, e.g. the betaines

- neutral ("non-ionic"), e.g. polyethylene oxide (PEO) or sugars. The PEO groups and the sugars are larger than the charged head groups, because otherwise sufficient amphiphilicity is not achieved.

- The hydrophobic part can consist of

- alkyl chains, fluorinated chains, siloxanes and other groups

- saturated or unsaturated chains. Unsaturated chains tend to crystallize less than saturated ones (a kink is formed). Therefore fluidity of the lamella is greater.

- one or two chains: one chain for example in fatty acids, two chains for example in lipids. Twochain surfactants are often more stable and form lamellae rather than vesicles because the shape parameter (Fig. 7.4) is closer to one.

- Long or short chains. Long chains form more stable surfactants than short chains.

- linear or branched chains. Branched chains do not form good lamellae (application: defoamers, wetting aids).

- Surfactants are sometimes classified according to the "hydrophilic-lipophilic balance". The smaller the "HLB value", the higher the lipophilic content. Initially, the HLB value was calculated from the number of hydrophilic and hydrophobic groups. Today, there are various other definitions. Table 10.1 shows applications for surfactants at the various HLB values.
- A molecular understanding of surfactant activity is mostly out of reach. Also for this reason (and because mixtures are often used), there is much empirical research.
- The production and in particular the purification of surfactants is costly. This is another reason why natural products and mixtures are often used.
- 10.3 Interfaces are often charged in water.

In water, almost all surfaces are charged. If the surface is not itself charged, there will be preferential adsorption of either H^+ or OH^- on the surface. Important charged surfaces and charged groups on surfaces are:

- Glass surfaces: Glass surfaces are negatively charged at neutral pH because the terminal SiOH groups are deprotonated.
- Other mineral surfaces: For Al₂O₃ and TiO₂, the charge depends on pH. These particles can be charged negatively or positively. The charge depends also on the crystallographic orientation of the surface. The isoelectric points of Al₂O₃ and TiO₂ are about 9 and about 6, respectively.
- Sulfates and sulfonates: Because the pK_A of sulfates and sulfonates is about 1, sulfates and sulfonates are pH stable. Sulfates and sulfonates are often parts of anionic surfactants (e.g. SDS, sodium dodecylsulfonate).

- carboxyl groups: Because the pK_A is 3– 4, normal fatty acids are not pH stable. At low pH, they are protonated and thus neutral. This can be an advantage if you want to manipulate the charge state externally (keyword: *responsive materials*). Carboxyl groups are carried, for example, by polyacrylic acid (PAA).
- Amines: Amines are often positively charged. The positive charge of proteins (when present)

Table 10.1: HLB values and use		
HLB value	Usage	Miscibility with H O ₂
1.5 to 3	Defoamer	insoluble
3 to 8	for W/O emulsions	milky when stirring
7 to 9	Wetting agent	
8 to 18	for O/W emulsions	stable (milky) emulsion
13 to 15	Washing active substances	clear emulsion / clear solution
12 to 18	Solubilizer	clear emulsion / clear solution
en.wikipedia.org/wiki/HLB-value Hans-Dieter Dörfler, Surface and Colloid Chemistry, VCH		

Weinheim, 1994, p. 198

is mainly due to amines. The quaternary amines ("quats", only these) are pH stable.

- Metal surfaces: Metal surfaces are often slightly negative in water because the quasi-free electron gas protrudes slightly further beyond the interface than the ionic hulls. Thus a dipole is formed. Caution: With metals, there is always the question of whether a voltage is present. This can occur by means of redox reactions (also at mixed electrodes).
- Adsorbed ionic surfactants: Surfactants readily adsorb to surfaces. When charged, they induce wettability by water.
- Neutral surfaces: Preferential adsorption of ions (e.g., more H⁺ than OH⁻) or a dipolar layer of an adsorbate also often occur on neutral surfaces.

The *isoelectric point* (IEP) is the pH value at which a surface (or also a protein) is neutral. To be distinguished from the IEP is the "point of zero charge". At this pH, colloidal particles carry no net charge. They may well be locally charged. This situation occurs, for example, with layered silicates (positive at the edges, negative on the surfaces).

Caution: Do not confuse the point of zero charge (a pH value) with the "potential of zero charge" in electrochemistry (an electrical potential).

Typical charges are on the order of a few $\mu C/cm^2$. A charge of 1 e/nm^{-2} corresponds to 16 $\mu C/cm^2.$

10.4 Excursus: Cathodic dip painting

A targeted destabilization of colloids is used in the coating of car bodies. The car body is negatively charged. OH^- is then formed in water at the surface, so the pH rises into the basic range. The coating is cationically stabilized with amines. Stabilization with anions (carboxylic acids) would



be cheaper, but then the body would have to be operated as an anode (the pH would have to be pushed into the acidic range, H⁺ would have to be formed). Running a metal as an anode always runs the risk of metal dissolution. To the extent that the ammonium salts are neutralized, the paint particles on the surface will precipitate. The mechanism is shown in Fig. 10.8. An advantage of electrodeposition coating is that cavities are also coated. When the exposed parts of the body are covered with paint, the current flow shifts to the still uncoated areas because the paint is electrically insulating. The process is intrinsically self-stabilizing.

10.5 Dielectric and electrostatic screening

Central to understanding the behavior of ions in water are the concepts of dielectric screening and electrostatic screening. Dielectric screening is caused by the dipole moment of the water molecules. When a field passes perpendicularly through a water-air interface, the field in water is weaker than in air by a factor of 78 due to the orientation of the dipoles at the surface (where 78 is the dielectric constant ε). The hydration shell around the ions screens the field of the ions by the same factor of 78.

Dielectric screening is allows ions to soluble in water in the first place. Dielectric screening leads to the hydration enthalpy. Because this is comparable in strength to the lattice energy of salts, salts dissolve in water.

The electrostatic screening is caused by the counterion cloud. The counterion cloud is an increased probability density for the occurrence of a counterion in the vicinity of an ion. The fact that counterion clouds cannot be multiple counterions is immediately understandable for reasons of electron neutrality. This already mentions a major weakness of this picture: One replaces in the framework of the Debye-Hückel theory the interaction between ion and counterion by an interaction between the ion and a residence probability density of the counterion. This substitution is typical for the mean-field theories. Not covered by the mean-field theories are the "correlations". Correlations in this context are effects which are not captured by the mean-field theory. The neglect of ion correlations is only one of a few shortcomings of the Debye-Hückel theory.

The difference between dielectric and electrostatic screening can be easily remembered by the following formula. It describes the course of the electric potential in the vicinity of a point charge, as it follows from the Debye-Hückel theory:

Glg. 10.5.1

$$\Psi = \frac{-e^2}{4\pi\varepsilon_0 r} \frac{1}{\varepsilon} \exp\left(-\frac{r}{r_D}\right)$$

The first term is the Coulomb potential, which also acts in a vacuum. This is attenuated – due to the dielectric screening – by the factor $1/\epsilon$. The exponential term captures the electro static screening. r_D is approximately the radius of the counterion cloud. Because of electrostatic screening, there can never be large-scale electric fields in equilibrium situations in water. They exist nevertheless, if

- they are alternating fields whose frequency is so high that the formation of the counterion cloud cannot follow the field, or
- the field in the electrolyte causes an electric current, which is dissipated via the electrodes.

The former situation occurs when the conductivity of electrolytes is to be determined. An alternating voltage with a frequency in the kHz range is used. The second situation occurs in electrophoresis.

Locally (on the scale of Debye length and below), electric fields do exist in water. They can even be much larger than the fields known from the macroscopic world. This is because at the macroscopic level, very strong fields eventually cause an electrical breakdown (e.g., an arc). This does not occur on the scale of the Debye length. One can express this fact also by the Debye length. On the scale of Debye length and below, the condition of electroneutrality may be violated. On larger scale not.

Two side notes:

- An equivalent of the Debye length also exists in plasmas and in semiconductors.⁵⁷
- In metals, the counterions of the electrons (the ionic trunks) are immobile. Therefore, electrostatic screening does not occur and electric waves travel through the wire in question at almost the speed of light.

The existence of the counterion cloud is a consequence of the *interplay of enthalpy and entropy*. If the pursuit of entropy did not exist, one counterion would condense to each ion. Indeed, there is

⁵⁷ https://de.wikipedia.org/wiki/Debye-Länge

often counterion *condensation*. Counterions are often tightly bound to the central ion or charged surface. However, because of the pursuit of entropy, some counterions always remain in a mobile state near the central ion or surface.

Before the value of the Debye length is derived, a remark on the strength of the electrostatic interaction: This is enormous. It is not perceived as enormous in everyday life only *because* it is screened. As an example, calculate the force between two spheres at a distance of 1 m, each containing 1 mol protons and 1 mol electrons (uncompensated). Consider also that the "strong interaction" which acts between the nucleons in atomic nuclei can hold a maximum of 82 protons in the atomic nucleus in the long run (whereas uranium with the nuclear charge number 92 is admittedly also almost stable).

Remember

In water, the electrostatic interaction is screened in two ways. The polarizability of water lowers all fields by a factor of about 78 (by the static dielectric constant). The counter ion cloud

additionally leads to an exponential decrease of the potential. It is valid $\psi = \frac{-e^2}{4\pi\epsilon_0 r} \frac{1}{\epsilon} \exp\left(-\frac{r}{r_D}\right)$

10.6 Organization of counterions at charged surfaces

The conditions at charged surfaces are quite extraordinarily complicated. Although the separation between the different "layers" (Fig. 10.9) is not always clear-cut, it is nevertheless possible to distinguish between different forms of attachment of counterions to charged interfaces. We order from the outside to the inside:

- Due to entropy, counter ions usually do not attach to the surface to the extent that the charge of the surface would be fully compensated by the adsorbed ions. A minority of ions remain at a certain distance from the surface and form the *diffuse double layer*. The thickness of this diffuse double layer (the Debye length) results from a balance between entropy and enthalpy. The thickness of the diffuse double layer depends on the salt concentration. Typical values are in the range of a few nanometers. The Debye length is discussed in Sect. 10.7.⁵⁸
- Some ions attach to the surface *without* stripping the hydration shell. These form the *outer Helmholtz layer*.
- Some ions attach to the surface, shedding the hydration shell. These form the inner Helmholtz layer. One also speaks of "adsorbed ions". The evidence for the difference between the outer and inner Helmholtz layer comes firstly from the kinetics of electrochemical reactions and secondly from studying the dependence of the double layer capacitance on the potential of the surface. The stripping of the hydration shell accounts for a significant contribution to the activation energy of electrochemical reactions. We pass over the effects of the two Helmholtz layers on the double layer capacitance.

Details of the potential profile at charged surfaces are fundamentally a difficult question. The measurement of the "surface potential" is fraught with the same conceptual and technical difficulties. "Surface potentials" are usually determined "electrokinetically". For particles this means the determination of the drift velocity v_{drift} in the electric field *E* ("electrophoresis"). For planar surfaces

⁵⁸ Do not confuse the diffuse double layer with the Nernst layer. The latter is many 100 μm thick. The Nernst layer is the unstirred layer within which all transport is diffusive.

one determines the streaming potential. In both cases there is a relation between the velocity on the one hand and the ζ potential (zeta potential) on the other. We only provide the equation adapted to electrophoresis (in its most simple form)⁵⁹

Glg. 10.6.1

$$\frac{\mathbf{v}_{drift}}{E} = \boldsymbol{\mu}_{ep} \approx \frac{\zeta \boldsymbol{\varepsilon} \boldsymbol{\varepsilon}_0}{\eta}$$

 μ_{ep} the electrophoretic mobility. Note: For colloids, the mobility depends only weakly on the radius. (For proteins, this is different.) ζ is the ζ potential. This raises the question of where on the potentialdistance curve the ζ potential is located (Fig. 10.10). The ζ potential is located at the "plane-ofzero-shear". At a certain distance from the surface, the distance-velocity relation is linear. (The "velocity" v here is the tangential velocity of the fluid relative to the surface). Extrapolating this relation to v = 0 yields the plane-of-zero-shear (Fig. 10.11). This has the important consequence that the hydrodynamic conditions at the surface are included in the ζ potential. Therefore, the detailed interpretation of the ζ potential is fraught with difficulties.



Fig. 10.9 Organization of counterions on charged surfaces. A distinction is made between the inner Helmholtz layer, the outer Helmholtz layer and the diffuse double layer. *en.wikipedia.org/wiki/Doublelayer_capacitance*



Fig. 10.10 The ζ potential en.wikipedia.org/wiki/Zeta_pot ential



Fig. 10.11 For the definition of slip plain www4.ncsu.edu/~hubbe/Defnitns/ ShearPln.htm

Two notes

- For planar surfaces, the ζ potential is inferred from the "streaming potential" or the "electroosmotic flow". Both are "electrokinetic phenomena", as is electrophoresis.
- The ζ potential can also be determined by electroacoustic means. If there is a density difference between particle and medium, a sound wave causes a relative motion and consequently a radio wave.

⁵⁹ For very small particles, $\mu \approx q/(6\pi\eta r_{\rm H})$ is more applicable, with *q* the charge and *r_H* the hydrodynamic radius.

Remember

- On charged surfaces, a distinction is made between the inner Helmholtz layer, the outer Helmholtz layer and the diffuse double layer.
- The ζ potential is the potential at the plane-of-zero-shear.

10.7 Debye length, elements of the Debye-Hückel theory

We derive the Debye length in the following. We restrict ourselves to planar interfaces. On the way to the Debye length, some elements of the Debye-Hückel theory are explained. The derivation starts from Maxwell's 1st law, which states that the divergence (the source density) of the electric field is proportional to the charge density.

$$\nabla \cdot E = \frac{\rho}{\varepsilon \varepsilon_0}$$

Reminder: The divergence is defined as

$$\nabla \cdot E = \frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{\partial z}$$
Glg. 10.7.2

We restrict ourselves to a planar surface. The field is along *z*. All gradients are along *z*. From Maxwell 1^{st} law we infer

$$\frac{\partial E_z}{\partial z} = \frac{\rho}{\varepsilon \varepsilon_0}$$
Glg. 10.7.3

We now use that the electric field is the negative gradient of an electric potential ψ :

$$E_z = -\nabla \psi = -\frac{\partial \psi}{\partial z}$$

Inserting this relation into Glg. 10.7.3 results in

$$\frac{\partial^2 \Psi}{\partial z^2} = -\frac{\rho}{\varepsilon \varepsilon_0}$$

This is the Poisson equation. For a given charge density distribution, the Poisson equation allows the electric field to be calculated. To do this, one must write a differential equation with source term (the right-hand side in Glg. 10.7.5) and - as always - with boundary conditions.

In water, the charge distribution is in turn a function of the potential. If one makes use of this, one can deduct from Glg. 10.7.5 into a closed differential equation in ψ . The charge distribution is subject to the Boltzmann law:

Glg. 10.7.4

Glg. 10.7.5
Glg. 10.7.8

$$\rho_{\pm}(z) = \pm e n_{\pm} \exp\left(\frac{\mp e \psi(z)}{k_B T}\right)$$

We consider 1-1 electrolytes in the following, i.e., only singly charged ions. For multiply charged ions it would be necessary to use Glg. 10.7.6. The charge would have to be taken into account. This would be a technical complication, which we avoid here. n_{\pm} is the number density of ions in the limiting case of $z \rightarrow \infty$. Because of electroneutrality, n_{\pm} and n_{-} (equal to n_{0}) are large. We call this parameter n_{0} and write

Glg. 10.7.7
$$n_{+} = n_{-} = n_{0}$$

Thus from Glg. 10.7.6

$$\rho = \rho_{-} + \rho_{+} = en_0 \left(-\exp\left(\frac{e\psi}{k_B T}\right) + \exp\left(\frac{-e\psi}{k_B T}\right) \right)$$

Insert into Glg. 10.7.5 results in

 $\frac{\partial^2 \psi}{\partial z^2} = -\frac{en_0}{\varepsilon \varepsilon_0} \left(-\exp\left(\frac{e\psi}{k_B T}\right) + \exp\left(\frac{-e\psi}{k_B T}\right) \right)$ Glg. 10.7.9

This is the *Poisson-Boltzmann equation*. It is a nonlinear partial differential equation in $\psi(z)$ (also $\psi(\vec{r})$), if one writes $(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2)\psi$) on the left hand side.⁶⁰

The Poisson-Boltzmann equation is the starting point of the Poisson-Boltzmann theory. The disadvantage of the Poisson-Boltzmann equation is that it is nonlinear in ψ , because ψ is in the exponent. Therefore, one usually has to solve the equation numerically. This can be done. Poisson-Boltzmann theory is successful. Apart from the nonlinearity, Poisson-Boltzmann theory has similar weaknesses and strengths as Debye-Hückel theory, which we will come to in a moment.

To get from Poisson-Boltzmann theory to Debye-Hückel theory, one linearizes the Poisson-Boltzmann equation in ψ . One assumes $\varepsilon \psi/(k_B T) \ll 1$ and Taylor-expands the exponential to first order:

$$\exp\left(\frac{e\psi}{k_BT}\right) \approx 1 + \frac{e\psi}{k_BT}$$

⁶⁰ Strictly speaking, Glg. 10.7.6 is an ordinary differential equation (in 1D).

Inserting this result into Glg. 10.7.9 leads to

$$\frac{\partial^2 \Psi}{\partial z^2} = \frac{en_0}{\varepsilon \varepsilon_0} \left[\left(1 + \frac{e\Psi}{k_B T} \right) - \left(1 - \frac{e\Psi}{k_B T} \right) \right] = \frac{2n_0}{\varepsilon \varepsilon_0} \frac{e^2 \Psi}{k_B T}$$

This is the desired linear partial differential equation in ψ .

Having obtained this equation from a Taylor expansion, one might suspect that it gives good results only for potentials less than k_B/e . The value of k_BT/e at room temperature is 25.7 mV.⁶¹ However, favorable coincidences cause the Debye-Hückel theory to give good results up to voltages of about 50 mV.

At Glg. 10.7.11 we make the ansatz

$$\Psi(z) = \Psi_{\delta} \exp\left(-\frac{z}{r_{D}}\right)$$
 Glg. 10.7.12

 ψ_{δ} is the potential at the bottom of the double layer (at the outer edge of the outer Helmholtz layer). r_D is the Debye length. Inserting into Glg. 10.7.11 leads to

$$r_D = \sqrt{\frac{\varepsilon \varepsilon_0 k_B T}{2n_0 e^2}}$$
Glg. 10.7.13

Without proof, we give the extension of this formula to multivalent ions. It is valid

$$r_D = \sqrt{\frac{\varepsilon \varepsilon_0 k_B T}{2e^2 N_A I}}$$
Glg. 10.7.14

The ionic strength *I* is defined as

$$I = \frac{1}{2} \sum_{i} z_i^2 c_i$$

 c_i is the concentration in mol/L. For 1-1 electrolytes, the ionic strength is identical to the salt concentration. For this purpose, consider NaCl:

Glg. 10.7.16
$$I = \frac{1}{2} \left(c_{Na^+} + c_{Cl^-} \right) = c_{NaCl}$$

Glo 10715

Glg. 10.7.11

⁶¹ The term k_BT/e also appears in the Nernst equation. There it is usually written as RT/F with $R = N_A k_B$ the gas constants and $F = N_A e$ of the Faraday constants.

For CaCl₂, the ionic strength is larger than the salt concentration:

Glg. 10.7.17

$$I = \frac{1}{2} \left(4c_{Ca} + c_{Cl^{-}} \right) = \frac{1}{2} \left(4c_{CaCl_{2}} + 2c_{CaCl_{2}} \right) = 3c_{CaCl_{2}}$$

For water at room temperature you can also remember that

$$r_D \approx \frac{0.3 \text{ nm}}{\sqrt{I[M]}}$$

Note: Addition of salt lowers the Debye length (Fig. 10.12).

In pure water at pH 7, H^+ and OH^- are the only ions that contribute to screening. The Debye length in pure water is about 1 μ m. In biofluids, the ionic strength is about 100 mM. The Debye length thus becomes about 1 nm. With such a small Debye length, the Debye-Hückel theory must reach its limits, and it does. Our lack of understanding of electrostatic interactions in water is a deep-seated problem in molecular biophysics.

Without proof we extend Glg. 10.7.12 to three dimensions:

$$\Psi = \frac{-e^2}{4\pi\varepsilon\varepsilon_0} \frac{1}{r} \exp\left(-\frac{r}{r_D}\right)$$

To check for correctness insert Glg. 10.7.11 and remember that the radial part of the ∇^2 -operator in spherical coordinates is given as $1/r^2 \partial_r/r^2 \partial_r$.

We calculate the Debye length a second time in the following, avoiding differential equations and using qualitative arguments which also do justice to the problem. This second derivation makes

transparent that the thickness of the diffuse double layer is due to the interplay between entropy and enthalpy. We conceive of the double layer as a *capacitor*. This capacitor strives to minimize its electrostatic energy. In this way, Coulomb attraction is taken into account. At the same time, the counterions forming one plate of the capacitor create an osmotic pressure. In this way, entropy is taken into account. The osmotic pressure counteracts the electrostatic attraction.

The electrical energy contained in a capacitor is given as $E = CU^2/2$ with $C = \varepsilon_0 A/d_C$ the capacitance, A the area, ε the dielectric constant, $\varepsilon_0 = 8.8 \ 10^{-12} \text{ C/(Vm)}$ the permittivity of the vacuum, d_C the distance between the two plates, and U the voltage. Note that the voltage acts is a fixed boundary condition here (as opposed to the charge). (The same problem exists in the other versions of the Debye-Hückel theory).



Glg. 10.7.19

A side note: The double layer capacitance is often measured and interpreted. Typical values are in the range of some $10 \,\mu\text{F/cm}^2$.

There is a pressure in the capacitor, because the capacitor hardly decreases its energy by decreasing the distance between the plates. The pressure is given as

Glg. 10.7.20

Glg. 10.7.21

$$p_{es} = -\frac{\mathrm{d}U_{es}}{\mathrm{d}V} = -\frac{1}{A}\frac{\mathrm{d}}{\mathrm{d}d_c}\left(\frac{1}{2}CU^2\right) = -\frac{1}{A}\frac{\mathrm{d}}{\mathrm{d}d_c}\left(\frac{1}{2}\frac{A\varepsilon\varepsilon_0}{d_c}U^2\right) = \frac{1}{2}\frac{\varepsilon\varepsilon_0U^2}{d_c^2}$$

The index es stands for electrostatic.

The net pressure, which results from entropy, is the *difference between* the osmotic pressures in the condenser and the bulk. The osmotic pressure in the condenser is

 $p_{osm} = RT \frac{n_B}{V} = RT \left(c_+ + c_- \right) = N_A k_B T \left(c_+ + c_- \right) = k_B T \left(n_+ + n_- \right)$ $n_{\pm} = n_0 \exp \left(-\frac{eU}{k_B T} \right) \approx n_0 \left(1 \mp \frac{eU}{k_B T} + \frac{1}{2} \left(\frac{eU}{k_B T} \right)^2 \right)$

Note that one must expand to second order to obtain a non-trivial result for the pressure. The osmotic force acting on the plate from the inside thus becomes

$$p_{osm} \approx k_B T n_0 \left(2 + \left(\frac{eU}{k_B T}\right)^2 \right)$$
Glg. 10.7.22

From this pressure, one must subtract the pressure acting from the outside $(2RTc_0 = 2k_BTn_0)$. One obtains

 $\Delta p_{osm} \approx k_B T n_0 \left(\frac{eU}{k_B T}\right)^2$ Glg. 10.7.23

We assume $p_{es} = \Delta p_{osm}$ equal and obtain

$$\frac{U^2}{2} \frac{\varepsilon \varepsilon_0}{d_c^2} \approx k_B T n_0 \left(\frac{eU}{k_B T}\right)^2$$

Dissolve to d_C leads to

 $d_C^2 \approx \frac{\varepsilon \varepsilon_0 k_B T}{2e^2 n_0}$

We identify the thickness calculated in this way with the Debye length. The fact that even the numerical factors agree with those from the longer calculation is a coincidence.

Glg. 10.7.24

Remember

- The diffuse double layer is the result of and interplay between entropy and enthalpy.
- The thickness of the diffuse double layer is the Debye length. In water at 298 K, $r_D \approx 0.3 \text{ nm}/(\text{I}[\text{mol/L}]^{1/2})$

10.8 Ion-specific effects and the Hofmeister series

The counterion cloud is the central prediction Debye-Hückel theory as furthermore also the starting point for the further discussions. We name (without justifications) an (incomplete) set of phenomena to which the Debye-Hückel theory makes statements:

- The forces between charged surfaces

We had calculated above only the course of the electric potential. The force-distance law, which is derived from the electrostatic part of the DLVO theory (section 10.9) also decays exponentially with distance. The characteristic length is the Debye length.

- The critical salt concentration at which electrostatic stabilization breaks down
 Why salt has an unfavorable effect on colloid stability is discussed in Sect. 10.9 is explained. This
 critical concentration goes by the name "critical coagulation concentration", ccc) in colloid science.
 According to Debye and Hückel, it depends on the charge number of the ions, but not on their
 chemical nature. The higher the charge number, the greater the tendency to salting out (the latter
 content of the Schulze-Hardy rule).
- The activity coefficients of ions in water At small concentrations, Debye's limiting law applies: $\log_{10} \gamma_{\pm} = -A|z_{\pm}z_{-}|\sqrt{I}$ with $A = 0.509 \text{ (L/mol)}^{1/2}$ for water at T = 298 K, z_{\pm} the charge numbers, and *I* the ionic strength.
- The mobility of ions in electric field (Kohlrausch's square root law)
 The counter ion cloud brakes the central ion.

According to the Debye-Onsager theory there is an "electrophoretic effect" and a "relaxation effect". Both scale with the root of the ionic strength (like the Debye length).

 The rate constants of reactions in solution and in particular their dependence on the salt concentration ("kinetic foreign salt effect").

The shortcomings of the Debye-Hückel theory include:

- The Debye-Hückel theory is based on a Taylor expansion in the voltage and should therefore only be valid for voltages significantly below 25.7 mV (25.7 mV = $k_BT/e = RT/F$). By chance, different terms compensate each other at higher voltages and therefore the Debye-Hückel theory is also applied at higher potentials.
- Ion correlations: The Debye-Hückel theory is a "mean-field" theory that replaces the individual ions with an averaged ion density.
- Finite ion radii

Debye-Hückel theory must fail when the Debye length approaches the ion radius (consider the hydration shell). Beyond 100 mM, deviations are expected. In the case of Debye's limit law, this can be seen, for example, in Fig. 10.13

- Van-der-Waals attraction

- H-bonds, hydration shell

The Debye-Hückel theory is universal in the sense that the chemical properties of an ion - apart from charge number - all play no role. If this were correct, e.g. a "sodium-potassium asymmetry", as it exists in nerve conduction, would remain completely without consequences. Those effects that depend on the chemical nature of the ions are grouped under the name "ion-specific effects" (ISEs). Among the ion-specific effects are

- -The deviation of the activity coefficient from Debye's limit law (Fig. 10.13)
- -The influence of ions on solubility, reactivities (also of enzymes) and the CMC
- -The influence of ions on the surface energy

One likes to systematize the ISEs along the Hofmeister series. In 1888, Hofmeister determined the critical salt concentration at which a certain protein (especially albumin from the hen's egg) precipitated and ranked the salts according to this concentration. Today, this concentration would be called the "critical coagulation concentration (ccc)." The Debye-Hückel theory makes a prediction for the ccc. As Hofmeister showed, it does not agree well with experiment. In particular, he also observed a "salting-in", not only a salting-out as predicted by the Debye-Hückel theory. A similar ordering as observed by Hofmeister is also found in many other ISEs. Caution is advised. Sometimes the sign of the ordering of the effects flips when concentrations are changed.

Hofmeister attributed the ISEs to the influence that the ions in question have on the structure of

the surrounding water. Ions which disturb this structure he called chaotropic; ions which stabilize it he called cosmotropic. Although this view is not entirely current today, some of the effects can be remembered using this idea. Note: In addition to "salting out," which can be understood using the Debye-Hückel theory, there is also "salting in." Further explanations on the Hofmeister series can be found in Fig. 10.14.

Remember

- The Debye-Hückel theory is the starting point for the discussion of electrostatic effects in water. It is universal.
- Debye-Hückel theory does not cover the ion-specific effects. These can arranged and ordered in the Hofmeister series.

10.9 Colloid stabilization according to DLVO theory, steric stabilization

In the context of DLVO theory, the interactions between colloidal particles are understood as a sum of van der Waals attraction and electrostatic repulsion. The electrostatic repulsion is described as an exponential law according to Debye-Hückel. (We omit the derivation of the interaction potential from the electric potential profile). It applies approximately





 V_{δ} is a prefactor. δ stands for the upper edge of the "outer Helmholtz-plane", at the same time the lower edge of the diffuse double layer). *D* is the distance between the surfaces of the two spheres (not,



Beyond an ionic strength of about 100 mM, many deviations from the Debye-Hückel theory occur. Shown here is log γ_{\pm} of KBr in water at 25°C (with $\gamma \pm$ the activity coefficients). The line is the prediction of Debye's limit law. *en.wikipedia.org/wiki/Debye-Hückel_theory*

for example, the distance between the sphere centers). DLVO theory in its simple form applies to distances much smaller than the sphere radius *a* (applies to $D \ll a$). This condition is quite realistic for technical polymer dispersions, where high solid fractions are used. The dispersions are packed as densely as possible, but flowability must be ensured. (A side note: A high solids content is easier to achieve with wide particle size distributions, because then the small particles fit into the gaps between the large particles).

For the attractive interaction applies

Glg. 10.9.2

$$V_{att} \approx -\frac{Aa}{12D}$$

A is the Hamaker constant.⁶² A quantifies the strength of the van der Waals (vdW) interactions. Typical values are on the order of 10^{-20} J. Note that the larger the particles, the stronger the attractive interaction, but the repulsive interaction (Glg. 10.9.1) is not size dependent. Thus, large particles tend to aggregate more than small particles. This is another reason to be interested in particles with a radius smaller than 1 µm in the context of colloid science.

Note: Glg. 10.9.2 contains the term 1/D (as opposed to $1/D^6$), although the distance dependence of



the vdW interaction between two molecules scales as $1/r^6$. For colloidal spheres, an inverse sixth power results when the sphere distance is much larger than the sphere radius (D >> a). Here, we consider the opposite case (D << a). Many different molecules contribute to the attraction. One has to integrate and in the course of these integrations a r^{-6} -law becomes a D^{-1} -law

⁶² This is an effective Hamaker constant. Write $A = (A_{11}^{1/2} - A_{22}^{1/2})^2$ with A_{11} and A_{22} the Hamaker constants of the particles and the liquid. Note that the interaction is attractive even for the case $A_{11} < A_{22}$. Two air bubbles in a liquid attract. There can be a net vdW repulsion if the two "particles" have different Hamaker constants. For this case, there is an even more complicated compound Hamaker constant that accounts for three different materials. This latter effective Hamaker constant can be negative. An air bubble and a solid particle in water can repel each other (due to the vdW interaction in connection with Archimedes' principle).

Basically, the Hamaker constant has the unit of one energy. It can be divided by k_BT . The Hamaker constant is usually slightly larger than k_BT . Note, however, that the Hamaker constant rarely competes directly with the thermal energy. There are almost always geometry factors still involved, including (Glg. 10.9.2).



As Fig. 10.15 illustrates, the sum of electrostatic repulsion and vdW attraction results in an aggregation barrier if - first - the prefactor before the repulsive term is large enough and if - second - the range of the repulsion is large enough. This also names the two central failure mechanisms of electrostatic stabilization. For example, the prefactor becomes small when charge on the particles is lost due to lack of pH stability. The range also becomes small when, after the addition of salt, the Debye length becomes small.

For the two reasons mentioned above, electrostatic colloid stabilization is not very robust. One can help oneself by additionally (or alternatively) applying *steric* stabilization (Fig. 10.16). Steric stabilization is achieved by polymer brushes. Polymer brushes here mean terminal anchored linear chains in a good solvent. Two polymer brushes always repel each other for entropic reasons. The preparation of brushes on latex particles is relatively simple for acrylate polymers: acrylic acid is added to the formulation at a concentration of about 1%. These relevant partial chains are water-soluble and therefore form the required brush-like structures on the surface. Non-ionic surfactants with their relatively long hydrophobic moieties also contribute to steric stabilization.

It should be noted in the margin a subtlety in the DLVO potential. The sum of repulsive and attractive potential leads to a flat secondary minimum at large distances. This minimum is usually of minor importance, but can have consequences. It can lead to flocculation (Sect. 10.10).

As far as quantitative details are concerned, the DLVO theory must have at least the same weaknesses as the Debye-Hückel theory. However, it explains some essential elements of colloid stability (and how it can be lost) well.

Remember

- The electrostatic repulsion creates an aggregation barrier (if the charge and the Debye length are large enough).
- Electrostatic colloid stabilization suffers from the addition of salt.
- Steric stabilization with polymer brushes provides a second mechanism for colloid stabilization.

10.10 Flocculation

Flocculation refers to a reversible accumulation of particles on each other. In contrast, "aggregation" is irreversible. Aggregation means aggregation into the primary minimum (Fig. 10.15). Dominant here is the vdW interaction. Aggregation is difficult to break up even by ultrasound and/or strong shear fluxes. Flocculation is already dissolved by moderate shear forces (e.g. generated by dipping a brush into the paint).

Flocculation is often desired because

- it has a favorable influence on the rheological properties during processing. Here, the shear thinning is to be mentioned above all
- a flowing of the film on the wall ("sagging") is avoided
- sedimentation of heavy pigments is hindered.

There are several mechanisms that lead to flocculation:

- A preferential interparticle spacing in the secondary minimum of the DLVO curve (Fig. 10.15).
- Bridging flocculation (Fig. 10.17) according to This mechanism requires weakly adsorbing chains.
- Depletion flocculation (Fig. 10.18). Depletion flocculation is caused by a bimodal (or multimodal) size distribution. If the smaller species does not fit into the gap between the larger particles, an osmotic vacuum is created in the gap.

Flocculation produces weak gels. In the terminology of rheology, these substances are called "Bingham fluids". They flow after a certain critical stress (the yield-stress) is exceeded. Such weak gels are also very common among foods (ketchup, mustard,). Pastes have similar properties.



Fig. 10.17 Mechanism of bridging flocculation community.dur.ac. uk/ sharon.cooper/lectures /colloids/interfacesweb1 .html



Fig. 10.18

Mechanism of depletion flocculation Fan, T.-H.; Tuinier, R., Hydrodynamic interaction of two colloids in nonadsorbing polymer solutions. Soft Matter **2010**, 6, 647.

11 Film formation from latex dispersions

11.1 General

- Literature on film formation:
 Keddie, J. L.; Routh, A. F., Fundamentals of Latex Film Formation: Processes and Properties. Springer: 2010.
- Mischke, P.; Brown, R., Film Formation in Modern Paint Systems. Vincentz Network: 2010.

Film formation in a way reverses the process of colloid generation. It is a controlled solidification by drying. In the following, we are concerned with coatings (as opposed to sintered bodies). We are not concerned with molecularly thin coatings. Typical thicknesses are $100 \,\mu\text{m}$. (In automotive engineering: more likely $150 \,\mu\text{m}$). This thickness allows to cover dust grains and to compensate a certain roughness. The material can dissipate mechanical energy to achieve some impact resistance. Some abrasion can be tolerated over the life of the paint.

A very important aspect of film formation is that polymers can relieve (relax) shrinkage-induced stresses. This is a special property of polymers whose glass transition temperature is not far above the working temperature. This is the role of polymers as *binders*.⁶³ The binder may well be present in such small quantities between the "pigments" that the "film" is porous and the "binder" only forms bridges between the particles. This is the case, for example, with interior wall paints. These would have to be permeable to moisture. With the exterior wall, this is different.

Example applications include:

- Protective coatings (automotive industry, shipbuilding, architecture, wood preservation...)
- Adhesives⁶⁴
- Rubber gloves
- Back coatings for carpets (a large but declining market).
- the most diverse types of inks (these usually not applied planar).⁶⁵ The "pigments" can be functional carriers of all kinds (photovoltaic, sensory, ...).
- Electrodes in lithium batteries consist of the "active", graphite for electrical conductivity and the polymer PVDF. They are applied as a film and then rolled.
- Auxiliary materials for paper production

The production of latex-based paints has a number of advantages. Because mainly water evaporates during drying (instead of organic solvents), latex-based paints are considered environmentally friendly.⁶⁶ Unfortunately, latex dispersions still contain "film-forming aids." These are organic molecules. You can smell these substances when water-based paints dry. Furthermore, latex dispersions can have a high solids content while maintaining moderate viscosity. Solution-based dispersions with a concentration of 50% or more (as is common with latex dispersions) are no longer flowable, but latex dispersions are. Third, emulsion polymerization is a relatively inexpensive

⁶⁶ Consider, however, that water-based processes (always) require the use of biocides. Biocides are playing an increasingly important role as water-based processes become more important. There is a complicated set of regulations. Below is the structure of isothiazolinone, an important component.



⁶³ The "CSH phases" in concrete play a comparable role. CSH stands for calcium silicate hydrate. These are fine and, within certain limits, flexible lamellae whose exact structure is not well known.

⁶⁴ With adhesives, stress relaxation is not a problem because the materials are soft.

⁶⁵ 3D printing is not considered in the following. In polymer 3D printing, the most common method is fused-deposition molding (FDM). There are other methods. FDM is based on cooling liquid polymer. No drying takes place.

manufacturing process available. Caution: Do not confuse emulsion polymerization with miniemulsion polymerization.

11.2 The film making process

The "film formation process" is commonly divided into three phases (Fig. 11.2):

Box 11.1

Emulsion polymerization

Emulsion polymerization does not produce dispersed polymer particles from emulsified monomer droplets in the course of polymerization. This latter process is at the core of miniemulsion polymerization. An essential aspect of miniemulsion polymerization is the stabilization of the emulsion against Ostwald ripening with a "hydrophobe" (section 3.5).

In emulsion polymerization, one starts with relatively large monomer droplets, which, however, only play the role of a monomer reservoir. The monomers must be readily soluble in water. The initiator is also watersoluble. A large number of micelles are present. Initially these are empty, later they swell with monomer. (Much later, these micelles become the polymer particles.) The initiator breaks down into two radicals in the water phase. After the monomer is easily soluble in water, oligomers are formed. Due to their size, oligomers are somewhat less soluble in water than the monomers. Therefore, sooner or later they enter the interior of the micelles. There, polymerization then proceeds further. In principle, the growing chains can of course also enter the (large) monomer droplets and form a chain there. However, because there are far fewer monomer droplets than micelles, the latter process is rare.

A certain disadvantage of emulsion polymerization is that it cannot be carried out continuously. It is a batch process. Attempts have been made to build appropriate tubular reactors. Reactor fouling – the risk of a solid phase forming – remained a problem.

A complication in emulsion polymerization can be that new particles are formed in a late phase. In seeded emulsion polymerization (also known as semi-batch polymerization), small particles are introduced and the particle nucleation phase is separated from the growth phase. In the "semi-batch process", not all reagents are present from the beginning. Rather, monomer, initiator and possibly other reagents are added from above during the reaction. In this way, one can counteract "compositional drift" in copolymerization, for example. One can also produce "core-shell particles" (e.g. with a hard core and a soft shell) by changing the monomer during polymerization. This creates "nanocomposite" particles. Nanocomposites, unlike copolymers, exhibit some spatial heterogeneity. Nanocomposites are also important because "latex blends" tend to segregate due to the small number of particles and therefore also the small mixing entropy.





Fig. 11.1

For emulsion polymerization

knowledge.ulprospector.com/4911/pc-fundamentalsemulsion-polymerization/

- Evaporation of the water ("stage I")
- Particle deformation ("stage II")
- Polymer interdiffusion ("stage II").

All three phases have their problems and open specific possibilities to adjust the film properties.

During Phase I ("water evaporation"), the latex can still flow. This is widely regarded as a problem because, for example, noses can form ("sagging"). To prevent this, a thickener is added. The thickener flocculates the dispersion (section 10.10). It is favorable to start the film formation with a

high solids content. This shortens the time during which the material can flow. The energy costs for drying and the transport costs may be reduced. A high solids content is achieved with wide particle size distributions, because then the small particles fit into the gaps between the large particles. Technical dispersions can have a solids content of 50% and higher.

Drying can be accelerated by convection and hot air. On fast-running belts, adhesive tapes or films are dried within a few seconds. Under normal ambient conditions, the evaporation rate of water is about 1 mm/day. There is a certain fundamental limit to the drying speed. There is a "laminar boundary layer" at every interface. Transport through this boundary layer is diffusive. This layer can be narrowed somewhat by vigorous convection, but it cannot be completely avoided. (A similar

boundary layer in electrochemistry is called the "Nernst layer". There it is several 100 μ m thick). The thickness of the boundary layer and the diffusivity of the water vapor in the boundary layer result in a "mass transfer coefficient" that must be accepted. A similar "mass transfer coefficient" also exists at all other phase boundaries.

During Phase I, the "coffee-stain effect" or "coffee-ring effect" often occurs. In this case, the material flows outward. A thickening is found at the edge of the film. The coffee-stain effect has two causes. First, the evaporation rate is increased at the edge. Second, the meniscus is anchored at the edge because the solidification has started there. Without this pinning, the droplet would contract laterally. Because of the pinning,





material flows outward - and remains there. It is not strictly always the material that flows to the outside. Sometimes a drying front also drives material from the outside to the inside.

During phase I, there is a concentration gradient of the particles between top and bottom. This will be insignificant if the evaporation is sufficiently slow. To quantify this argument, one defines a suitably normalized evaporation rate, also called "Peclet number" as

Glg. 11.2.1

$$Pe \approx \frac{\tau_{diff}}{\tau_{dry}} = \frac{H^2 / D}{H / E} = \frac{H}{DE}$$

H is the film thickness, *D* is the diffusivity of the polymer particles and *E* (in units of m/s) is the evaporation rate. If the solid fraction is small, one can use the Stokes-Einstein diffusivity for *D* $(D_{SE} = k_{\rm B}T/(6\pi\eta a))$. Otherwise, one must use the cooperative diffusion coefficient. The latter is defined via Fick's law $(J = -D_{coop}\nabla c)$. When repulsive interactions dominate, the cooperative diffusion coefficient is larger than the Stokes-Einstein diffusivity. Mass transport is more efficient than predicted by Stokes-Einstein because the particles "push each other forward" (hence the name "cooperative").

When the Peclet number is high (when the film dries "fast" in the sense that diffusion becomes ineffective), a skin often forms on the top of the film. This is a problem because this skin can (can, not must) form cracks and wrinkles. This later leads to film defects. The skin can also slow down further drying. Accumulation of particles at the top of the film will only lead to a skin if the particles deform and coalesce there. This will preferentially be the case if the particles are soft. Therefore, the extent and type of skin formation also depends on the glass transition temperature of the polymer material.

The Peclet number plays a central role in the process of "autostratification" (also "self-stratification"). It would be technically attractive if films with graded properties (functionally graded materials) were to form spontaneously during the drying process. For example, one might want good adhesion on the substrate side and good scratch resistance on the air side. Currently, such coatings are created as multilayer systems. Coatings in the automotive industry consist of three sub-layers. First, an electrocoat is applied. This is optimized for adhesion and corrosion protection. Electro deposition ensures that the paint is deposited everywhere. This is a pH-induced precipitation. The colloids in question are not pH stable. It must be a cathodic (rather than an anodic process) because anodic processes tend to dissolve the metal. The pH unstable colloids are therefore stabilized with amines (instead of carboxylic acids, which would be cheaper). Above the KTL layer (KTL for cathodic dip coating) is the "base-coat". This layer contains a large proportion of the color pigments. Above this is the "top-coat" (often made of polyurethane). This is optimized for scratch resistance.

The formation of concentration gradients and their fixation in the dry film can be caused by the flow of water towards the water-air interface. For this, the Peclet number must be around 1. The particles then initially accumulate on the surface of the film. If one type of particle diffuses faster than the other particle type (e.g. because the particles in question are smaller), the concentration of the small particles equalizes, but that of the large particles does not (or only partially). When diffusion comes to a standstill at this point because the film solidifies, the large particles are enriched on the surface. Autostratification is thus achieved. According to



Fig. 11.3 Alkyd resins are the modern technical version of linseed oil, which used to be widely used by painters as a binder. *www.pcimag.com/articles/99678development-of-low-color-alkyd-resinswith-high-content-of-biobased-succinicacid*



the idea developed above, the large particles should be enriched at the top. It turns out that sometimes the small particles are enriched at the top. We will ignore the reasons here. Multi-component diffusion can be very multifaceted and complicated. In principle, one could always imagine using such a mechanism with small molecules dissolved in water (in the "serum"). However, small molecules diffuse so quickly that you would have to dry a very thick film within seconds in order to freeze a concentration gradient (to make the Peclet number of the order of one). This is impractical.

We come to phase II of film formation, particle deformation. First: The particles deform only if

they are sufficiently soft. The temperature must not be far below the glass transition temperature. In the context of coatings, this leads to the "film formation dilemma". As a rule, coatings should be mechanically robust. A glass transition temperature above room temperature is desired. But this is exactly what stands in the way of film formation, because hard spheres cannot deform sufficiently. There is a "minimum film formation temperature" (MFT, or MFFT according to minimum film formation temperature), which can be determined with a "film drawing bench" (Fig. 11.4). The film forming bench essentially is a substrate with a temperature gradient.

One of the ways out of the film formation dilemma is to add plasticizers ("coalescing aids") to the dispersion, which evaporate more slowly than the water. These are small molecules. These coalescing aids produce the odor that is perceived when painting. (Organic solvents have been replaced by



Fig. 11.5 The flow of water may be driven by negative capillary pressure, which occurs at the water/air interface.

water as a continuous phase.⁶⁷) Under certain circumstances, the film-forming aids are as problematic from an environmental point of view as the organic solvents. People like to refer to latex dispersions as part of "green chemistry." This is only partially correct.

The second way to cure a soft coating is chemical crosslinking There are several ways to achieve this:

- Radical crosslinking, thermally initiated
- Radical crosslinking, UV-initiated
- Oxygen-induced crosslinking (alkyd resins, Fig. 11.3)
- pH-induced crosslinking, where the pH decreases during drying because ammonia evaporates.

If the particles are *not* sufficiently deformable, two separate problems occur: First, the gusset phase can fill with air. Then the film is white. Second, cracking can occur. Cracks on the one hand and a white film on the other are also present in Fig. 11.4 as separate phenomena. It is sometimes said that a failed film formation leads to a powder. This is rather rarely the case. Most often, flakes are formed. Capillary forces usually lead to irreversible adhesion of particles to each other.

Note. Until the interstices fill with air, the films usually largely clear. This is true even for small glass spheres (often made according to Stöber, Sect. 10.1). The capillary forces are so large that even elastic bodies with considerable rigidity are deformed.

⁶⁷ Do not confuse a solvent with the continuous phase of a dispersion. The polymer in a latex dispersion is insoluble in water.

There are three different mechanisms that can drive particle deformation. These are negative capillary pressure, which occurs at the water/air interface (Fig. 11.5). It can further be driven by the water/polymer surface tensions ("wet sintering") or by the air/polymer surface tension ("dry sintering"). These mechanisms play a role in the classification of film formation scenarios according to Routh and Russel (Fig. 11.8) play a role. The kinetics of the sintering process are discussed in Box 11.2 is discussed.

Box 11.2

Sintering according to Frenkel

The simplest model for the sintering of polymer particles is by Frenkel. It predicts that

$$\theta^2 \approx \frac{\gamma}{a\eta} t$$

 γ is the surface tension between polymer and water (or also polymer and air). η is the viscosity of the polymer (!). In general, the polymer will be viscoelastic, of course. *a* is the particle radius. The angle θ is explained in **Fehler! Verweisquelle konnte nicht gefunden werden.**



The fact that the particle radius *a* is in the denominator in the Frenkel equation can be justified with a simple dimensional argument. The right side must be dimensionless. γ must be in the numerator, η must be in the denominator. The particle radius can be used to give this ratio the correct dimension. However, this does not explain why θ^2 is proportional to $\gamma/(a\eta) t$. After all, it could also be the size θ or θ^3 . The reasoning for the square leads into the details. We omit it. (For a corresponding static situation under an external normal force *F*, according to the Hertz model $\theta^3 = F/(a^2 \text{ K})$ with *K* an effective modulus, approximately equal to the shear modulus).

The Frenkel equation predicts that small particles sinter faster than large particles because a is in the denominator on the right-hand side. One may take this as a variant of the general wisdom that capillary effect increases in relative importance on small scales. Here capillary forces compete with viscous friction.

Fig. 11.6

Sintering particles

The kinetics are determined by a pressure equilibrium. In addition to the various capillary pressures and surface tensions, the hydrodynamic pressure also plays a role. The latter is usually presented as a consequence of "Darcy flow". In a porous medium Darcy postulates the following relation between flow velocity v and pressure gradient ∇p :

Glg. 11.2.2

$$\mathbf{v} = -\frac{\kappa}{\eta} \nabla p$$

 η is the viscosity of the liquid, κ is the "permeability". κ has the dimension of m^2 and corresponds approximately to the area of the pore cross-section. One can justify Glg. 11.2.2 with the law of Hagen-Poiseuille. Under certain conditions, Darcy's law becomes an equation analogous to Fick's second law for diffusion. Let ϕ be the local water content (a volume fraction). Let the porous medium be elastic on short time scales. Then the pore walls exert a negative pressure on the water phase, given as

Glg. 11.2.3 $p_{elas} = K(\phi - \phi_0)$

K is a modulus (unit: Pascal). ϕ_0 is the initial water content. A continuity equation applies to the water

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = -\nabla \cdot \mathbf{v}$$

J is the flow. κ is the pore cross-section, κ was assumed constant here for simplicity. If the permeability is not constant, it must stop below divergence ($\nabla \cdot$...). We require local hydrostatic equilibrium ($p = p_{elas}$)



Half of the latex particles are labeled with donor and half with acceptor molecules. The donor dyes fluoresce. The acceptor dyes can fluoresce, but do not always do so. When donor and acceptor dyes are in close proximity, "Förster Resonant Energy Transfer" occurs. This is a nearfield electromagnetic effect. Electromagnetism is more complicated than we are used to, when the distance between two antennas is comparable to the size of the antennas. Then the "near-field effects" occur. One of these effects is the energy transfer between two dyes. (Near-field effects are used when batteries are charged via a coil without cables).

This energy transfer has a characteristic signature in the decay curves (**Fehler! Verweisquelle konnte nicht gefunden werden.**). The decay curves are histograms of the time delays between the exciting lamp pulse and the arrival of the fluorescence photon. In the absence of energy transfer, this histogram is essentially an exponential function. In lin-log representation, the result is a straight line. In the presence of FRET, the curve in question is curved upward.

We form the divergence, use Glg. 11.2.4 and arrive at

Glg. 11.2.6

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = -\nabla \cdot \mathbf{v} = \frac{\kappa}{\eta} K \nabla^2 \phi$$

The role of diffusivity is taken by $\kappa K/\eta$. Assume $K \approx 10^6$ Pa (a rubber), assume $\kappa \approx 10 \times 10$, and assume $\eta \approx 10^{-3}$ Pa s. This results in an effective diffusion constant of 10^{-7} m²/s corresponding to 10^{-4} cm²/s. This value is slightly higher than typical diffusion constants. Note: The Darcy flow is not a Brownian motion. It is a convective flow in a porous medium.

The behavior of moist porous media can be very complicated. This field of research is also called "soil mechanics" because such processes often occur in soils.

A side note: When particle deformation is driven by sintering, instability occurs. It is the analog of the Rayleigh instability (Sect. 3.4). The local capillary pressure is γ_{PW}/r with γ_{PW} the surface tension

Glg. 11.2.5

between polymer and water and r the pore radius. The narrow pores collapse and empty the water into neighboring areas with larger pore radius. A drying front occurs.

This brings us to phase III of film formation: interdiffusion. When a film has become clear, film formation is not yet complete. The film does not yet have mechanical strength. To create mechanical strength, the polymer chains must be given time to diffuse across particle boundaries and form a transient interlocking network. This process is called "polymer welding" in another context. This process was first studied with neutron scattering. Somewhat less elaborate instrumentally is a fluorescence method, based on nonradiative energy transfer between donor and acceptor dyes (Box 11.4).

11.3 Different scenarios of film formation

Depending on the conditions, the film formation process can take different courses. Routh and Russel have summarized these scenarios diagrammatically in a "map". They have chosen two main parameters: the Peclet number (Glg. 11.2.1) and a time for particle deformation normalized to the drying time. The various surface tensions are left out as parameters in this representation. The phenomenon of laterally propagating drying fronts is also largely left out. The Routh-Russel model is summarized in Fig. 11.8.

