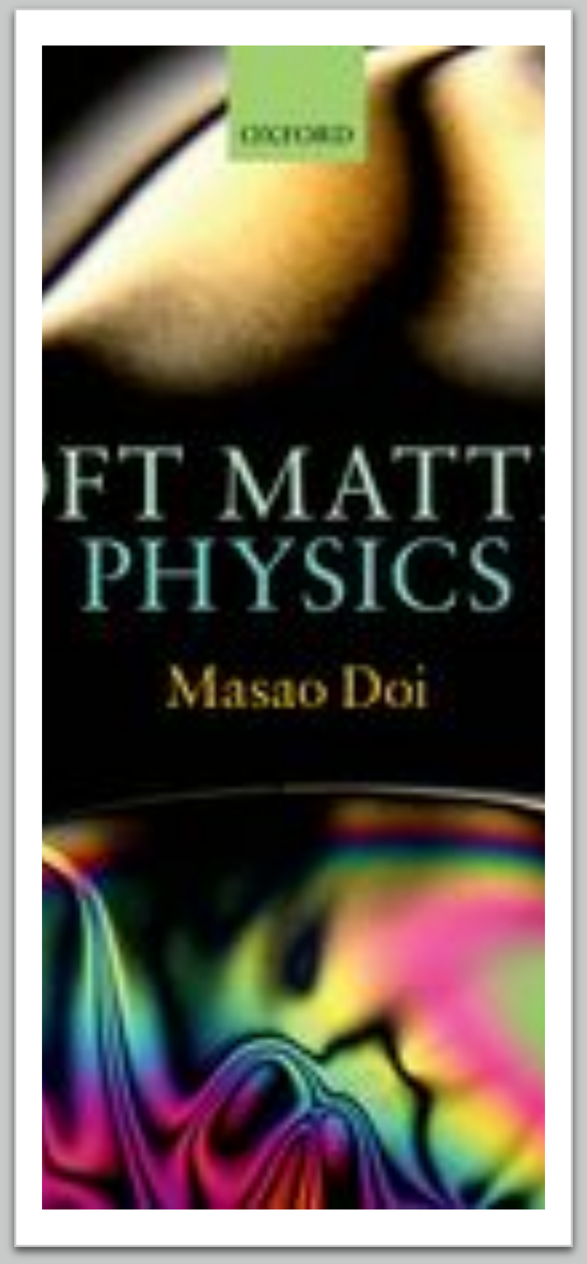


Surfaces & Surfactants

Surfaces & Interfaces

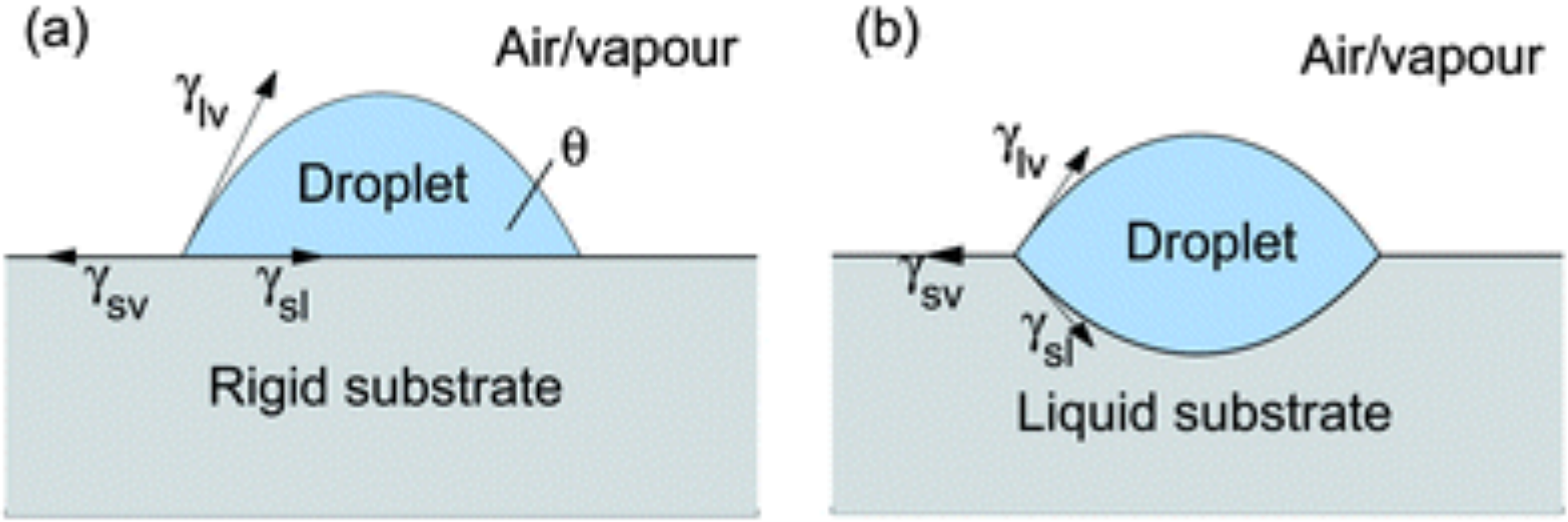
Surfaces, or more generally, interfaces are important in soft matter by two reasons.

First, the weak forces associated with surfaces, such as surface tension and inter-surface forces, play an important role in the flow and deformation of soft matter. For example, surface tension is the force governing the behaviour of liquid droplets.

Second, many soft matter systems, especially colloidal dispersions, are composed of several different phases and have large interfacial area within the material. In such materials, the interfacial properties are crucially important for the bulk properties. For example, whether colloidal dispersions are stable or not is determined by the inter-surface force.

Equilibrium shape of a fluid

Young and Neumann triangle equations



Surface tension

A small liquid droplet placed on a plate usually takes the shape of spherical cap or pancake. The shape changes if the plate is tilted, but it recovers the original shape when the plate is set back. This phenomenon indicates that the fluid droplet on a plate has an equilibrium shape.

The force which gives the equilibrium shape to a fluid is the force associated with the fluid surface. A surface is a special place forthe fluid molecules.

Molecules in a fluid usually attract each other. If such a molecule sits in the bulk region (the region far from the surface), it has a negative potential energy $-z\epsilon$, where z is the coordination number and $-\epsilon$ is the van der Waals energy between neighbouring molecules. On the other hand, if the molecule is at the surface, approximately half of the neighbours are lost and the potential energy is about $-(z/2)\epsilon$.

Surface tension

Therefore the molecules at the surface have a potential energy about $(z/2)\epsilon$ higher than the molecules in the bulk.

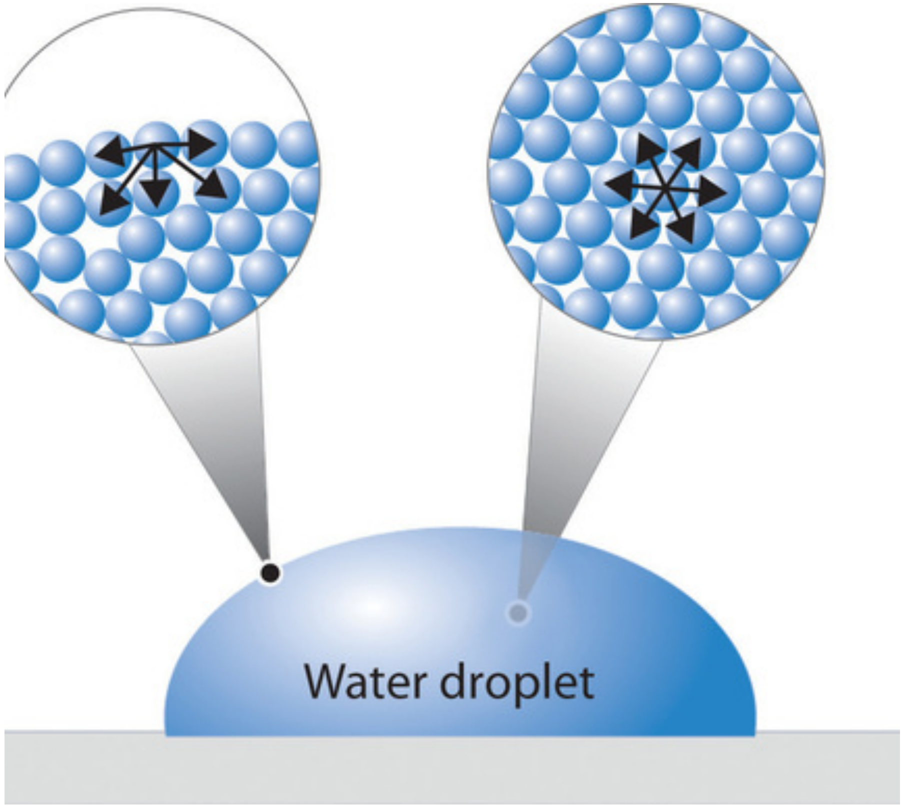
The excess energy associated with the surface is called the surface energy. (More precisely, it should be called the surface free energy, and its definition will be given later.) The surface energy is proportional to the surface area of the fluid, and the energy per unit area of the surface is called the surface energy density (or surface tension), denoted by γ.

Since the surface area of a fluid depends on the fluid shape, the equilibrium shape of a fluid is uniquely determined by the condition that the free energy of the system is a minimum. If there are no other forces acting on the fluid, the fluid takes a spherical shape, the one which minimizes the surface area for a given volume.

Surface tension

A liquid droplet on a substrate takes the shape of a spherical cap.

Molecular origin of surface tension.



Methods to measure the surface tension.

A liquid is set in the region bounded by the U-shaped supporting wire and a straight bounding wire. The force acting on the bounding wire is given by 2γa.

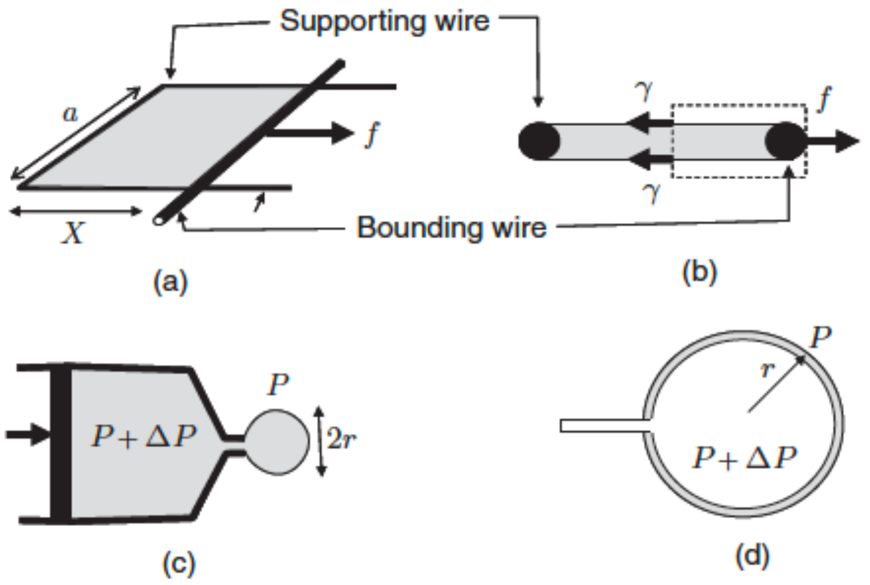
The liquid in the dashed box is pulled to the right by the force f exerted on the bounding wire and is pulled to the left by the surface tension 2γa.

Laplace pressure

To make a liquid droplet by injection of the liquid through a syringe, an excess pressure ΔP must be applied.

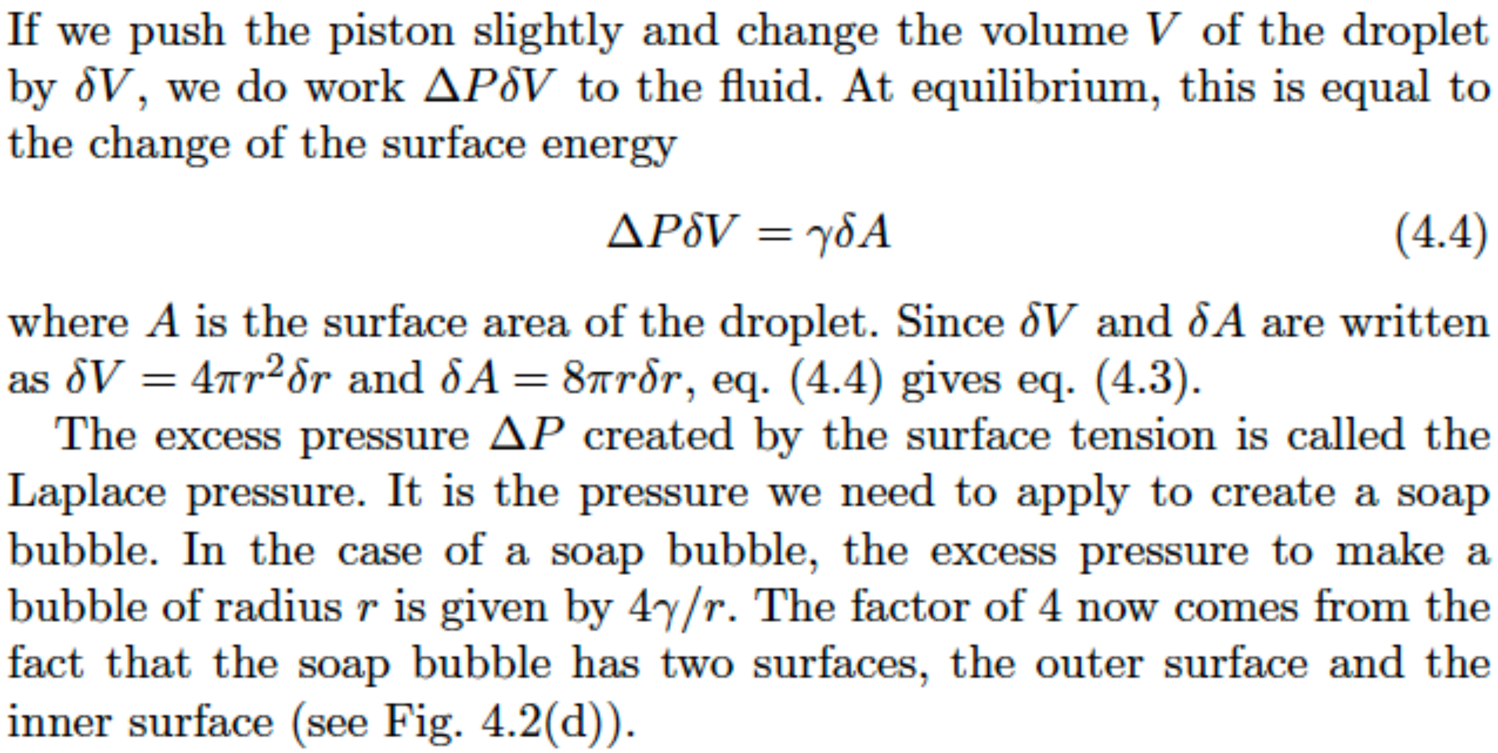
The excess pressure at equilibrium is the Laplace pressure. For a droplet of radius r, the Laplace pressure is ΔP = 2γ/r.

The excess pressure ΔP needed to blow a soap bubble is given by ΔP = 4γ/r.



Laplace pressure

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



If we push the piston slightly and change the volume V of the droplet by δV, we do work $\Delta P \delta V$ to the fluid. At equilibrium, this is equal to the change of the surface energy

$$\Delta P \delta V = \gamma \delta A \tag{4.4}$$

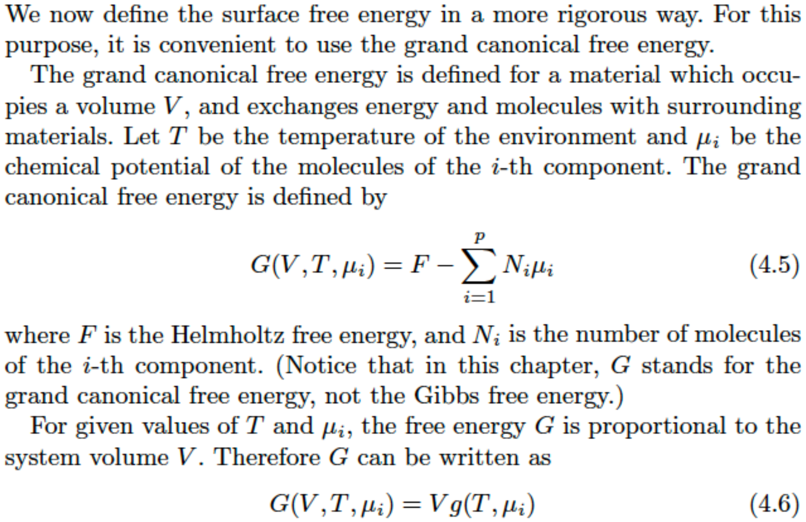
where A is the surface area of the droplet. Since δV and δA are written as $\delta V = 4\pi r^2 \delta r$ and $\delta A = 8\pi r \delta r$, eq. (4.4) gives eq. (4.3).

The excess pressure ΔP created by the surface tension is called the Laplace pressure. It is the pressure we need to apply to create a soap bubble. In the case of a soap bubble, the excess pressure to make a bubble of radius r is given by $4\gamma/r$. The factor of 4 now comes from the fact that the soap bubble has two surfaces, the outer surface and the inner surface (see Fig. 4.2(d)).

Soap bubbles

Grand canonical free energy

$$G(V,T,\mu_i) = -VP(T,\mu_i)$$



We now define the surface free energy in a more rigorous way. For this purpose, it is convenient to use the grand canonical free energy.

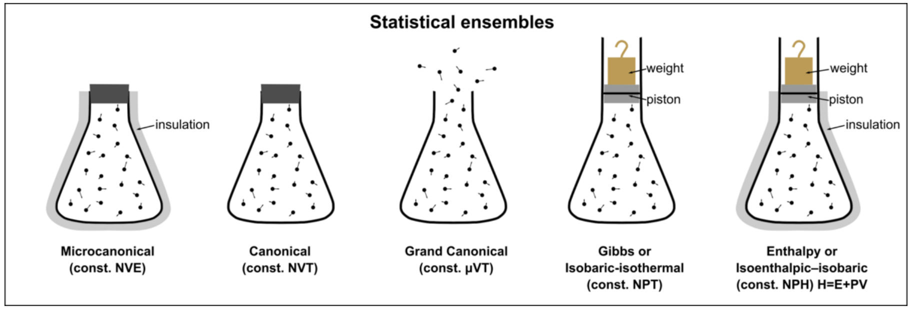
The grand canonical free energy is defined for a material which occupies a volume V, and exchanges energy and molecules with surrounding materials. Let T be the temperature of the environment and μ_i be the chemical potential of the molecules of the i-th component. The grand canonical free energy is defined by

$$G(V,T,\mu_i) = F - \sum_{i=1}^{p} N_i\mu_i \tag{4.5}$$

where F is the Helmholtz free energy, and N_i is the number of molecules of the i-th component. (Notice that in this chapter, G stands for the grand canonical free energy, not the Gibbs free energy.)

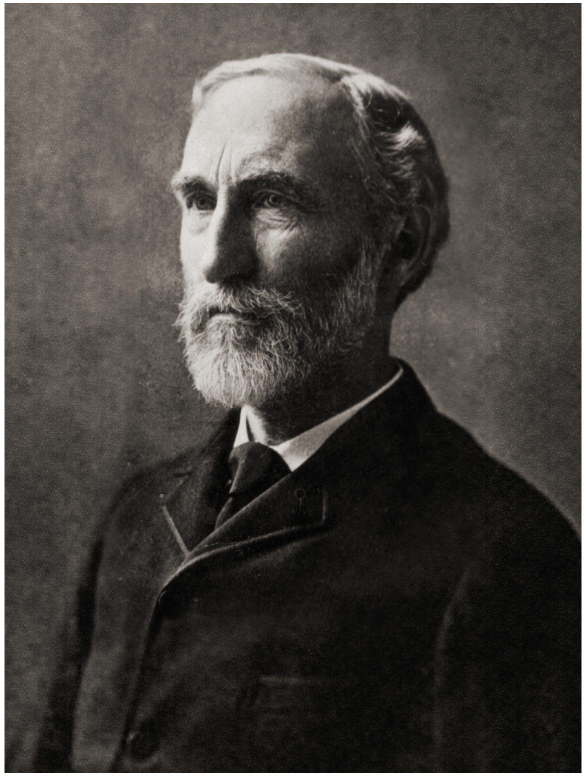
For given values of T and μ_i, the free energy G is proportional to the system volume V. Therefore G can be written as

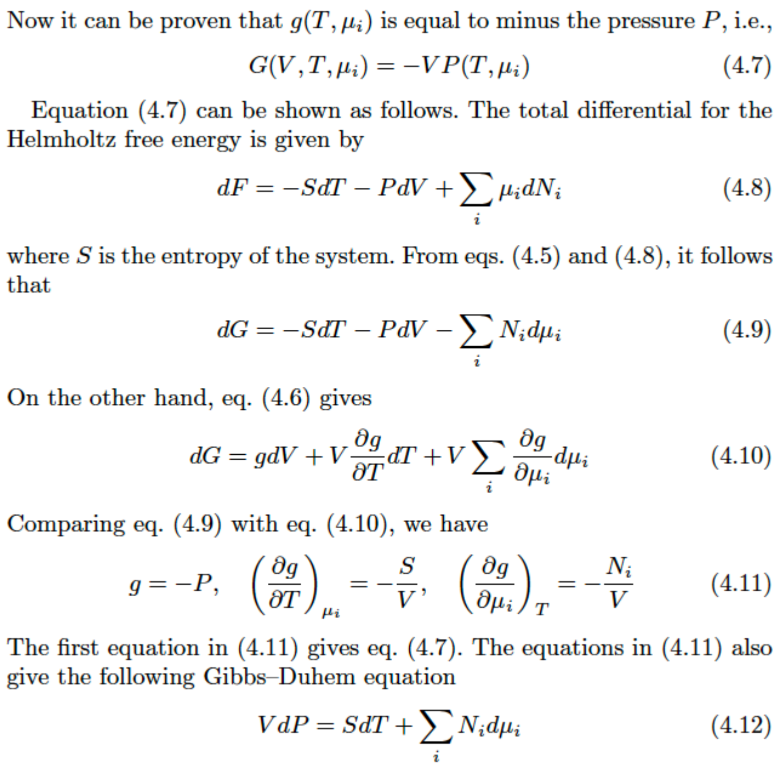
$$G(V,T,\mu_i) = Vg(T,\mu_i) \tag{4.6}$$



Gibbs-Duhem equation

$$VdP = SdT + \sum_i N_i d\mu_i$$





Now it can be proven that $g(T, \mu_i)$ is equal to minus the pressure P, i.e.,

$$G(V, T, \mu_i) = -VP(T, \mu_i) \tag{4.7}$$

Equation (4.7) can be shown as follows. The total differential for the Helmholtz free energy is given by

$$dF = -SdT - PdV + \sum_i \mu_i dN_i \tag{4.8}$$

where S is the entropy of the system. From eqs. (4.5) and (4.8), it follows that

$$dG = -SdT - PdV - \sum_i N_i d\mu_i \tag{4.9}$$

On the other hand, eq. (4.6) gives

$$dG = gdV + V\frac{\partial g}{\partial T}dT + V\sum_i \frac{\partial g}{\partial \mu_i}d\mu_i \tag{4.10}$$

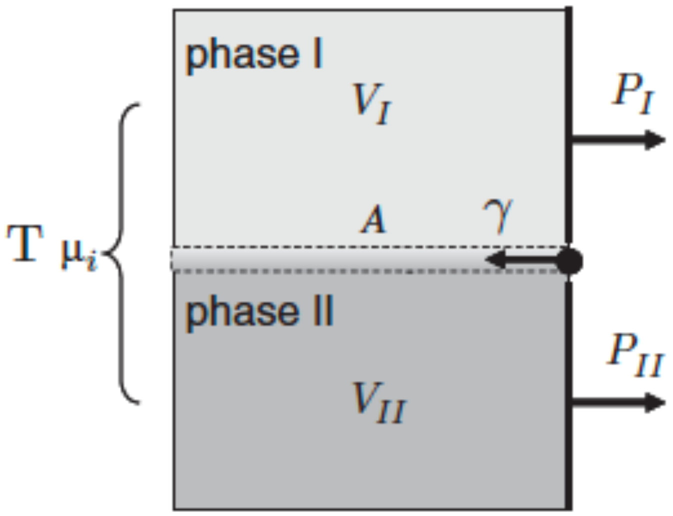
Comparing eq. (4.9) with eq. (4.10), we have

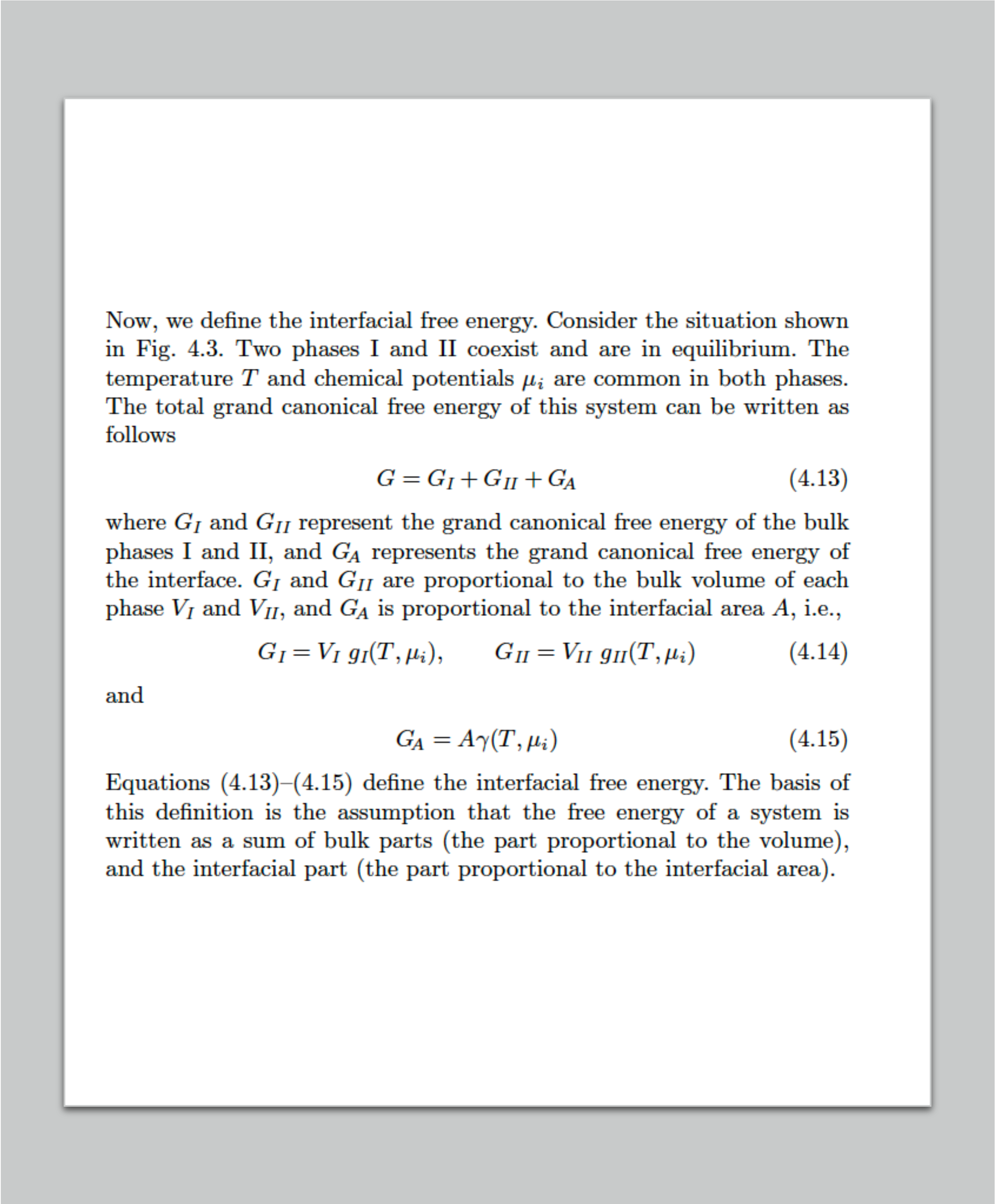
$$g = -P, \quad \left(\frac{\partial g}{\partial T}\right)_{\mu_i} = -\frac{S}{V}, \quad \left(\frac{\partial g}{\partial \mu_i}\right)_T = -\frac{N_i}{V} \tag{4.11}$$

The first equation in (4.11) gives eq. (4.7). The equations in (4.11) also give the following Gibbs–Duhem equation

$$VdP = SdT + \sum_i N_i d\mu_i \tag{4.12}$$

Interfacial free energy





Now, we define the interfacial free energy. Consider the situation shown in Fig. 4.3. Two phases I and II coexist and are in equilibrium. The temperature T and chemical potentials μ_i are common in both phases. The total grand canonical free energy of this system can be written as follows

$$G = G_I + G_{II} + G_A \tag{4.13}$$

where G_I and G_{II} represent the grand canonical free energy of the bulk phases I and II, and G_A represents the grand canonical free energy of the interface. G_I and G_{II} are proportional to the bulk volume of each phase V_I and V_{II}, and G_A is proportional to the interfacial area A, i.e.,

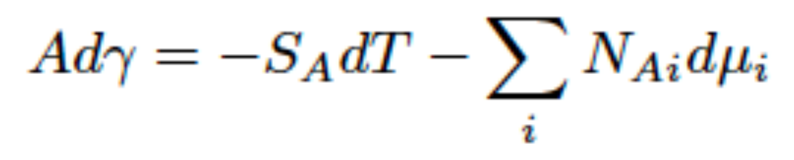
$$G_I = V_I\, g_I(T, \mu_i), \qquad G_{II} = V_{II}\, g_{II}(T, \mu_i) \tag{4.14}$$

and

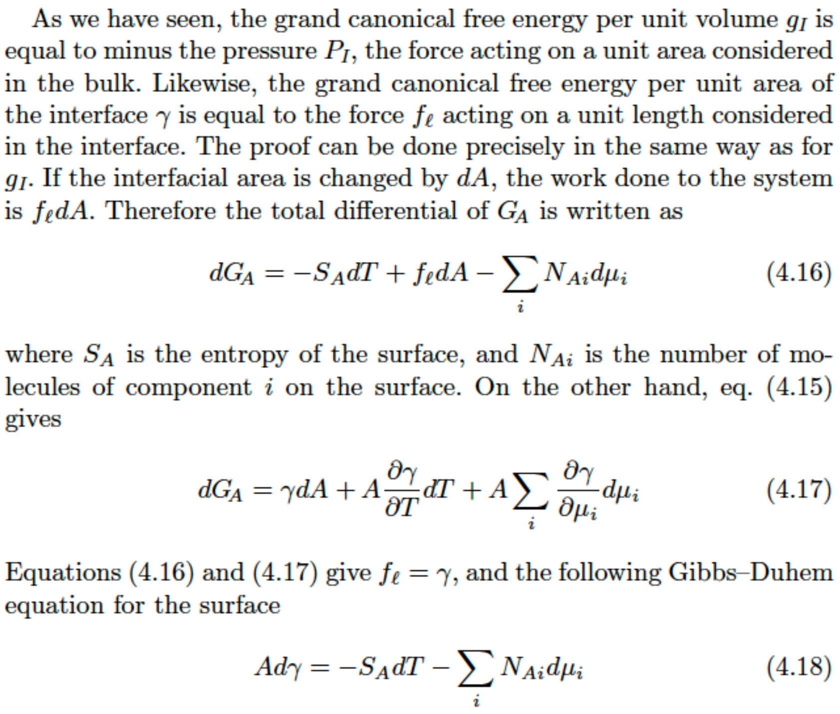
$$G_A = A\gamma(T, \mu_i) \tag{4.15}$$

Equations (4.13)–(4.15) define the interfacial free energy. The basis of this definition is the assumption that the free energy of a system is written as a sum of bulk parts (the part proportional to the volume), and the interfacial part (the part proportional to the interfacial area).

Gibbs-Duhem equation for the surface



$$A d\gamma = -S_A dT - \sum_i N_{Ai} d\mu_i$$



As we have seen, the grand canonical free energy per unit volume g_I is equal to minus the pressure P_I, the force acting on a unit area considered in the bulk. Likewise, the grand canonical free energy per unit area of the interface γ is equal to the force f_ℓ acting on a unit length considered in the interface. The proof can be done precisely in the same way as for g_I. If the interfacial area is changed by dA, the work done to the system is $f_\ell dA$. Therefore the total differential of G_A is written as

$$dG_A = -S_A dT + f_\ell dA - \sum_i N_{Ai} d\mu_i \qquad (4.16)$$

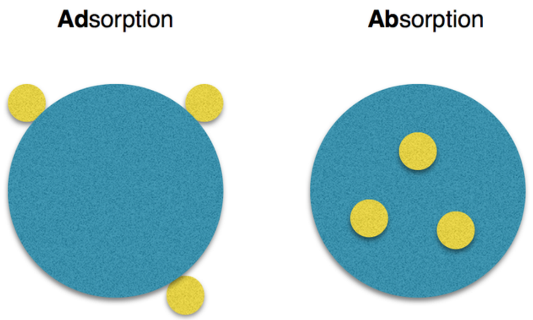
where S_A is the entropy of the surface, and N_{Ai} is the number of molecules of component i on the surface. On the other hand, eq. (4.15) gives

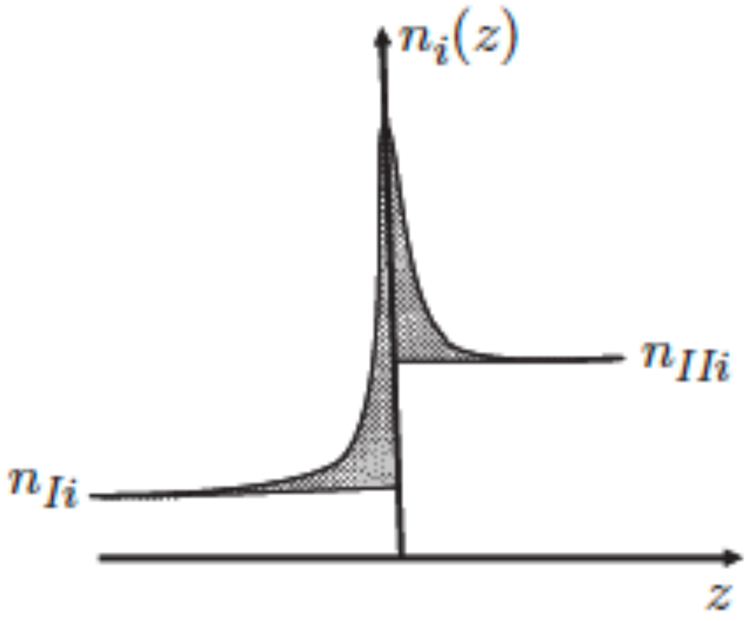
$$dG_A = \gamma dA + A\frac{\partial \gamma}{\partial T} dT + A \sum_i \frac{\partial \gamma}{\partial \mu_i} d\mu_i \qquad (4.17)$$

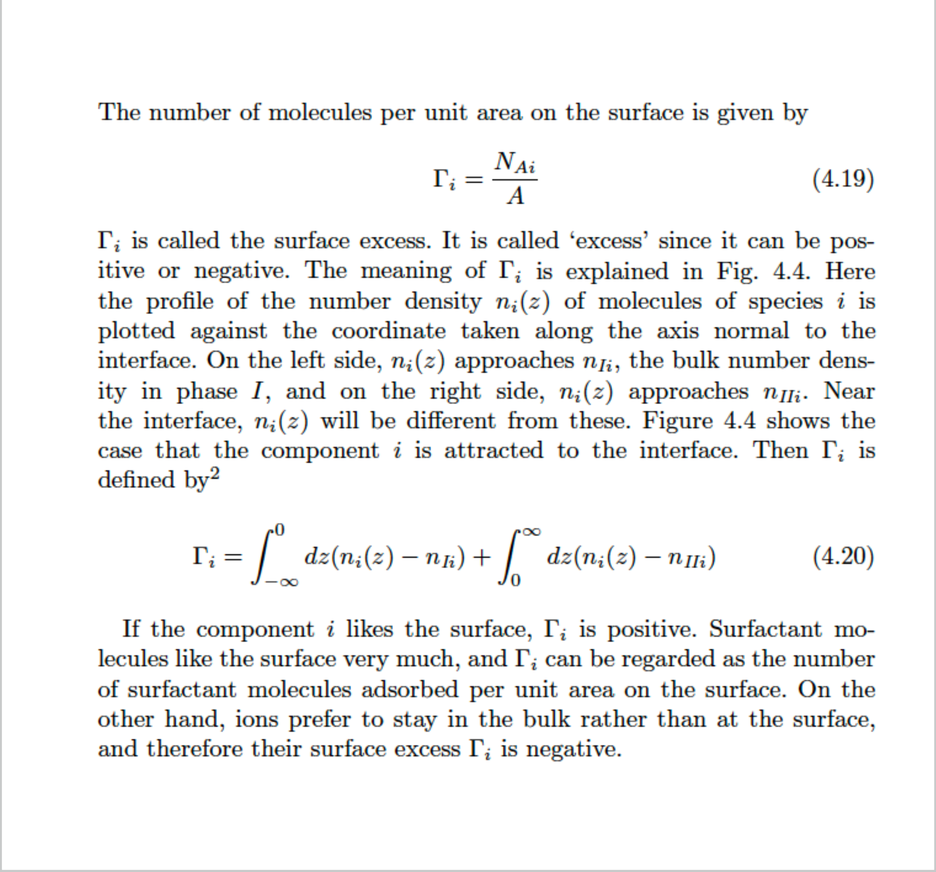
Equations (4.16) and (4.17) give $f_\ell = \gamma$, and the following Gibbs–Duhem equation for the surface

$$A d\gamma = -S_A dT - \sum_i N_{Ai} d\mu_i \qquad (4.18)$$

Surface excess







The number of molecules per unit area on the surface is given by

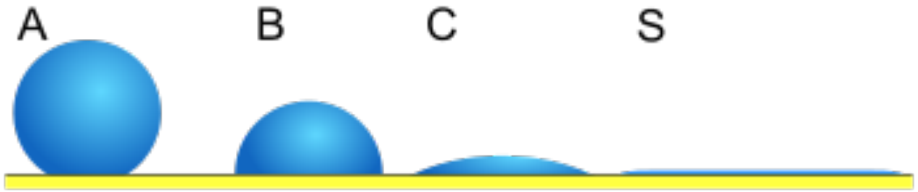
$$\Gamma_i = \frac{N_{Ai}}{A} \tag{4.19}$$

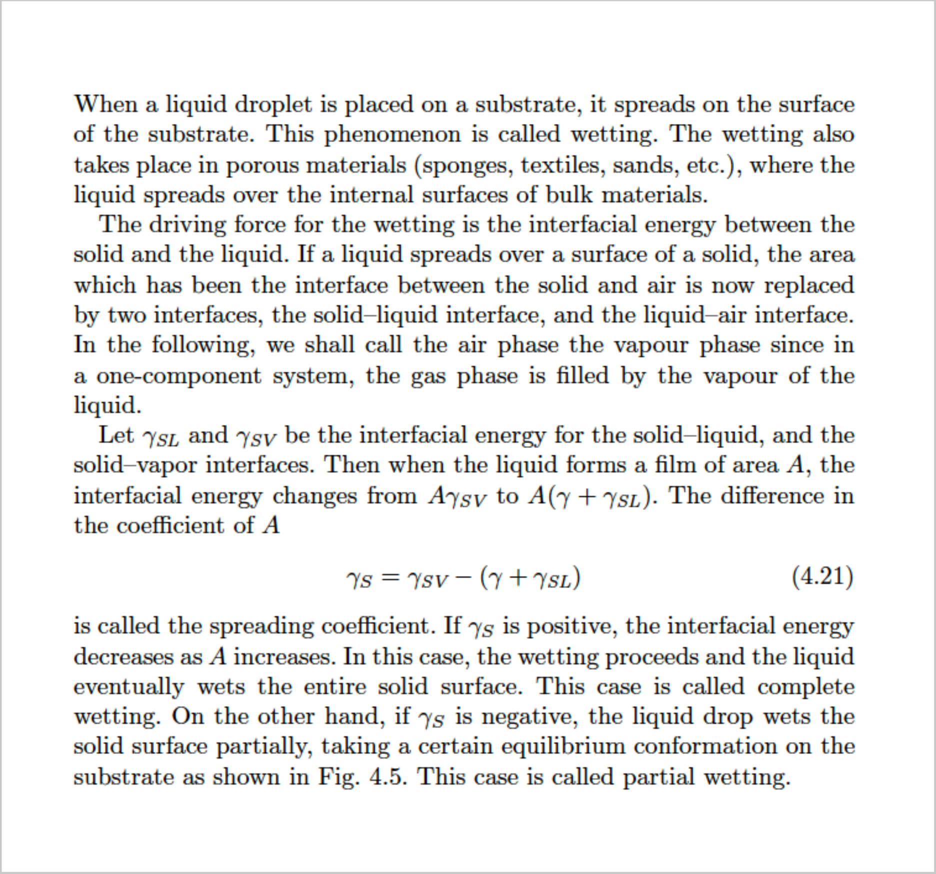
Γ_i is called the surface excess. It is called 'excess' since it can be positive or negative. The meaning of Γ_i is explained in Fig. 4.4. Here the profile of the number density $n_i(z)$ of molecules of species i is plotted against the coordinate taken along the axis normal to the interface. On the left side, $n_i(z)$ approaches n_{Ii}, the bulk number density in phase I, and on the right side, $n_i(z)$ approaches n_{IIi}. Near the interface, $n_i(z)$ will be different from these. Figure 4.4 shows the case that the component i is attracted to the interface. Then Γ_i is defined by[2]

$$\Gamma_i = \int_{-\infty}^{0} dz(n_i(z) - n_{Ii}) + \int_{0}^{\infty} dz(n_i(z) - n_{IIi}) \tag{4.20}$$

If the component i likes the surface, Γ_i is positive. Surfactant molecules like the surface very much, and Γ_i can be regarded as the number of surfactant molecules adsorbed per unit area on the surface. On the other hand, ions prefer to stay in the bulk rather than at the surface, and therefore their surface excess Γ_i is negative.

Wetting





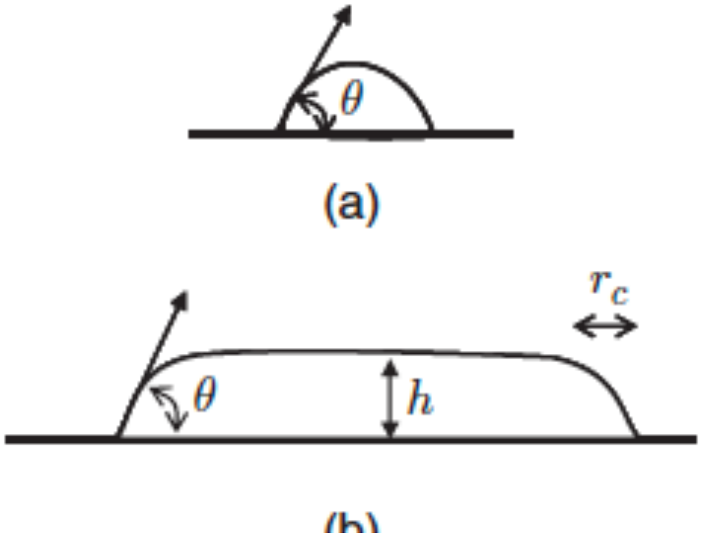
When a liquid droplet is placed on a substrate, it spreads on the surface of the substrate. This phenomenon is called wetting. The wetting also takes place in porous materials (sponges, textiles, sands, etc.), where the liquid spreads over the internal surfaces of bulk materials.

The driving force for the wetting is the interfacial energy between the solid and the liquid. If a liquid spreads over a surface of a solid, the area which has been the interface between the solid and air is now replaced by two interfaces, the solid–liquid interface, and the liquid–air interface. In the following, we shall call the air phase the vapour phase since in a one-component system, the gas phase is filled by the vapour of the liquid.

Let γ_{SL} and γ_{SV} be the interfacial energy for the solid–liquid, and the solid–vapor interfaces. Then when the liquid forms a film of area A, the interfacial energy changes from $A\gamma_{SV}$ to $A(\gamma + \gamma_{SL})$. The difference in the coefficient of A

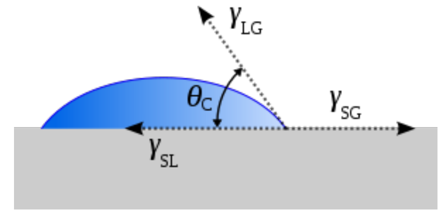
$$\gamma_S = \gamma_{SV} - (\gamma + \gamma_{SL}) \tag{4.21}$$

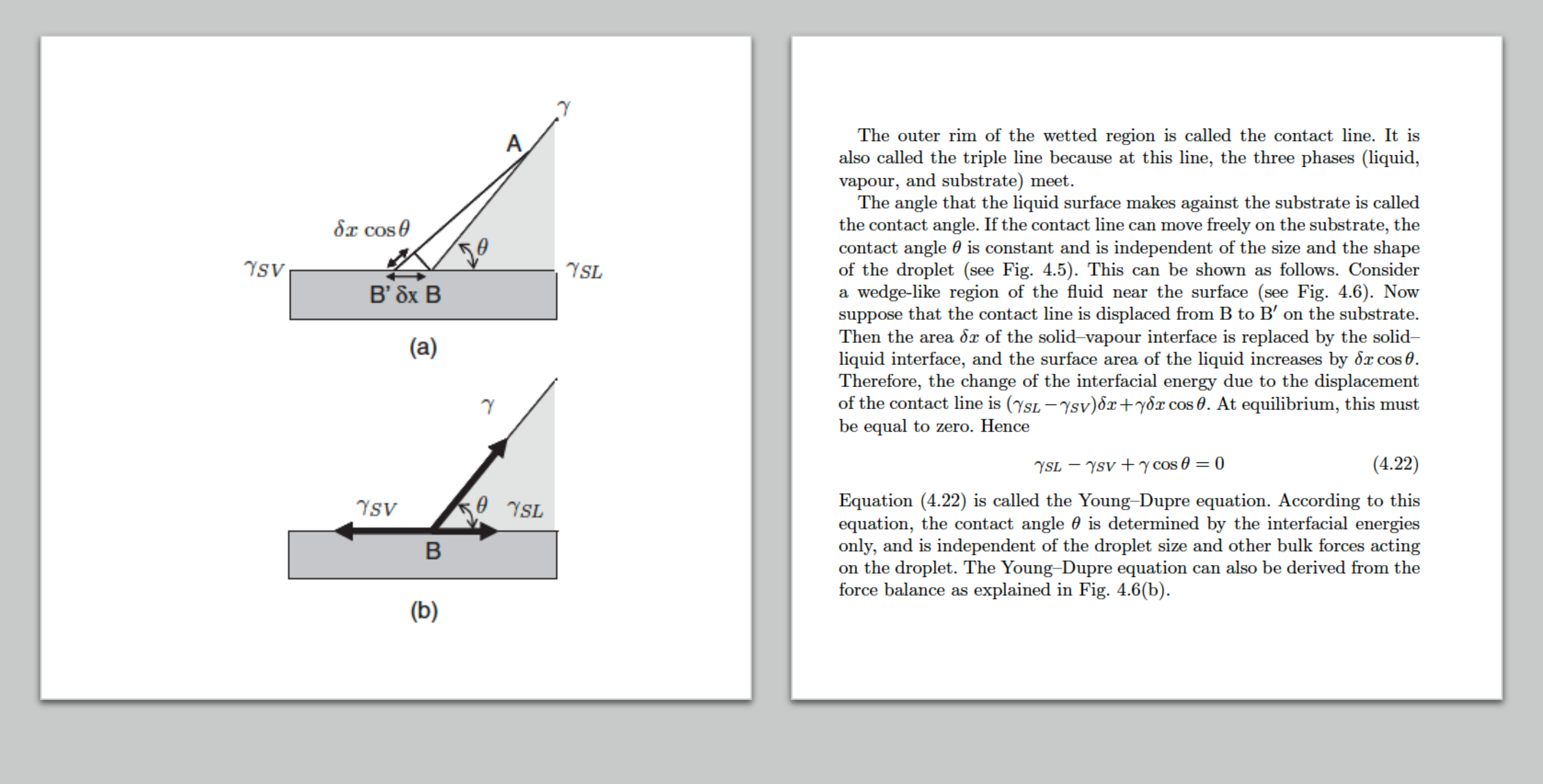
is called the spreading coefficient. If γ_S is positive, the interfacial energy decreases as A increases. In this case, the wetting proceeds and the liquid eventually wets the entire solid surface. This case is called complete wetting. On the other hand, if γ_S is negative, the liquid drop wets the solid surface partially, taking a certain equilibrium conformation on the substrate as shown in Fig. 4.5. This case is called partial wetting.



Young’s equation

$$\gamma_{SL} - \gamma_{SV} + \gamma \cos\theta = 0$$





The outer rim of the wetted region is called the contact line. It is also called the triple line because at this line, the three phases (liquid, vapour, and substrate) meet.

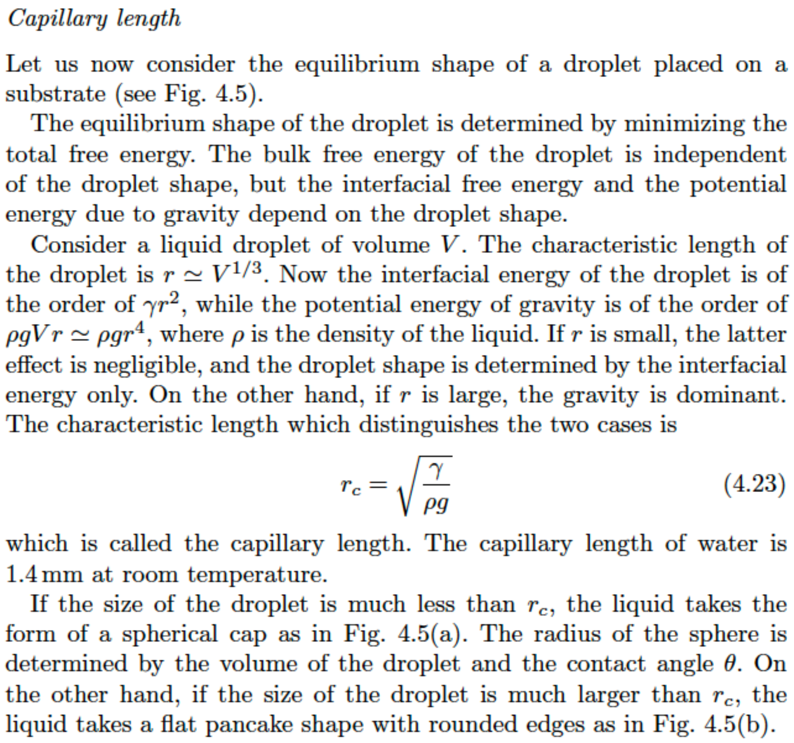
The angle that the liquid surface makes against the substrate is called the contact angle. If the contact line can move freely on the substrate, the contact angle θ is constant and is independent of the size and the shape of the droplet (see Fig. 4.5). This can be shown as follows. Consider a wedge-like region of the fluid near the surface (see Fig. 4.6). Now suppose that the contact line is displaced from B to B$'$ on the substrate. Then the area δx of the solid–vapour interface is replaced by the solid–liquid interface, and the surface area of the liquid increases by $\delta x \cos\theta$. Therefore, the change of the interfacial energy due to the displacement of the contact line is $(\gamma_{SL} - \gamma_{SV})\delta x + \gamma \delta x \cos\theta$. At equilibrium, this must be equal to zero. Hence

$$\gamma_{SL} - \gamma_{SV} + \gamma \cos\theta = 0 \tag{4.22}$$

Equation (4.22) is called the Young–Dupre equation. According to this equation, the contact angle θ is determined by the interfacial energies only, and is independent of the droplet size and other bulk forces acting on the droplet. The Young–Dupre equation can also be derived from the force balance as explained in Fig. 4.6(b).

Capillary length

$$r_c = \sqrt{\frac{\gamma}{\rho g}}$$



Capillary length

Let us now consider the equilibrium shape of a droplet placed on a substrate (see Fig. 4.5).

The equilibrium shape of the droplet is determined by minimizing the total free energy. The bulk free energy of the droplet is independent of the droplet shape, but the interfacial free energy and the potential energy due to gravity depend on the droplet shape.

Consider a liquid droplet of volume V. The characteristic length of the droplet is $r \simeq V^{1/3}$. Now the interfacial energy of the droplet is of the order of γr^2, while the potential energy of gravity is of the order of $\rho g V r \simeq \rho g r^4$, where ρ is the density of the liquid. If r is small, the latter effect is negligible, and the droplet shape is determined by the interfacial energy only. On the other hand, if r is large, the gravity is dominant. The characteristic length which distinguishes the two cases is

$$r_c = \sqrt{\frac{\gamma}{\rho g}} \tag{4.23}$$

which is called the capillary length. The capillary length of water is 1.4 mm at room temperature.

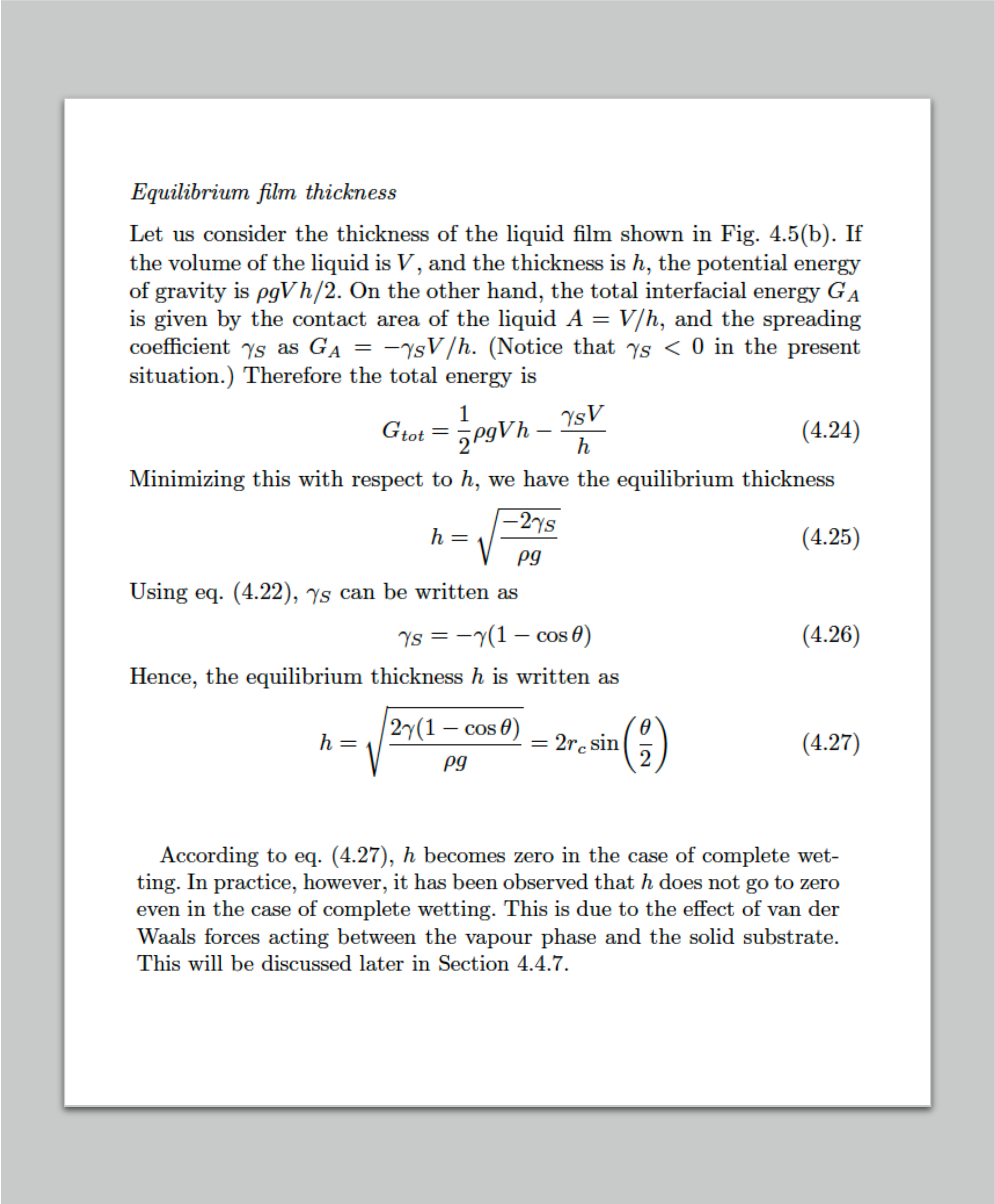
If the size of the droplet is much less than r_c, the liquid takes the form of a spherical cap as in Fig. 4.5(a). The radius of the sphere is determined by the volume of the droplet and the contact angle θ. On the other hand, if the size of the droplet is much larger than r_c, the liquid takes a flat pancake shape with rounded edges as in Fig. 4.5(b).

The capillary length will vary for different liquids and different conditions. Here is a picture of a water droplet on a lotus leaf.

Film thickness

(b)

$$h = \sqrt{\frac{2\gamma(1-\cos\theta)}{\rho g}} = 2r_c \sin\left(\frac{\theta}{2}\right)$$



Equilibrium film thickness

Let us consider the thickness of the liquid film shown in Fig. 4.5(b). If the volume of the liquid is V, and the thickness is h, the potential energy of gravity is $\rho gVh/2$. On the other hand, the total interfacial energy G_A is given by the contact area of the liquid $A = V/h$, and the spreading coefficient γ_S as $G_A = -\gamma_S V/h$. (Notice that $\gamma_S < 0$ in the present situation.) Therefore the total energy is

$$G_{tot} = \frac{1}{2}\rho gVh - \frac{\gamma_S V}{h} \tag{4.24}$$

Minimizing this with respect to h, we have the equilibrium thickness

$$h = \sqrt{\frac{-2\gamma_S}{\rho g}} \tag{4.25}$$

Using eq. (4.22), γ_S can be written as

$$\gamma_S = -\gamma(1-\cos\theta) \tag{4.26}$$

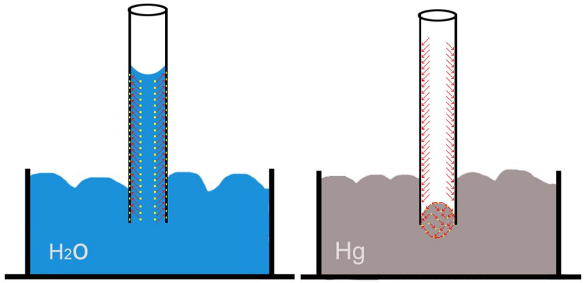
Hence, the equilibrium thickness h is written as

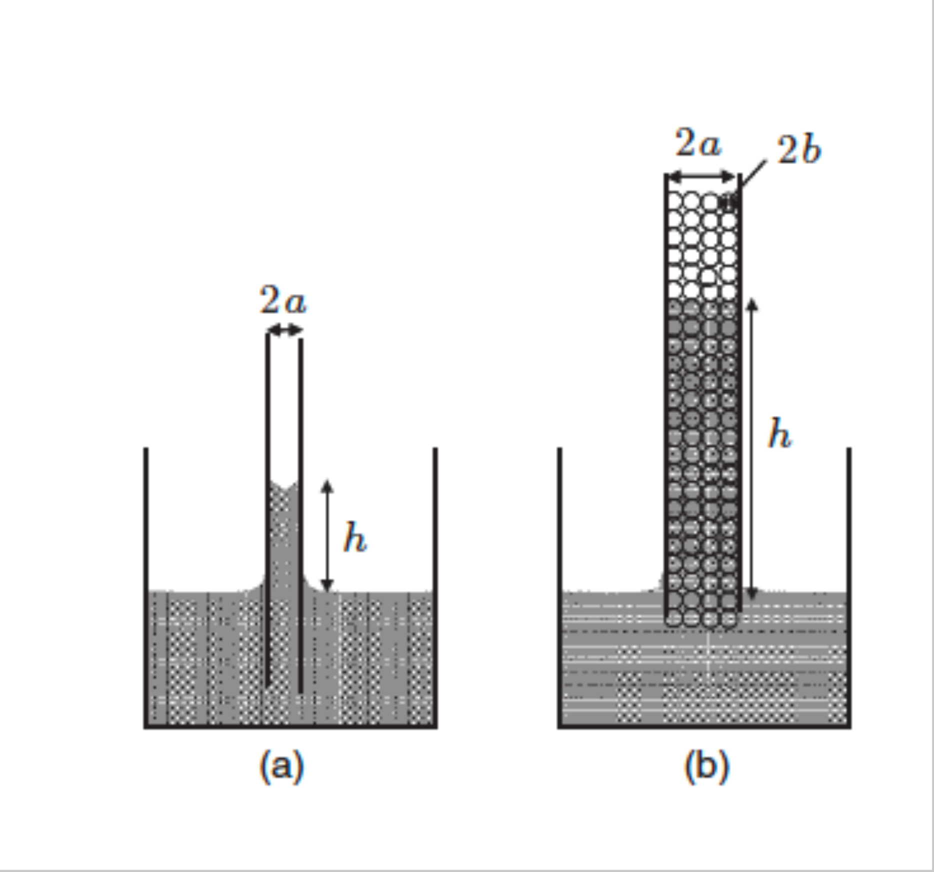
$$h = \sqrt{\frac{2\gamma(1-\cos\theta)}{\rho g}} = 2r_c \sin\left(\frac{\theta}{2}\right) \tag{4.27}$$

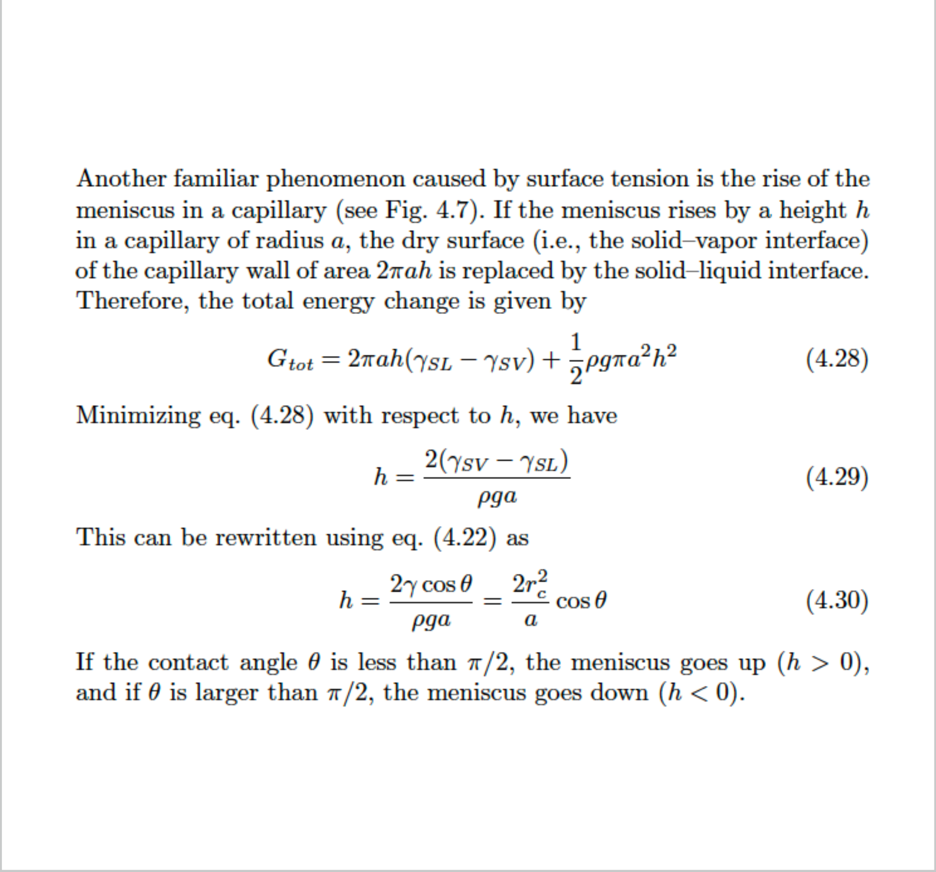
According to eq. (4.27), h becomes zero in the case of complete wetting. In practice, however, it has been observed that h does not go to zero even in the case of complete wetting. This is due to the effect of van der Waals forces acting between the vapour phase and the solid substrate. This will be discussed later in Section 4.4.7.

Capillary rise

$$h = \frac{2\gamma\cos\theta}{\rho g a}$$







Another familiar phenomenon caused by surface tension is the rise of the meniscus in a capillary (see Fig. 4.7). If the meniscus rises by a height h in a capillary of radius a, the dry surface (i.e., the solid–vapor interface) of the capillary wall of area $2\pi a h$ is replaced by the solid–liquid interface. Therefore, the total energy change is given by

$$G_{tot} = 2\pi a h(\gamma_{SL} - \gamma_{SV}) + \frac{1}{2}\rho g \pi a^2 h^2 \qquad (4.28)$$

Minimizing eq. (4.28) with respect to h, we have

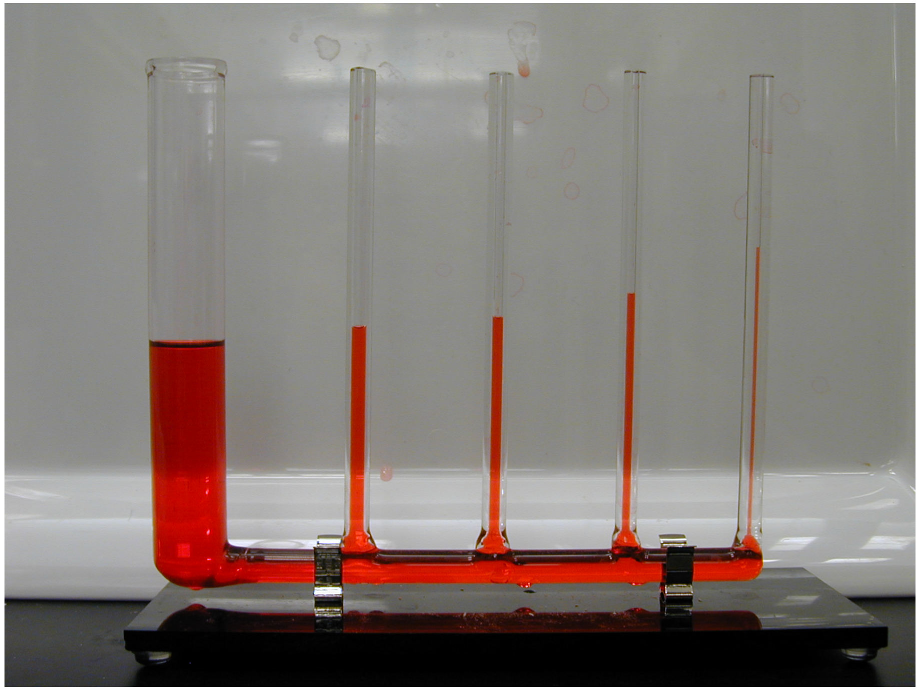
$$h = \frac{2(\gamma_{SV} - \gamma_{SL})}{\rho g a} \qquad (4.29)$$

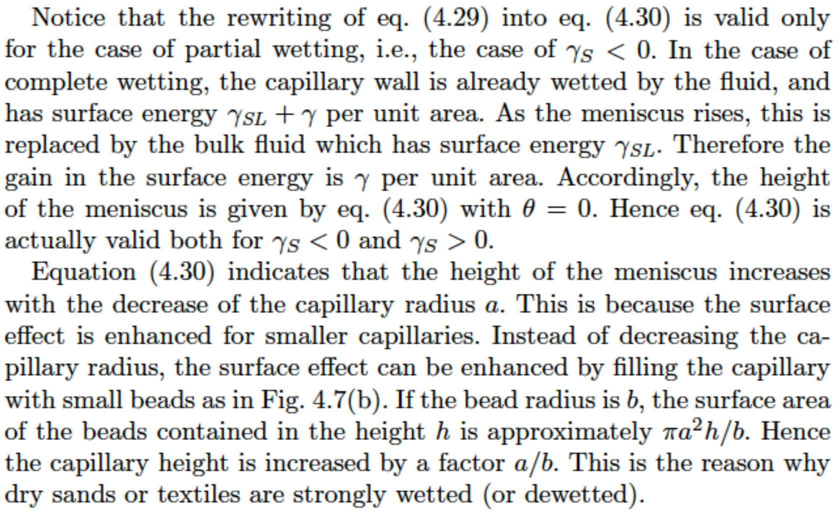
This can be rewritten using eq. (4.22) as

$$h = \frac{2\gamma\cos\theta}{\rho g a} = \frac{2r_c^2}{a}\cos\theta \qquad (4.30)$$

If the contact angle θ is less than $\pi/2$, the meniscus goes up ($h > 0$), and if θ is larger than $\pi/2$, the meniscus goes down ($h < 0$).

Effect of the capillary radius





Notice that the rewriting of eq. (4.29) into eq. (4.30) is valid only for the case of partial wetting, i.e., the case of $\gamma_S < 0$. In the case of complete wetting, the capillary wall is already wetted by the fluid, and has surface energy $\gamma_{SL} + \gamma$ per unit area. As the meniscus rises, this is replaced by the bulk fluid which has surface energy γ_{SL}. Therefore the gain in the surface energy is γ per unit area. Accordingly, the height of the meniscus is given by eq. (4.30) with $\theta = 0$. Hence eq. (4.30) is actually valid both for $\gamma_S < 0$ and $\gamma_S > 0$.

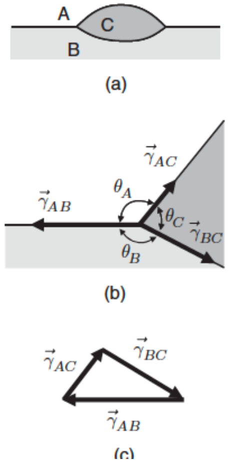
Equation (4.30) indicates that the height of the meniscus increases with the decrease of the capillary radius a. This is because the surface effect is enhanced for smaller capillaries. Instead of decreasing the capillary radius, the surface effect can be enhanced by filling the capillary with small beads as in Fig. 4.7(b). If the bead radius is b, the surface area of the beads contained in the height h is approximately $\pi a^2 h/b$. Hence the capillary height is increased by a factor a/b. This is the reason why dry sands or textiles are strongly wetted (or dewetted).

Liquid droplet on liquid

(a) Oil droplet placed on the surface of water.

(b) The contact angles around the triple line of three phases A, B, and C.

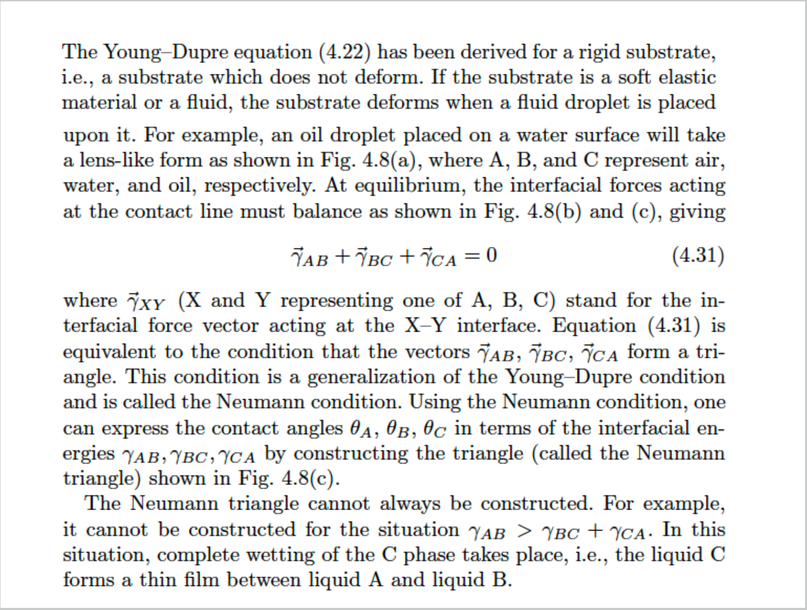
(c) The Neumann triangle representing the force balance at the triple line.



(a)

(b)

(c)



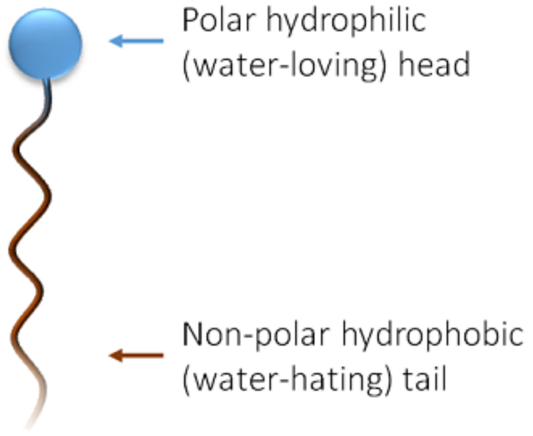
The Young–Dupre equation (4.22) has been derived for a rigid substrate, i.e., a substrate which does not deform. If the substrate is a soft elastic material or a fluid, the substrate deforms when a fluid droplet is placed upon it. For example, an oil droplet placed on a water surface will take a lens-like form as shown in Fig. 4.8(a), where A, B, and C represent air, water, and oil, respectively. At equilibrium, the interfacial forces acting at the contact line must balance as shown in Fig. 4.8(b) and (c), giving

$$\vec{\gamma}_{AB} + \vec{\gamma}_{BC} + \vec{\gamma}_{CA} = 0 \qquad (4.31)$$

where $\vec{\gamma}_{XY}$ (X and Y representing one of A, B, C) stand for the interfacial force vector acting at the X–Y interface. Equation (4.31) is equivalent to the condition that the vectors $\vec{\gamma}_{AB}$, $\vec{\gamma}_{BC}$, $\vec{\gamma}_{CA}$ form a triangle. This condition is a generalization of the Young–Dupre condition and is called the Neumann condition. Using the Neumann condition, one can express the contact angles θ_A, θ_B, θ_C in terms of the interfacial energies $\gamma_{AB}, \gamma_{BC}, \gamma_{CA}$ by constructing the triangle (called the Neumann triangle) shown in Fig. 4.8(c).

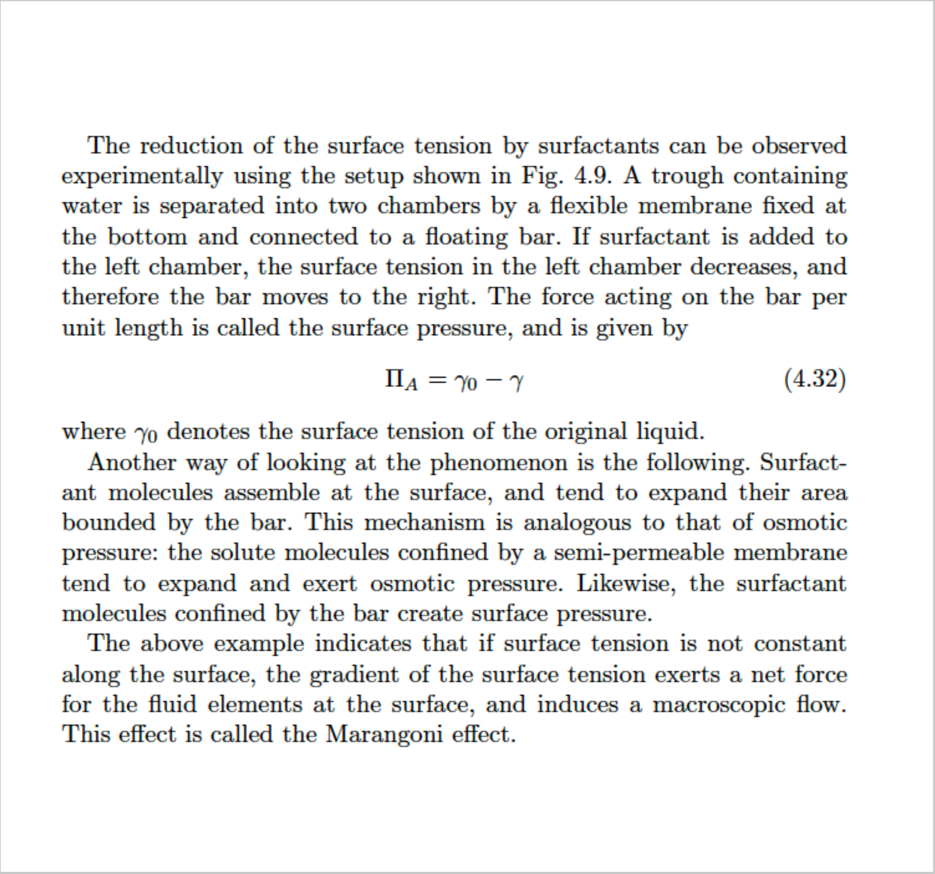
The Neumann triangle cannot always be constructed. For example, it cannot be constructed for the situation $\gamma_{AB} > \gamma_{BC} + \gamma_{CA}$. In this situation, complete wetting of the C phase takes place, i.e., the liquid C forms a thin film between liquid A and liquid B.

Surfactants



Polar hydrophilic (water-loving) head

Non-polar hydrophobic (water-hating) tail



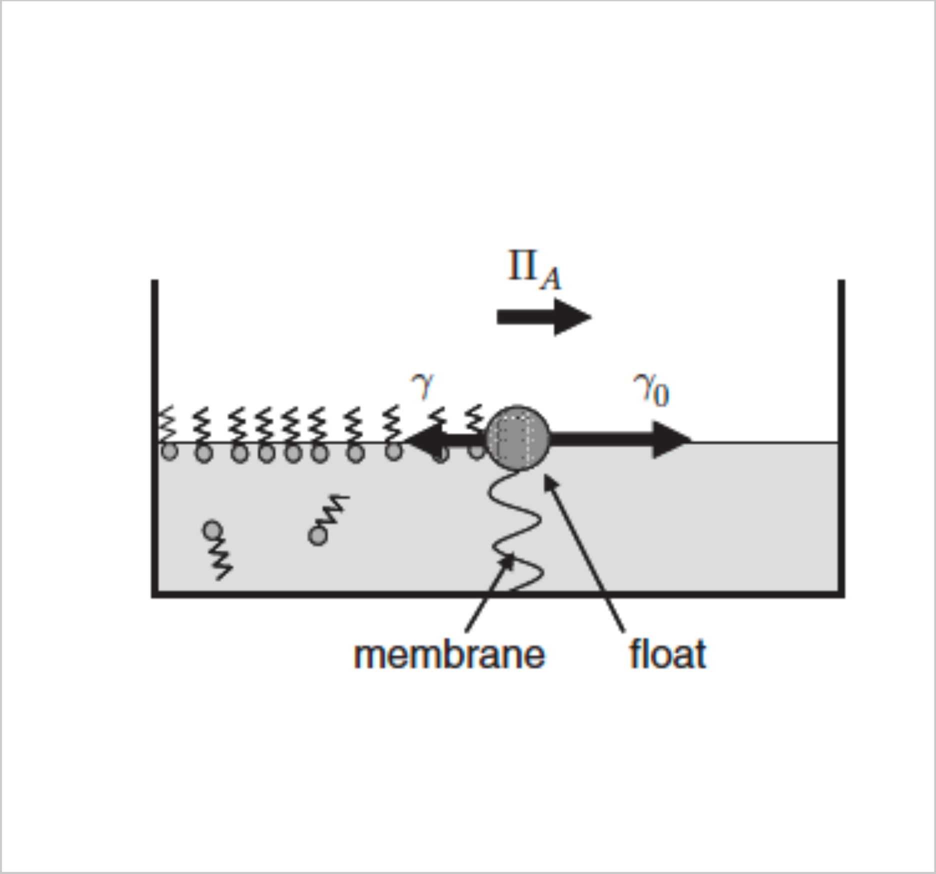
The reduction of the surface tension by surfactants can be observed experimentally using the setup shown in Fig. 4.9. A trough containing water is separated into two chambers by a flexible membrane fixed at the bottom and connected to a floating bar. If surfactant is added to the left chamber, the surface tension in the left chamber decreases, and therefore the bar moves to the right. The force acting on the bar per unit length is called the surface pressure, and is given by

$$\Pi_A = \gamma_0 - \gamma \tag{4.32}$$

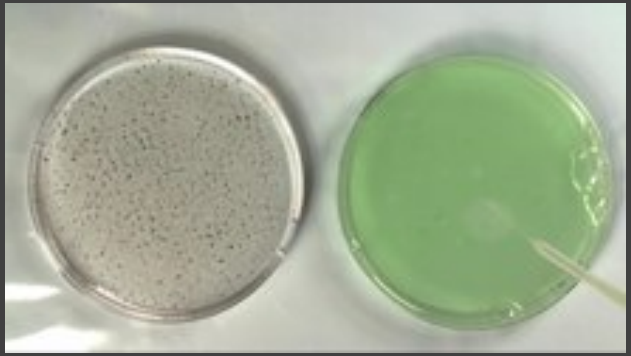
where γ_0 denotes the surface tension of the original liquid.

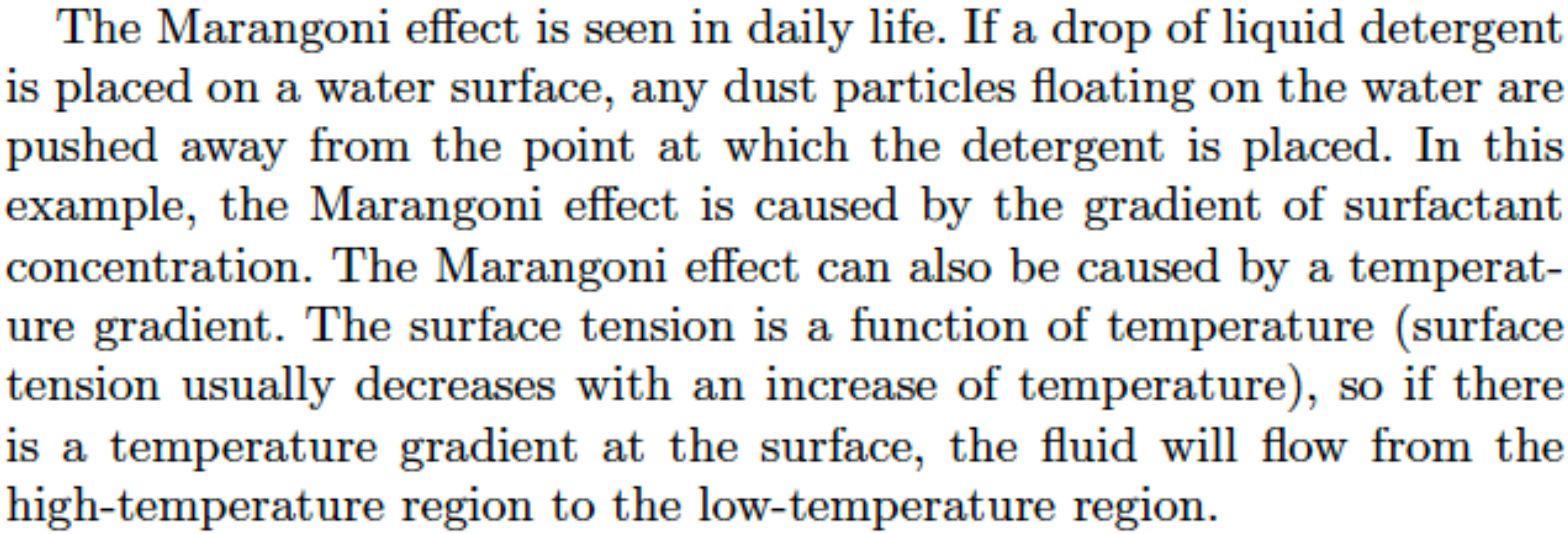
Another way of looking at the phenomenon is the following. Surfactant molecules assemble at the surface, and tend to expand their area bounded by the bar. This mechanism is analogous to that of osmotic pressure: the solute molecules confined by a semi-permeable membrane tend to expand and exert osmotic pressure. Likewise, the surfactant molecules confined by the bar create surface pressure.

The above example indicates that if surface tension is not constant along the surface, the gradient of the surface tension exerts a net force for the fluid elements at the surface, and induces a macroscopic flow. This effect is called the Marangoni effect.



Marangoni effect

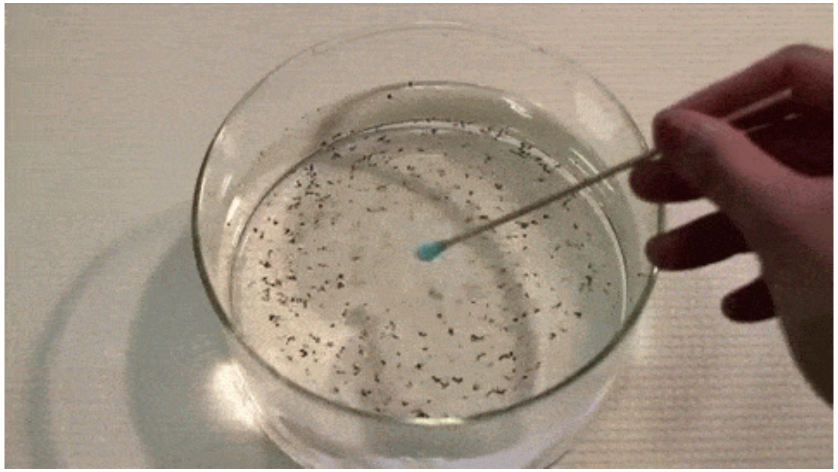


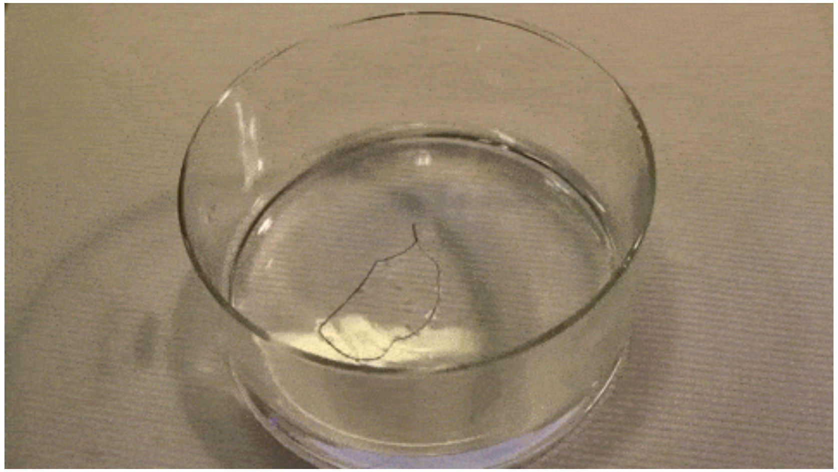


The Marangoni effect is seen in daily life. If a drop of liquid detergent is placed on a water surface, any dust particles floating on the water are pushed away from the point at which the detergent is placed. In this example, the Marangoni effect is caused by the gradient of surfactant concentration. The Marangoni effect can also be caused by a temperature gradient. The surface tension is a function of temperature (surface tension usually decreases with an increase of temperature), so if there is a temperature gradient at the surface, the fluid will flow from the high-temperature region to the low-temperature region.

Marangoni effect

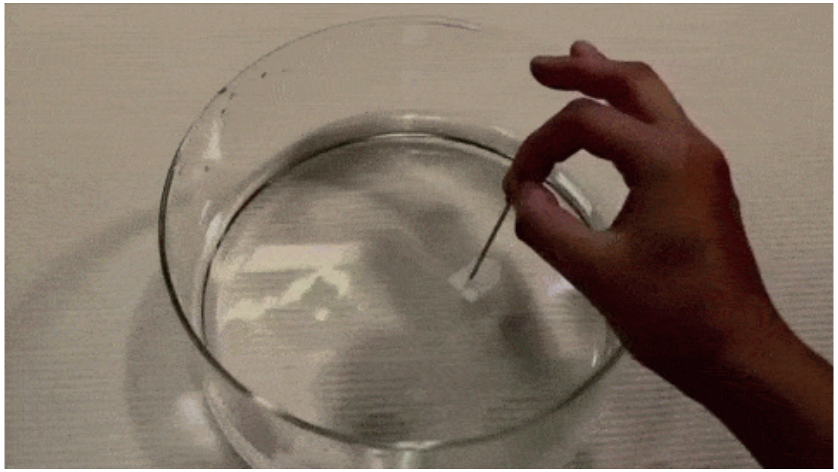
Fluid will flow from areas of lower surface tension to areas of higher surface tension. And this causes the pepper flakes to spread away and makes the string to expand.

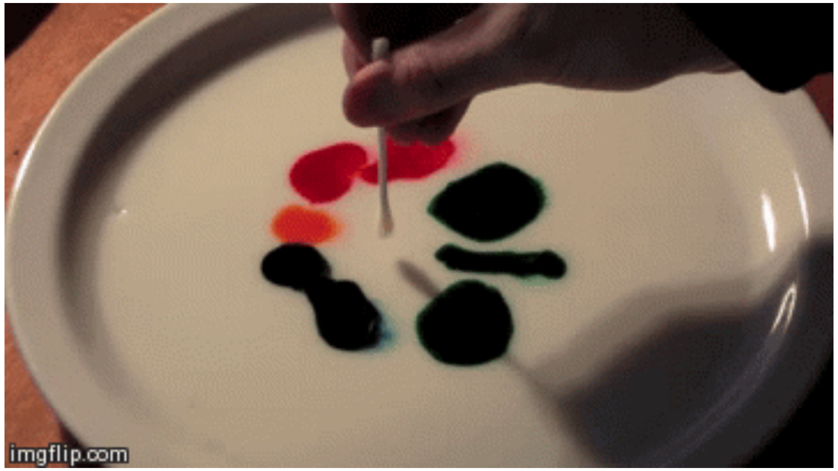




Marangoni effect

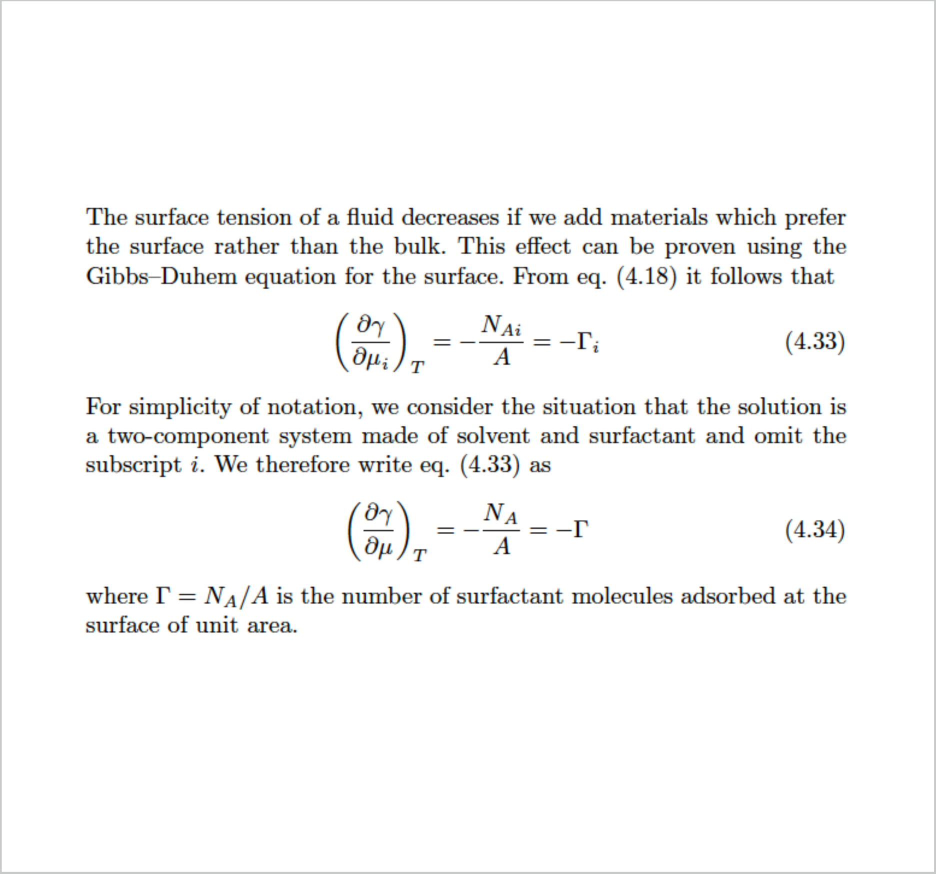
Fluid will flow from areas of lower surface tension to areas of higher surface tension. And this propels the small boat and makes the dye to fan out.





Surface adsorption
&
Langmuir equation

$$\Gamma = \frac{n\Gamma_s}{n_s + n}$$



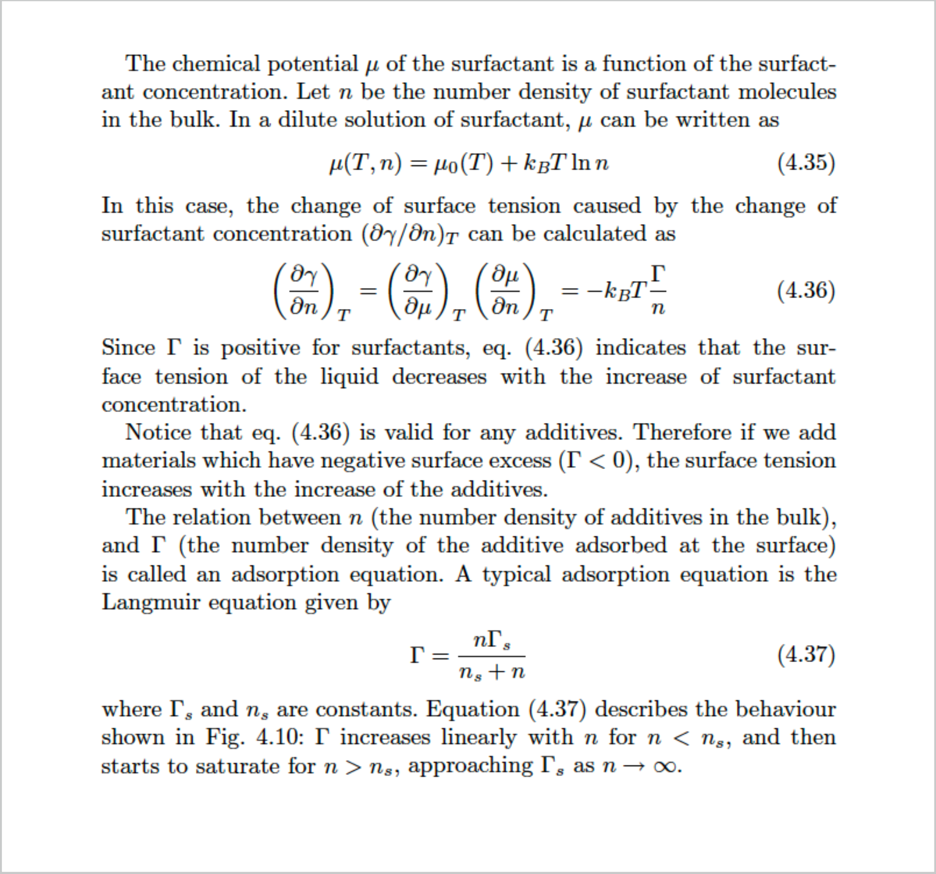
The surface tension of a fluid decreases if we add materials which prefer the surface rather than the bulk. This effect can be proven using the Gibbs–Duhem equation for the surface. From eq. (4.18) it follows that

$$\left(\frac{\partial \gamma}{\partial \mu_i}\right)_T = -\frac{N_{Ai}}{A} = -\Gamma_i \qquad (4.33)$$

For simplicity of notation, we consider the situation that the solution is a two-component system made of solvent and surfactant and omit the subscript i. We therefore write eq. (4.33) as

$$\left(\frac{\partial \gamma}{\partial \mu}\right)_T = -\frac{N_A}{A} = -\Gamma \qquad (4.34)$$

where $\Gamma = N_A/A$ is the number of surfactant molecules adsorbed at the surface of unit area.



The chemical potential μ of the surfactant is a function of the surfactant concentration. Let n be the number density of surfactant molecules in the bulk. In a dilute solution of surfactant, μ can be written as

$$\mu(T, n) = \mu_0(T) + k_B T \ln n \qquad (4.35)$$

In this case, the change of surface tension caused by the change of surfactant concentration $(\partial\gamma/\partial n)_T$ can be calculated as

$$\left(\frac{\partial \gamma}{\partial n}\right)_T = \left(\frac{\partial \gamma}{\partial \mu}\right)_T \left(\frac{\partial \mu}{\partial n}\right)_T = -k_B T \frac{\Gamma}{n} \qquad (4.36)$$

Since Γ is positive for surfactants, eq. (4.36) indicates that the surface tension of the liquid decreases with the increase of surfactant concentration.

Notice that eq. (4.36) is valid for any additives. Therefore if we add materials which have negative surface excess ($\Gamma < 0$), the surface tension increases with the increase of the additives.

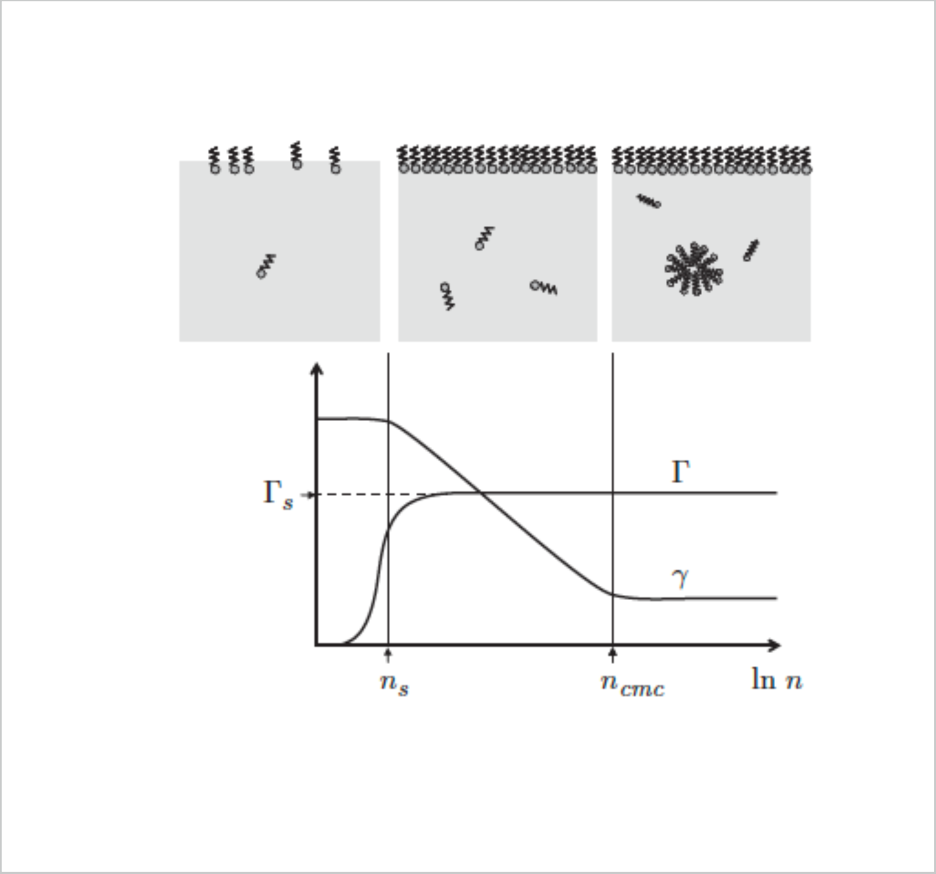
The relation between n (the number density of additives in the bulk), and Γ (the number density of the additive adsorbed at the surface) is called an adsorption equation. A typical adsorption equation is the Langmuir equation given by

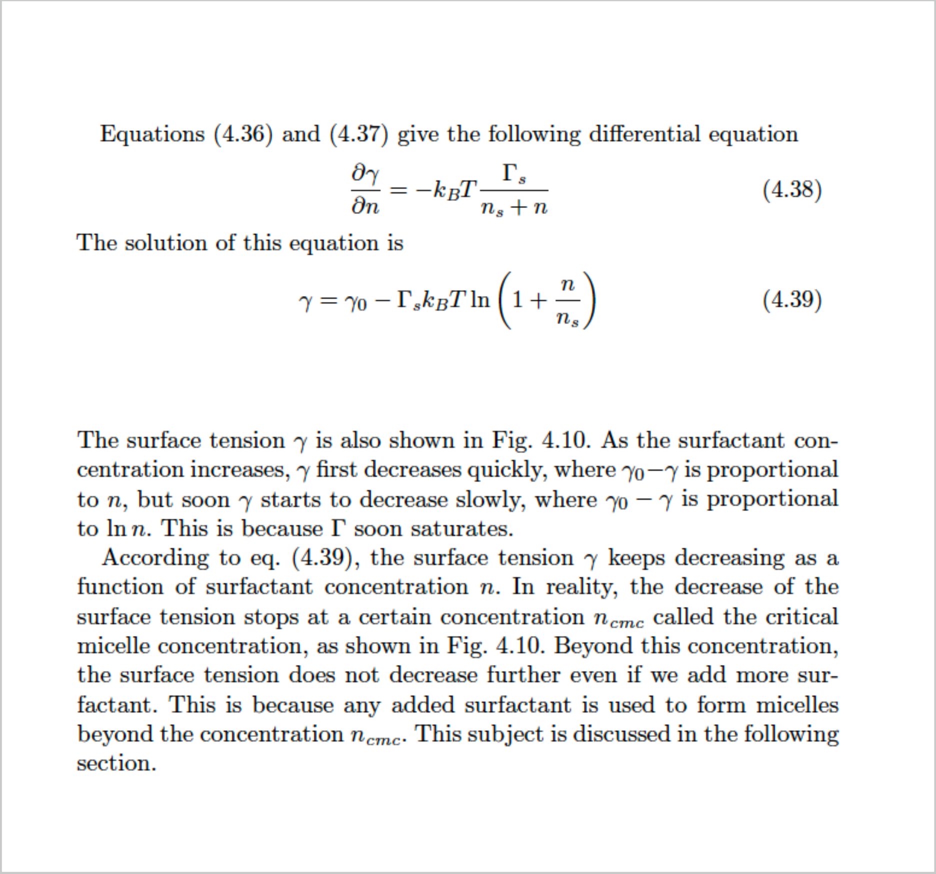
$$\Gamma = \frac{n\Gamma_s}{n_s + n} \qquad (4.37)$$

where Γ_s and n_s are constants. Equation (4.37) describes the behaviour shown in Fig. 4.10: Γ increases linearly with n for $n < n_s$, and then starts to saturate for $n > n_s$, approaching Γ_s as $n \to \infty$.

Surface tension & Langmuir equation

$$\gamma = \gamma_0 - \Gamma_s k_B T \ln\left(1 + \frac{n}{n_s}\right)$$





Equations (4.36) and (4.37) give the following differential equation

$$\frac{\partial \gamma}{\partial n} = -k_B T \frac{\Gamma_s}{n_s + n} \tag{4.38}$$

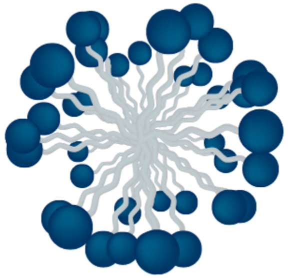
The solution of this equation is

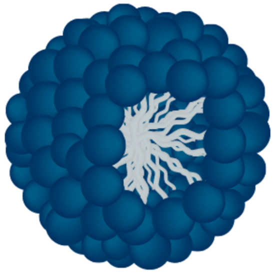
$$\gamma = \gamma_0 - \Gamma_s k_B T \ln\left(1 + \frac{n}{n_s}\right) \tag{4.39}$$

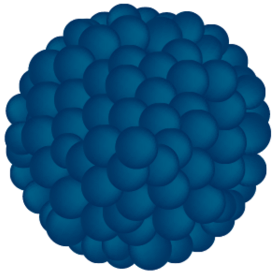
The surface tension γ is also shown in Fig. 4.10. As the surfactant concentration increases, γ first decreases quickly, where $\gamma_0 - \gamma$ is proportional to n, but soon γ starts to decrease slowly, where $\gamma_0 - \gamma$ is proportional to $\ln n$. This is because Γ soon saturates.

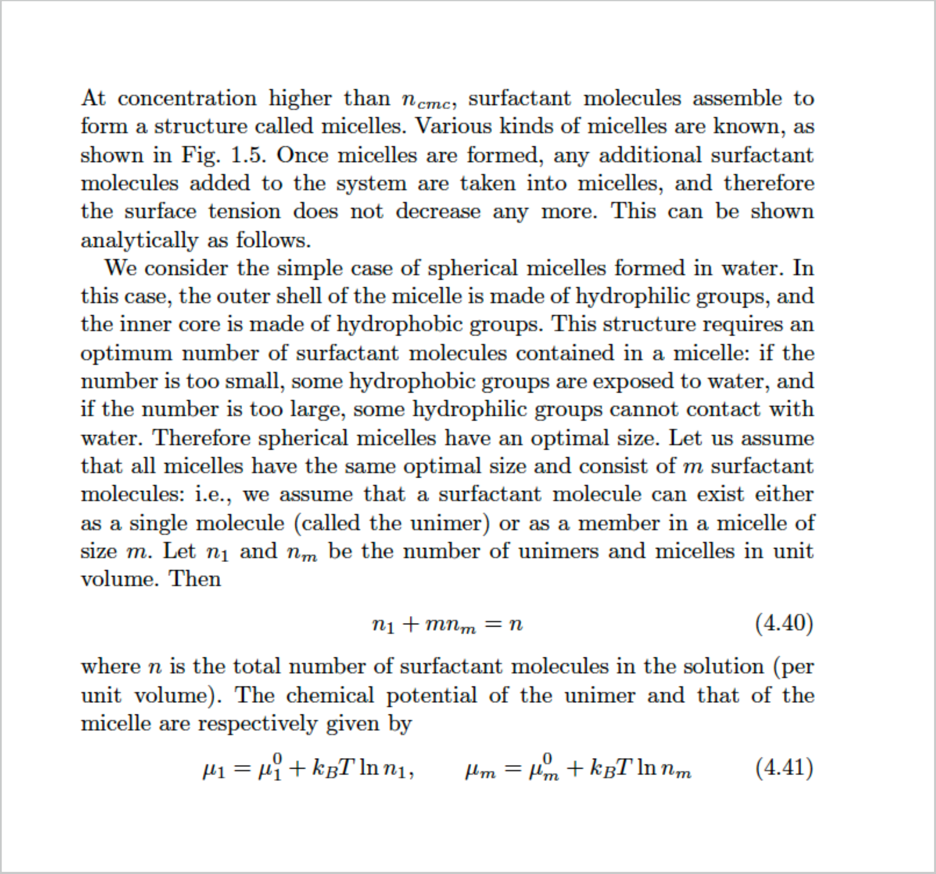
According to eq. (4.39), the surface tension γ keeps decreasing as a function of surfactant concentration n. In reality, the decrease of the surface tension stops at a certain concentration n_{cmc} called the critical micelle concentration, as shown in Fig. 4.10. Beyond this concentration, the surface tension does not decrease further even if we add more surfactant. This is because any added surfactant is used to form micelles beyond the concentration n_{cmc}. This subject is discussed in the following section.

Micelles & cmc


Profile of a micelle


Surfactant molecules complete micelle


Complete micelle

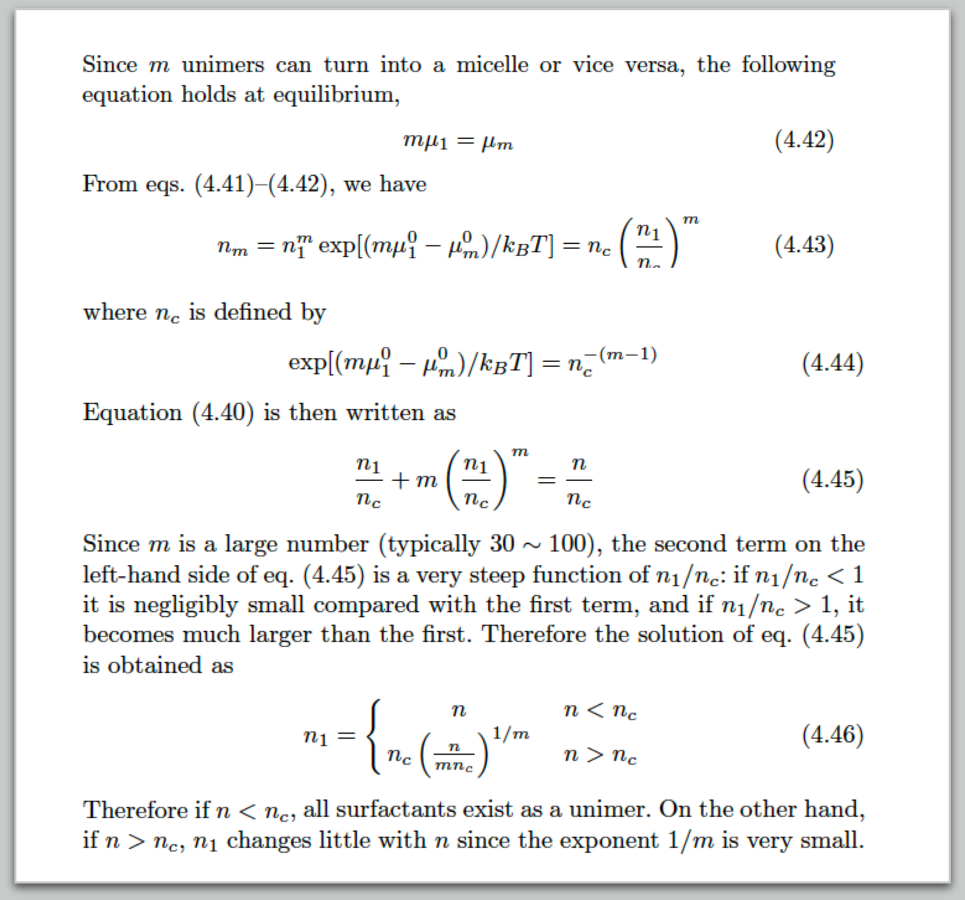

At concentration higher than n_{cmc}, surfactant molecules assemble to form a structure called micelles. Various kinds of micelles are known, as shown in Fig. 1.5. Once micelles are formed, any additional surfactant molecules added to the system are taken into micelles, and therefore the surface tension does not decrease any more. This can be shown analytically as follows.

We consider the simple case of spherical micelles formed in water. In this case, the outer shell of the micelle is made of hydrophilic groups, and the inner core is made of hydrophobic groups. This structure requires an optimum number of surfactant molecules contained in a micelle: if the number is too small, some hydrophobic groups are exposed to water, and if the number is too large, some hydrophilic groups cannot contact with water. Therefore spherical micelles have an optimal size. Let us assume that all micelles have the same optimal size and consist of m surfactant molecules: i.e., we assume that a surfactant molecule can exist either as a single molecule (called the unimer) or as a member in a micelle of size m. Let n_1 and n_m be the number of unimers and micelles in unit volume. Then

$$n_1 + mn_m = n \tag{4.40}$$

where n is the total number of surfactant molecules in the solution (per unit volume). The chemical potential of the unimer and that of the micelle are respectively given by

$$\mu_1 = \mu_1^0 + k_B T \ln n_1, \qquad \mu_m = \mu_m^0 + k_B T \ln n_m \tag{4.41}$$


Since m unimers can turn into a micelle or vice versa, the following equation holds at equilibrium,

$$m\mu_1 = \mu_m \tag{4.42}$$

From eqs. (4.41)–(4.42), we have

$$n_m = n_1^m \exp[(m\mu_1^0 - \mu_m^0)/k_B T] = n_c \left(\frac{n_1}{n_c}\right)^m \tag{4.43}$$

where n_c is defined by

$$\exp[(m\mu_1^0 - \mu_m^0)/k_B T] = n_c^{-(m-1)} \tag{4.44}$$

Equation (4.40) is then written as

$$\frac{n_1}{n_c} + m\left(\frac{n_1}{n_c}\right)^m = \frac{n}{n_c} \tag{4.45}$$

Since m is a large number (typically $30 \sim 100$), the second term on the left-hand side of eq. (4.45) is a very steep function of n_1/n_c: if $n_1/n_c < 1$ it is negligibly small compared with the first term, and if $n_1/n_c > 1$, it becomes much larger than the first. Therefore the solution of eq. (4.45) is obtained as

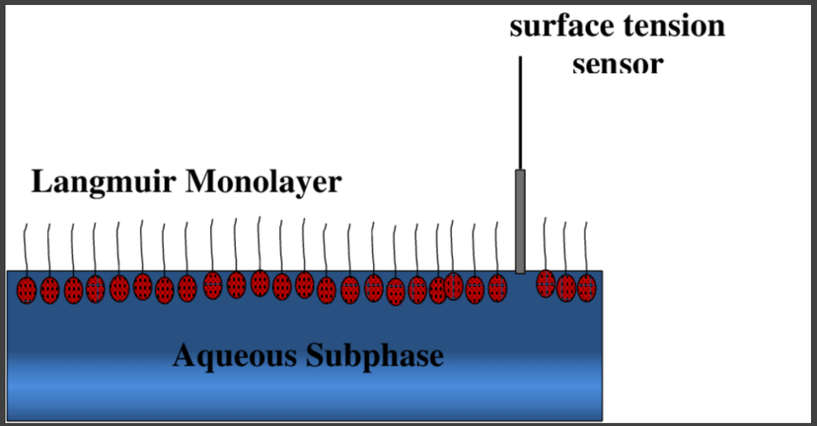
$$n_1 = \begin{cases} n & n < n_c \\ n_c \left(\frac{n}{mn_c}\right)^{1/m} & n > n_c \end{cases} \tag{4.46}$$

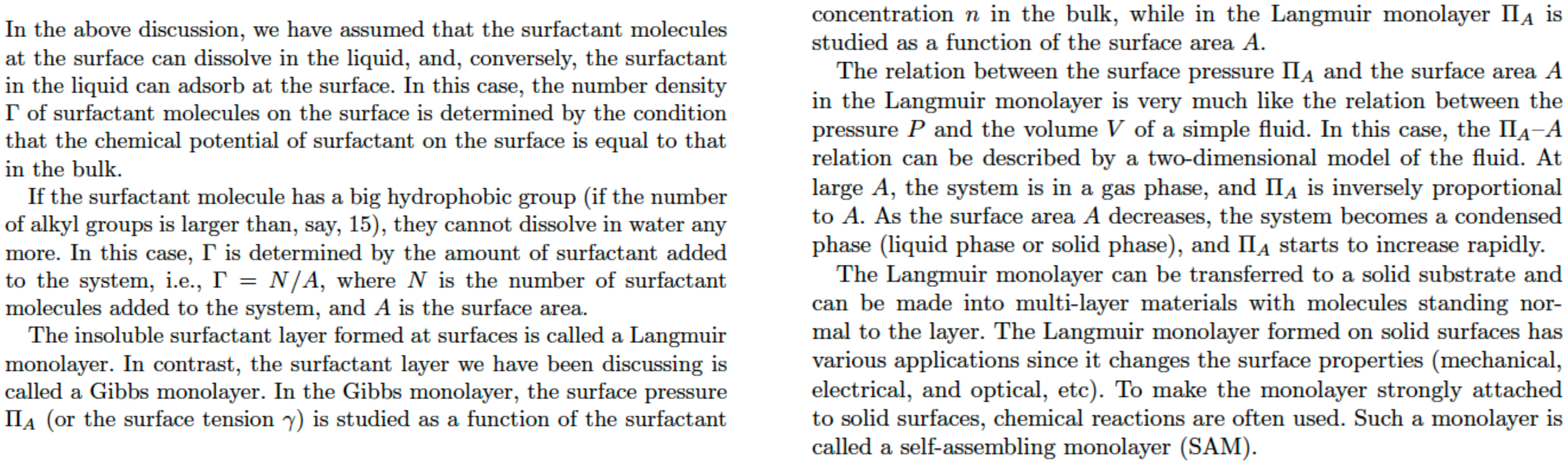
Therefore if $n < n_c$, all surfactants exist as a unimer. On the other hand, if $n > n_c$, n_1 changes little with n since the exponent $1/m$ is very small.

Physically, the reason why n_1 changes little is that added surfactant molecules are taken into the micelles, and do not remain as unimers. One can see from eqs. (4.43) and (4.46) that the number density of micelles n_m is essentially zero for $n < n_c$ and is equal to n/m for $n > n_c$. Therefore n_c is identical to n_{cmc}, the concentration at which micelles start to appear. Since the chemical potential μ_1 of the unimer changes little with n for $n > n_{cmc}$, the surface tension γ ceases to decrease with further addition of surfactants for $n > n_{cmc}$.

Statistical mechanical theory has been developed for other types of micelles (cylindrical, lamellar) shown in Fig. 4.10, and the size distribution and n_{cmc} have been discussed for such micelles.

Gibbs & Langmuir monolayers





In the above discussion, we have assumed that the surfactant molecules at the surface can dissolve in the liquid, and, conversely, the surfactant in the liquid can adsorb at the surface. In this case, the number density Γ of surfactant molecules on the surface is determined by the condition that the chemical potential of surfactant on the surface is equal to that in the bulk.

If the surfactant molecule has a big hydrophobic group (if the number of alkyl groups is larger than, say, 15), they cannot dissolve in water any more. In this case, Γ is determined by the amount of surfactant added to the system, i.e., $\Gamma = N/A$, where N is the number of surfactant molecules added to the system, and A is the surface area.

The insoluble surfactant layer formed at surfaces is called a Langmuir monolayer. In contrast, the surfactant layer we have been discussing is called a Gibbs monolayer. In the Gibbs monolayer, the surface pressure Π_A (or the surface tension γ) is studied as a function of the surfactant concentration n in the bulk, while in the Langmuir monolayer Π_A is studied as a function of the surface area A.

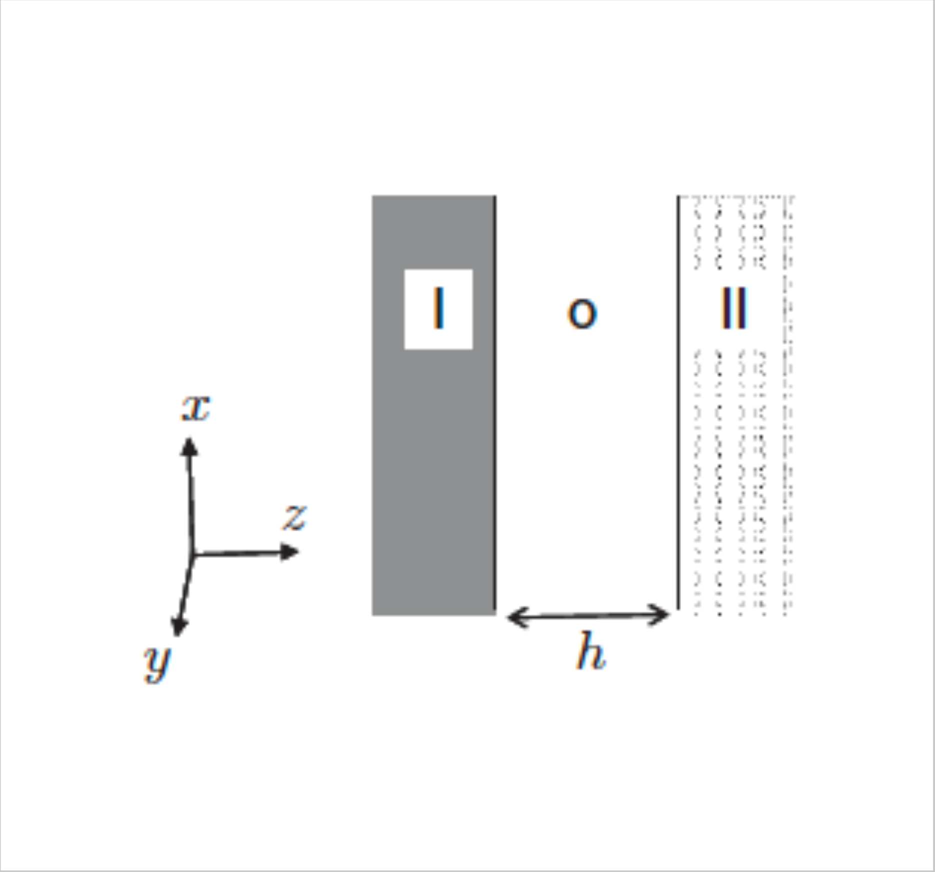
The relation between the surface pressure Π_A and the surface area A in the Langmuir monolayer is very much like the relation between the pressure P and the volume V of a simple fluid. In this case, the Π_A–A relation can be described by a two-dimensional model of the fluid. At large A, the system is in a gas phase, and Π_A is inversely proportional to A. As the surface area A decreases, the system becomes a condensed phase (liquid phase or solid phase), and Π_A starts to increase rapidly.

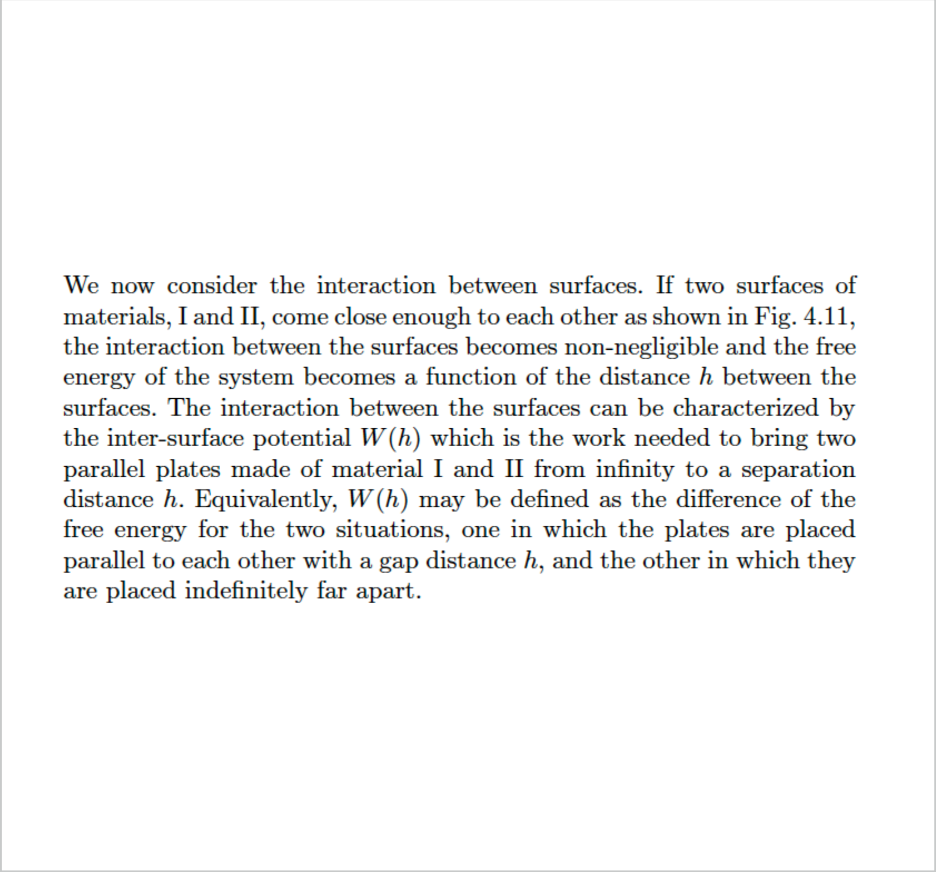
The Langmuir monolayer can be transferred to a solid substrate and can be made into multi-layer materials with molecules standing normal to the layer. The Langmuir monolayer formed on solid surfaces has various applications since it changes the surface properties (mechanical, electrical, and optical, etc). To make the monolayer strongly attached to solid surfaces, chemical reactions are often used. Such a monolayer is called a self-assembling monolayer (SAM).

Interaction between surfaces

For a large surface, W(h) is proportional to the area A of the surface.

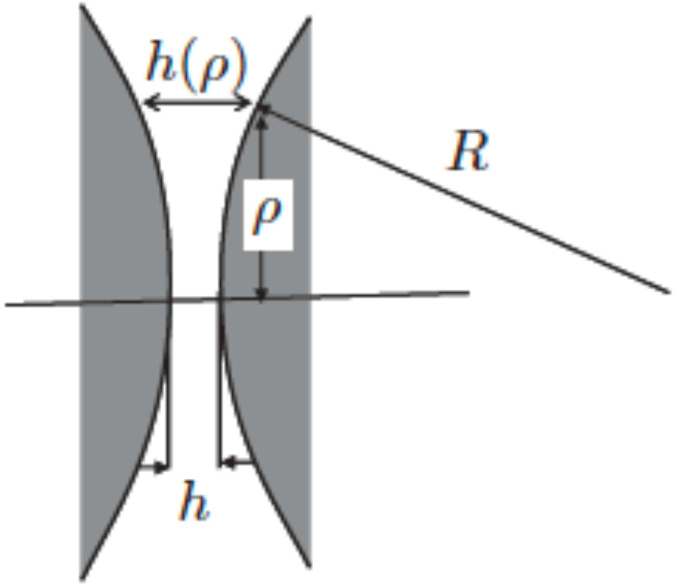
The potential per unit area w(h) = W(h)/A is called the inter-surface potential density.





We now consider the interaction between surfaces. If two surfaces of materials, I and II, come close enough to each other as shown in Fig. 4.11, the interaction between the surfaces becomes non-negligible and the free energy of the system becomes a function of the distance h between the surfaces. The interaction between the surfaces can be characterized by the inter-surface potential $W(h)$ which is the work needed to bring two parallel plates made of material I and II from infinity to a separation distance h. Equivalently, $W(h)$ may be defined as the difference of the free energy for the two situations, one in which the plates are placed parallel to each other with a gap distance h, and the other in which they are placed indefinitely far apart.

Derjaguin approximation



Consider two spherical particles of radius R placed with the gap distance h. The distance h(ρ) represents the surface-to-surface distance along a parallel line separated by a distance ρ from the line connecting the centres of the particles. For ρ <<R, h(ρ) is approximated as

$$\tilde{h}(\rho) = h + 2(R - \sqrt{R^2 - \rho^2}) \approx h + \frac{\rho^2}{R}$$

Consider a ring-like region on the surface of the particle bounded by two cylinders of radius ρ and ρ+dρ. If ρ<< R, the area of the ring is 2πρdρ, and the interaction energy is w(h)2πρdρ. Integrating this with respect to ρ, we have the interaction potential between the particles:

$$U(h) = \int_0^R w(\tilde{h}) 2\pi\rho d\rho$$

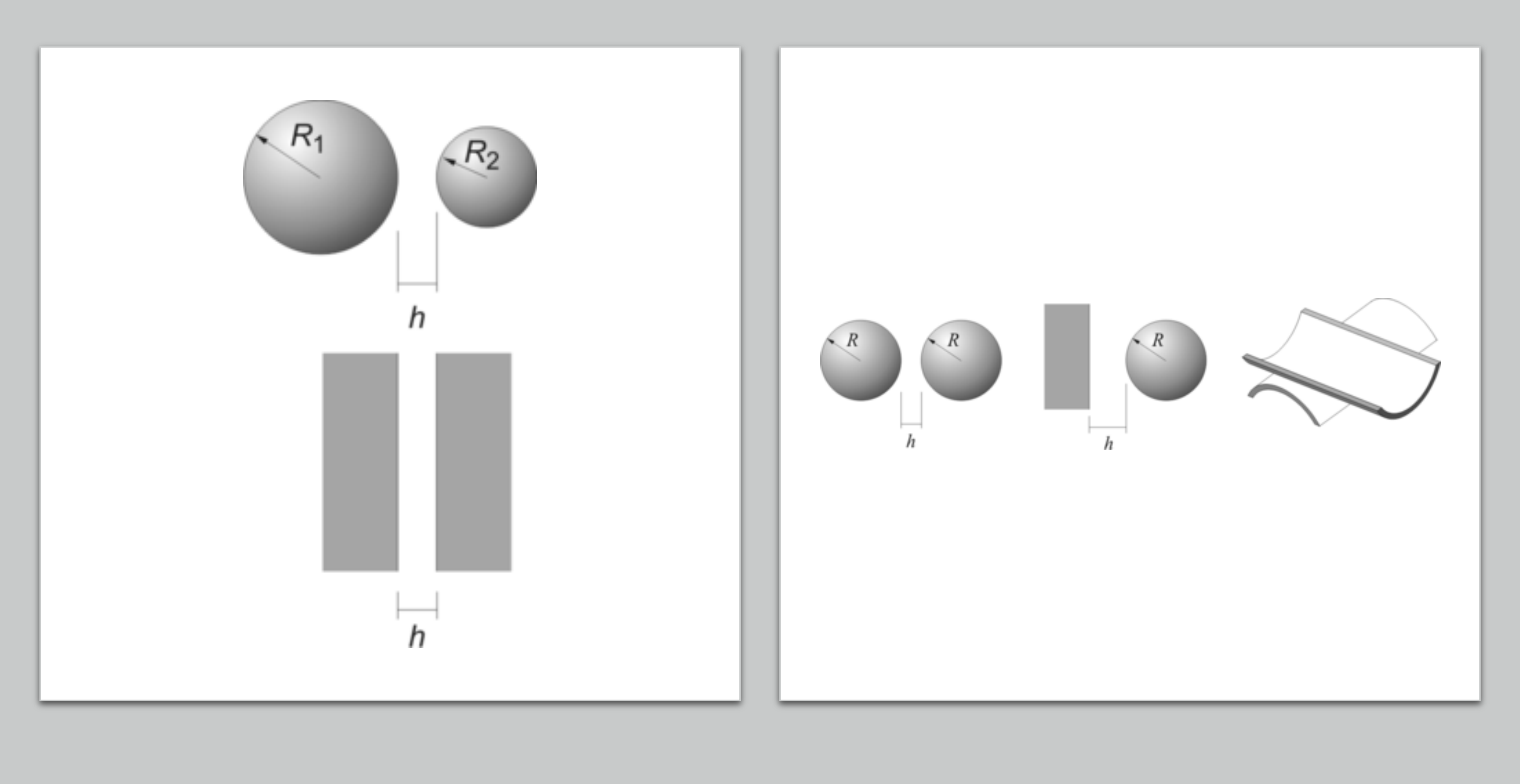
By using a new variable $x = h+\rho^2/R$, the right-hand side is rewritten as

$$U(h) = \pi R \int_h^\infty w(x) dx$$

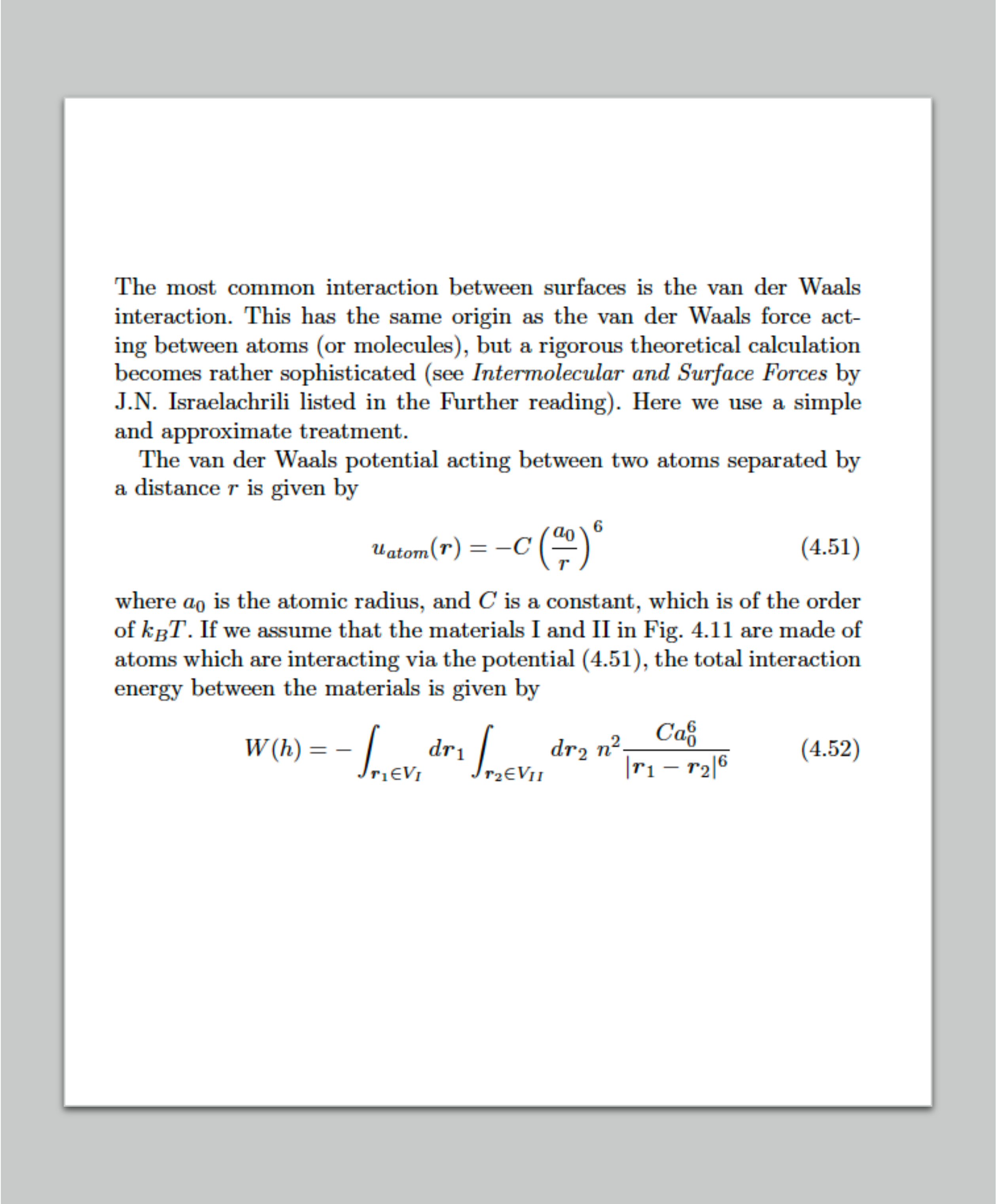
where the upper bound of the integral has been replaced by ∞. If the spheres have different radii, say R1 and R2, U(h) is given by

$$U(h) = 2\pi \frac{R_1 R_2}{R_1 + R_2} \int_h^\infty w(x) dx$$

Derjaguin approximation



van der Waals forces



The most common interaction between surfaces is the van der Waals interaction. This has the same origin as the van der Waals force acting between atoms (or molecules), but a rigorous theoretical calculation becomes rather sophisticated (see *Intermolecular and Surface Forces* by J.N. Israelachrili listed in the Further reading). Here we use a simple and approximate treatment.

The van der Waals potential acting between two atoms separated by a distance r is given by

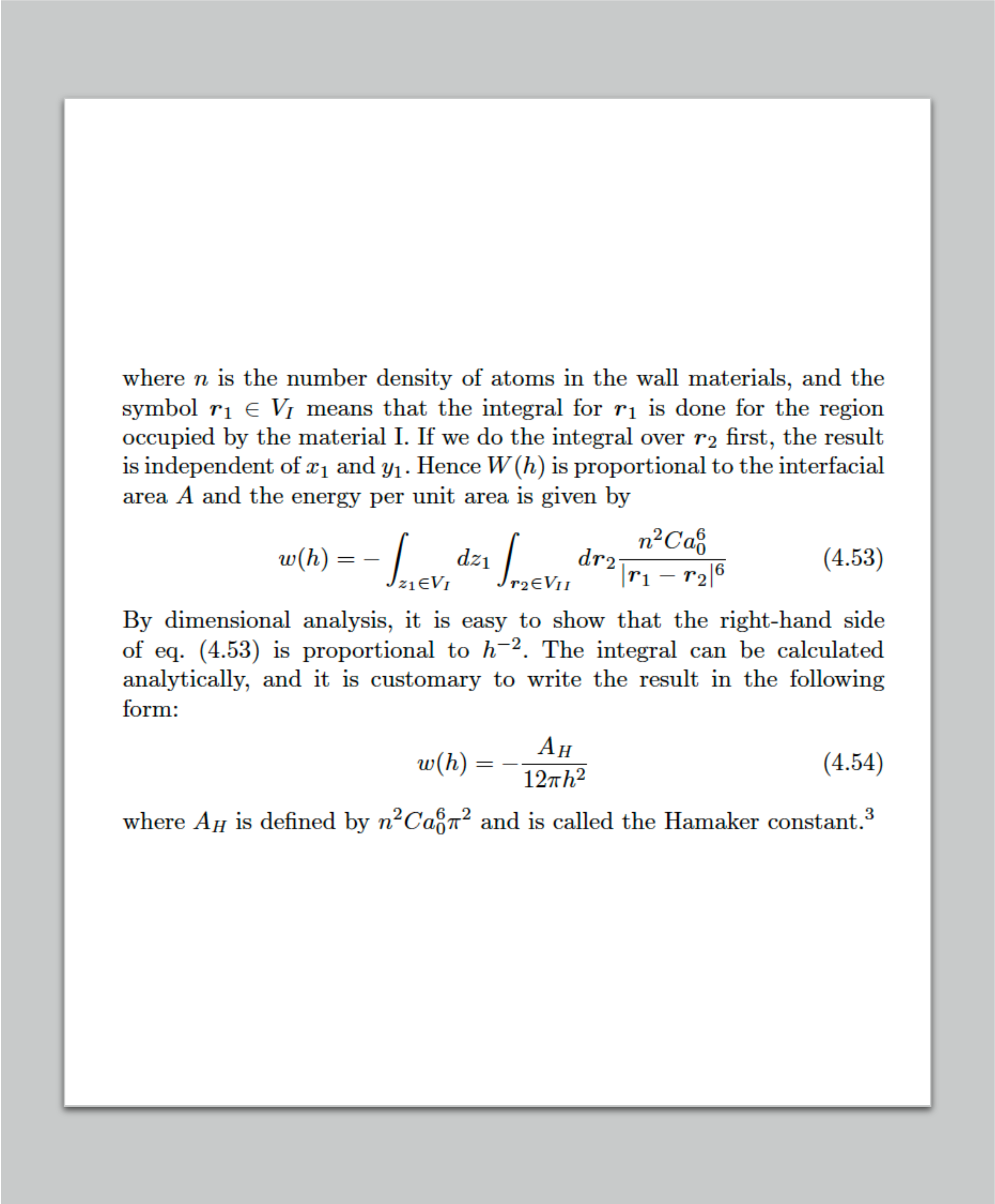
$$u_{atom}(\boldsymbol{r}) = -C\left(\frac{a_0}{r}\right)^6 \tag{4.51}$$

where a_0 is the atomic radius, and C is a constant, which is of the order of k_BT. If we assume that the materials I and II in Fig. 4.11 are made of atoms which are interacting via the potential (4.51), the total interaction energy between the materials is given by

$$W(h) = -\int_{\boldsymbol{r}_1 \in V_I} d\boldsymbol{r}_1 \int_{\boldsymbol{r}_2 \in V_{II}} d\boldsymbol{r}_2 \; n^2 \frac{Ca_0^6}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|^6} \tag{4.52}$$

van der Waals forces

$$w(h) = -\frac{A_H}{12\pi h^2}$$



where n is the number density of atoms in the wall materials, and the symbol $\boldsymbol{r}_1 \in V_I$ means that the integral for $\boldsymbol{r}_1$ is done for the region occupied by the material I. If we do the integral over $\boldsymbol{r}_2$ first, the result is independent of x_1 and y_1. Hence $W(h)$ is proportional to the interfacial area A and the energy per unit area is given by

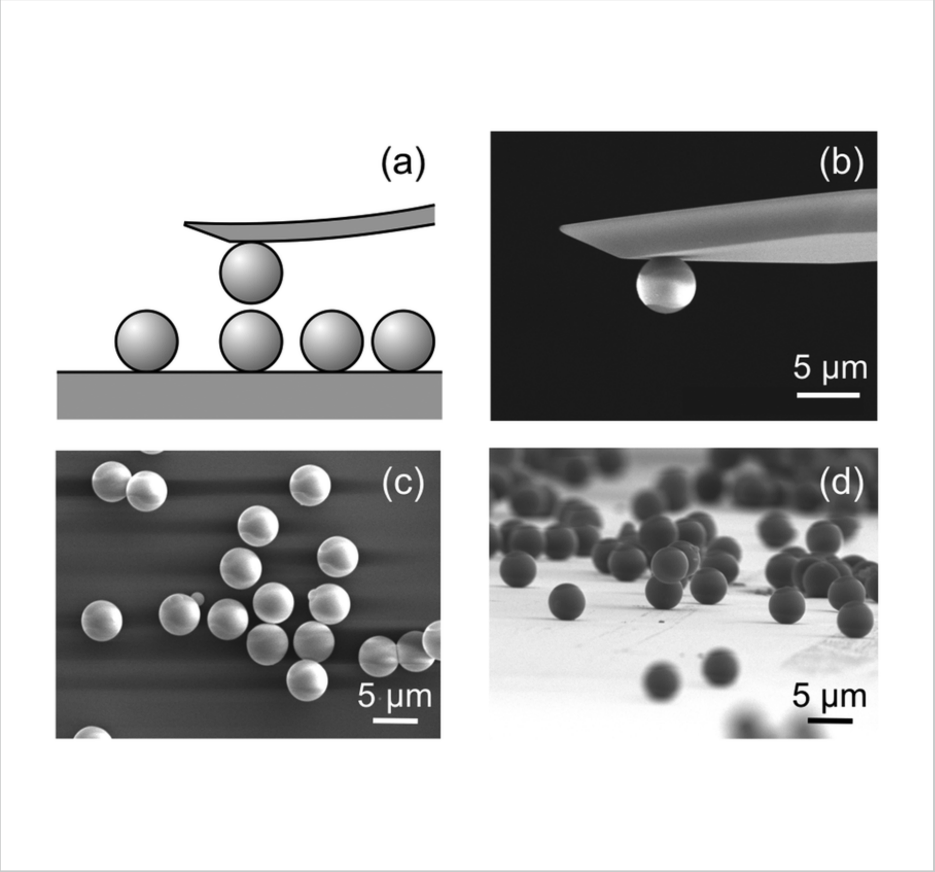
$$w(h) = -\int_{z_1 \in V_I} dz_1 \int_{\boldsymbol{r}_2 \in V_{II}} d\boldsymbol{r}_2 \frac{n^2 C a_0^6}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|^6} \tag{4.53}$$

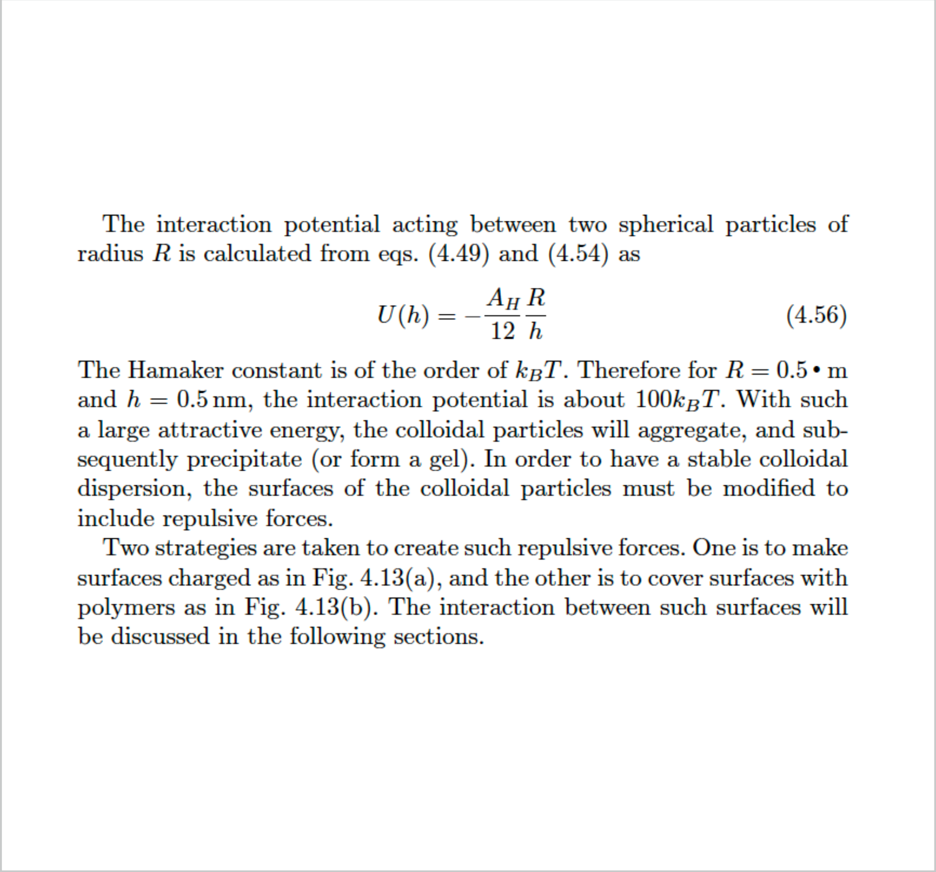
By dimensional analysis, it is easy to show that the right-hand side of eq. (4.53) is proportional to h^{-2}. The integral can be calculated analytically, and it is customary to write the result in the following form:

$$w(h) = -\frac{A_H}{12\pi h^2} \tag{4.54}$$

where A_H is defined by $n^2 C a_0^6 \pi^2$ and is called the Hamaker constant.[3]

Strength of the van der Waals force





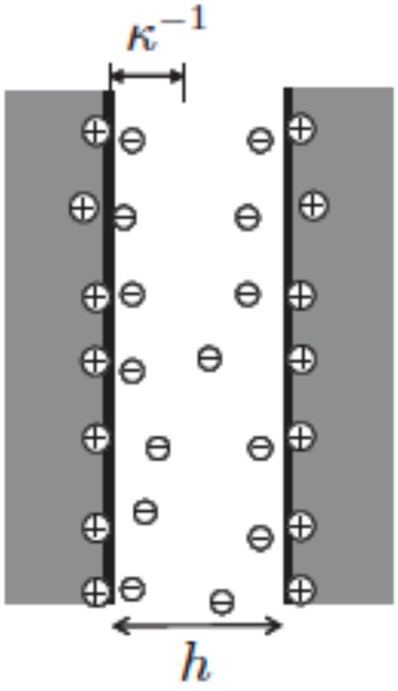
The interaction potential acting between two spherical particles of radius R is calculated from eqs. (4.49) and (4.54) as

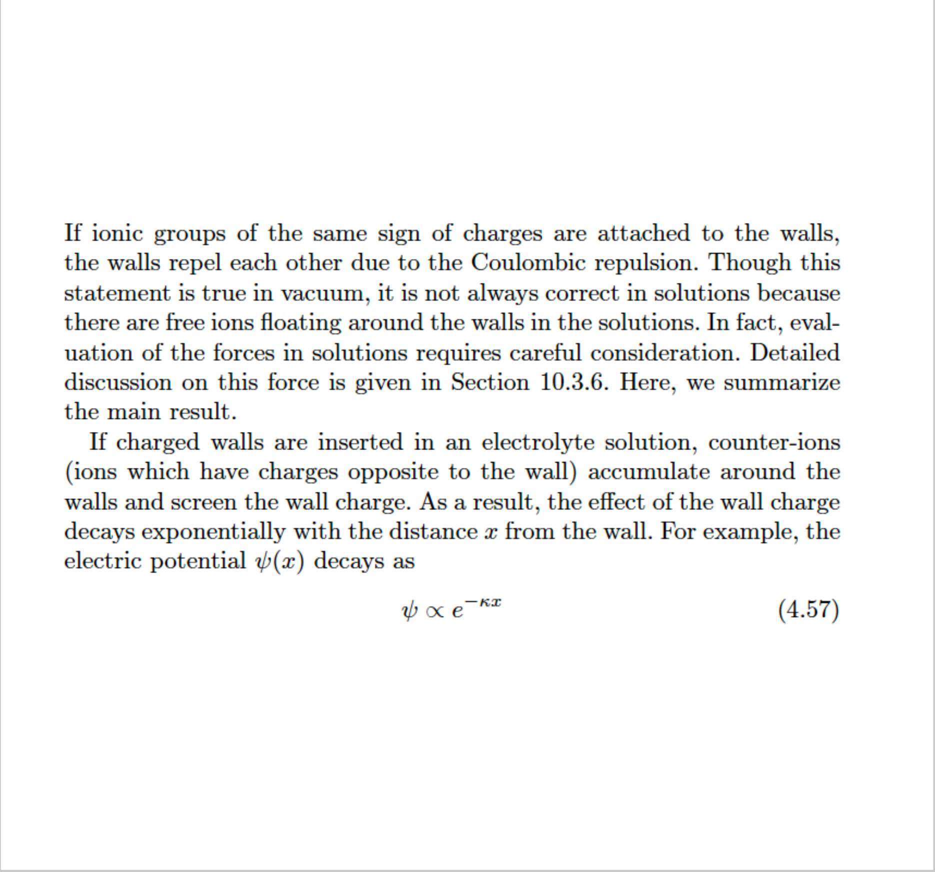
$$U(h) = -\frac{A_H}{12}\frac{R}{h} \tag{4.56}$$

The Hamaker constant is of the order of k_BT. Therefore for $R = 0.5 \bullet \mathrm{m}$ and $h = 0.5\,\mathrm{nm}$, the interaction potential is about $100k_BT$. With such a large attractive energy, the colloidal particles will aggregate, and subsequently precipitate (or form a gel). In order to have a stable colloidal dispersion, the surfaces of the colloidal particles must be modified to include repulsive forces.

Two strategies are taken to create such repulsive forces. One is to make surfaces charged as in Fig. 4.13(a), and the other is to cover surfaces with polymers as in Fig. 4.13(b). The interaction between such surfaces will be discussed in the following sections.

Charged surfaces



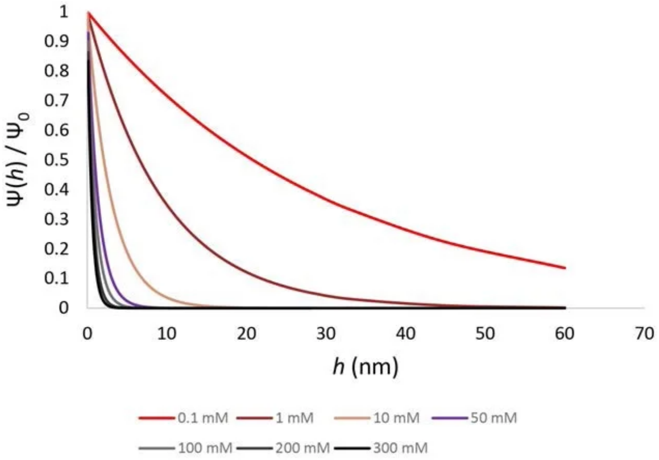


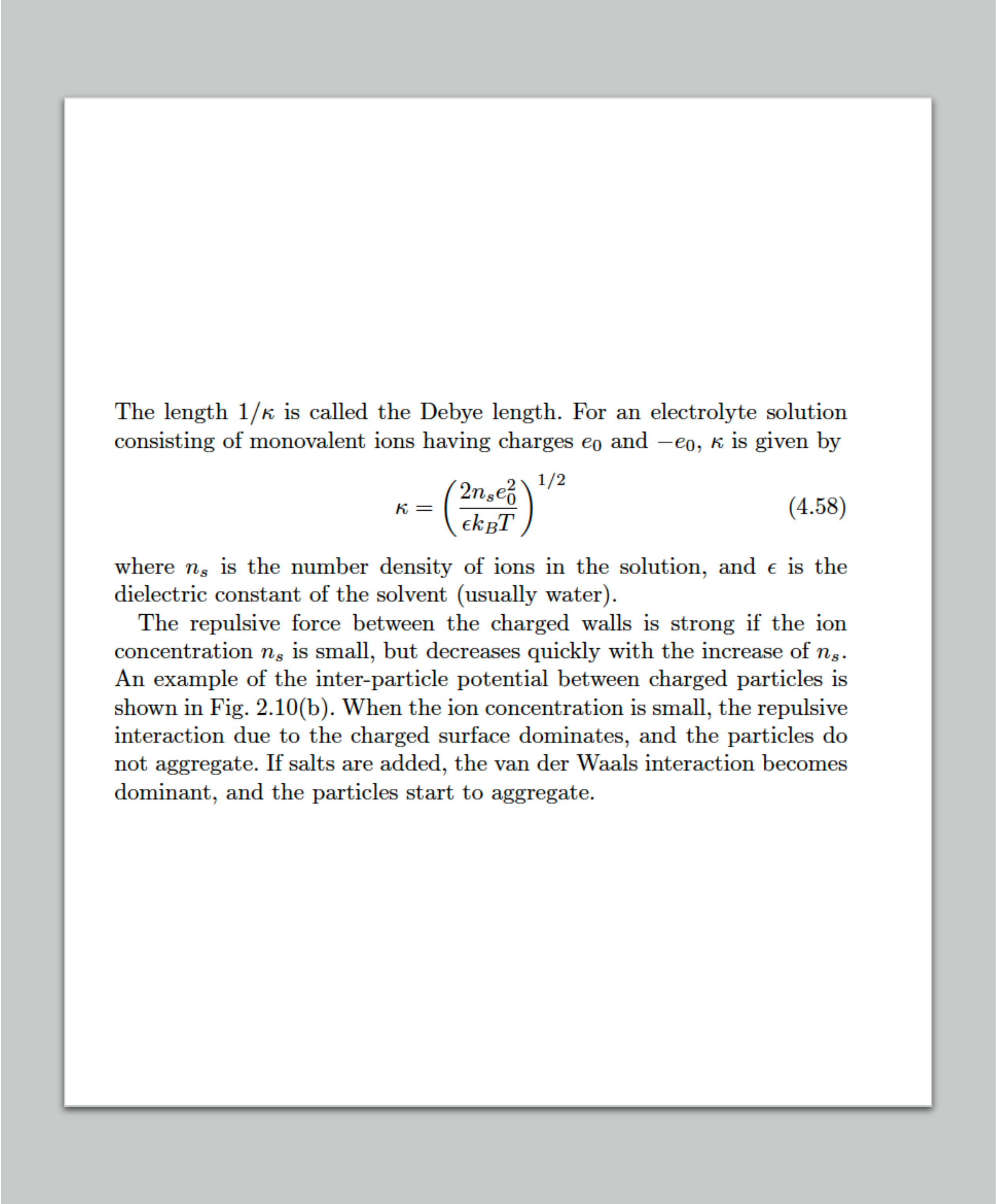
If ionic groups of the same sign of charges are attached to the walls, the walls repel each other due to the Coulombic repulsion. Though this statement is true in vacuum, it is not always correct in solutions because there are free ions floating around the walls in the solutions. In fact, evaluation of the forces in solutions requires careful consideration. Detailed discussion on this force is given in Section 10.3.6. Here, we summarize the main result.

If charged walls are inserted in an electrolyte solution, counter-ions (ions which have charges opposite to the wall) accumulate around the walls and screen the wall charge. As a result, the effect of the wall charge decays exponentially with the distance x from the wall. For example, the electric potential $\psi(x)$ decays as

$$\psi \propto e^{-\kappa x} \qquad (4.57)$$

Debye length





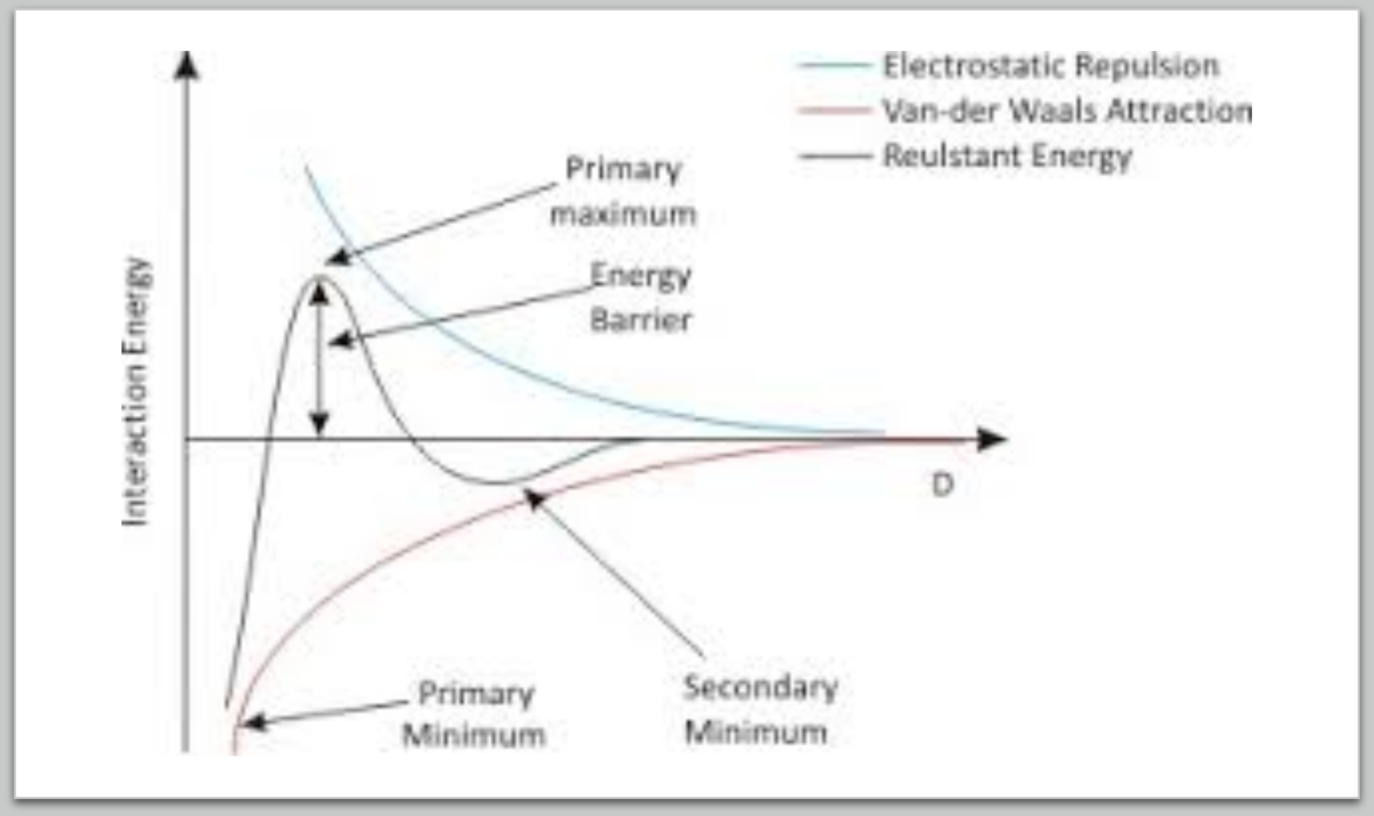
The length $1/\kappa$ is called the Debye length. For an electrolyte solution consisting of monovalent ions having charges e_0 and $-e_0$, κ is given by

$$\kappa = \left(\frac{2n_s e_0^2}{\epsilon k_B T} \right)^{1/2} \tag{4.58}$$

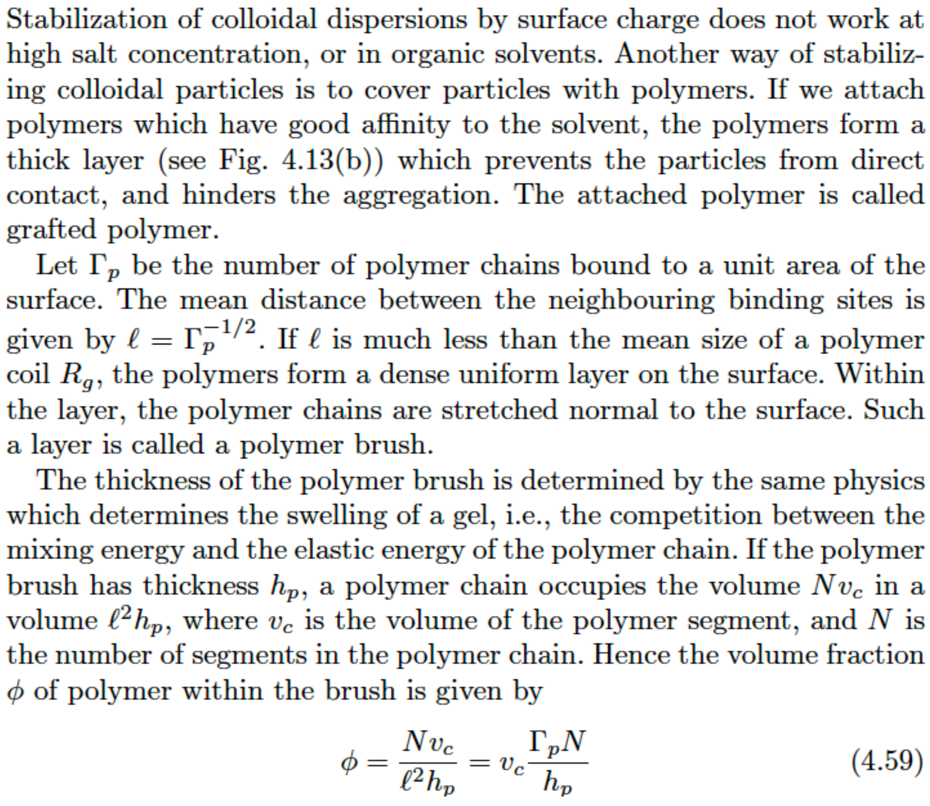
where n_s is the number density of ions in the solution, and ϵ is the dielectric constant of the solvent (usually water).

The repulsive force between the charged walls is strong if the ion concentration n_s is small, but decreases quickly with the increase of n_s. An example of the inter-particle potential between charged particles is shown in Fig. 2.10(b). When the ion concentration is small, the repulsive interaction due to the charged surface dominates, and the particles do not aggregate. If salts are added, the van der Waals interaction becomes dominant, and the particles start to aggregate.

DLVO potential



Polymer grafted surfaces

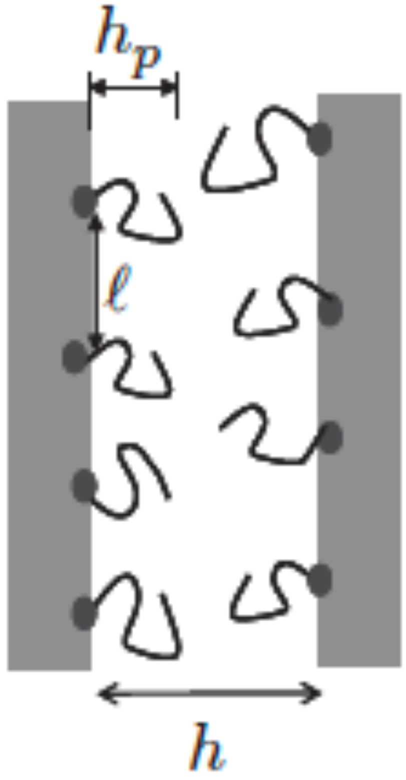


Stabilization of colloidal dispersions by surface charge does not work at high salt concentration, or in organic solvents. Another way of stabilizing colloidal particles is to cover particles with polymers. If we attach polymers which have good affinity to the solvent, the polymers form a thick layer (see Fig. 4.13(b)) which prevents the particles from direct contact, and hinders the aggregation. The attached polymer is called grafted polymer.

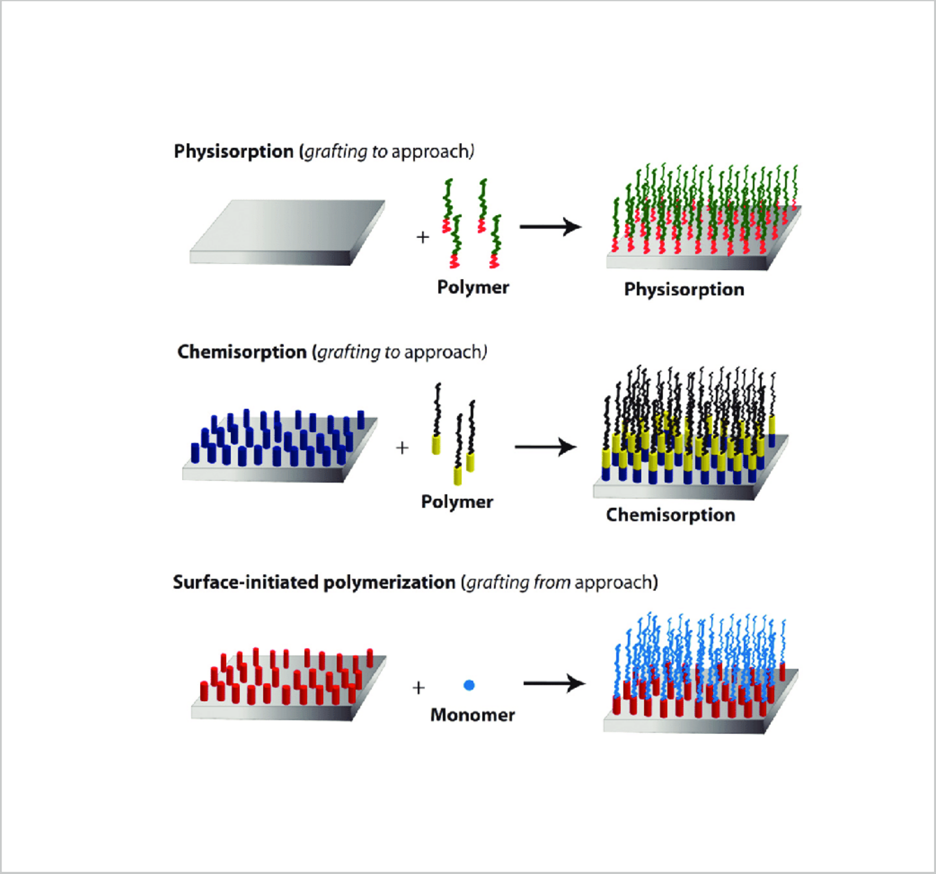
Let Γ_p be the number of polymer chains bound to a unit area of the surface. The mean distance between the neighbouring binding sites is given by $\ell = \Gamma_p^{-1/2}$. If ℓ is much less than the mean size of a polymer coil R_g, the polymers form a dense uniform layer on the surface. Within the layer, the polymer chains are stretched normal to the surface. Such a layer is called a polymer brush.

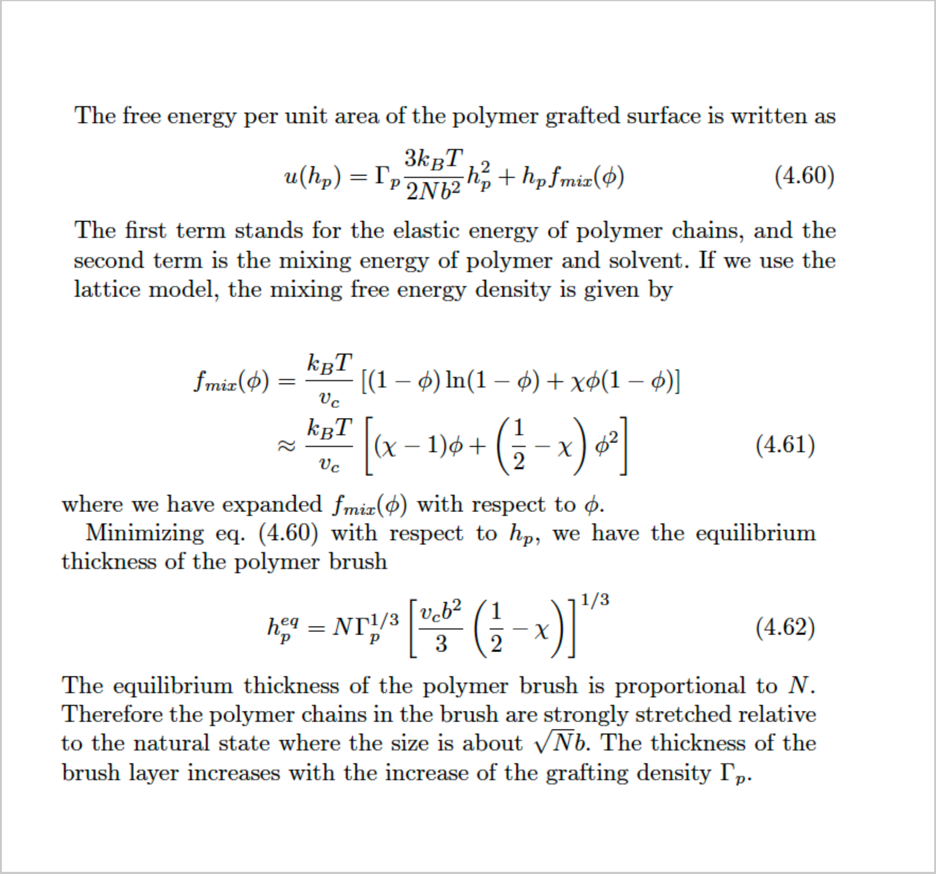
The thickness of the polymer brush is determined by the same physics which determines the swelling of a gel, i.e., the competition between the mixing energy and the elastic energy of the polymer chain. If the polymer brush has thickness h_p, a polymer chain occupies the volume Nv_c in a volume $\ell^2 h_p$, where v_c is the volume of the polymer segment, and N is the number of segments in the polymer chain. Hence the volume fraction ϕ of polymer within the brush is given by

$$\phi = \frac{Nv_c}{\ell^2 h_p} = v_c \frac{\Gamma_p N}{h_p} \tag{4.59}$$



Grafted polymers





The free energy per unit area of the polymer grafted surface is written as

$$u(h_p) = \Gamma_p \frac{3k_BT}{2Nb^2} h_p^2 + h_p f_{mix}(\phi) \tag{4.60}$$

The first term stands for the elastic energy of polymer chains, and the second term is the mixing energy of polymer and solvent. If we use the lattice model, the mixing free energy density is given by

$$\begin{aligned} f_{mix}(\phi) &= \frac{k_BT}{v_c}\left[(1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)\right] \\ &\approx \frac{k_BT}{v_c}\left[(\chi-1)\phi + \left(\frac{1}{2}-\chi\right)\phi^2\right] \end{aligned} \tag{4.61}$$

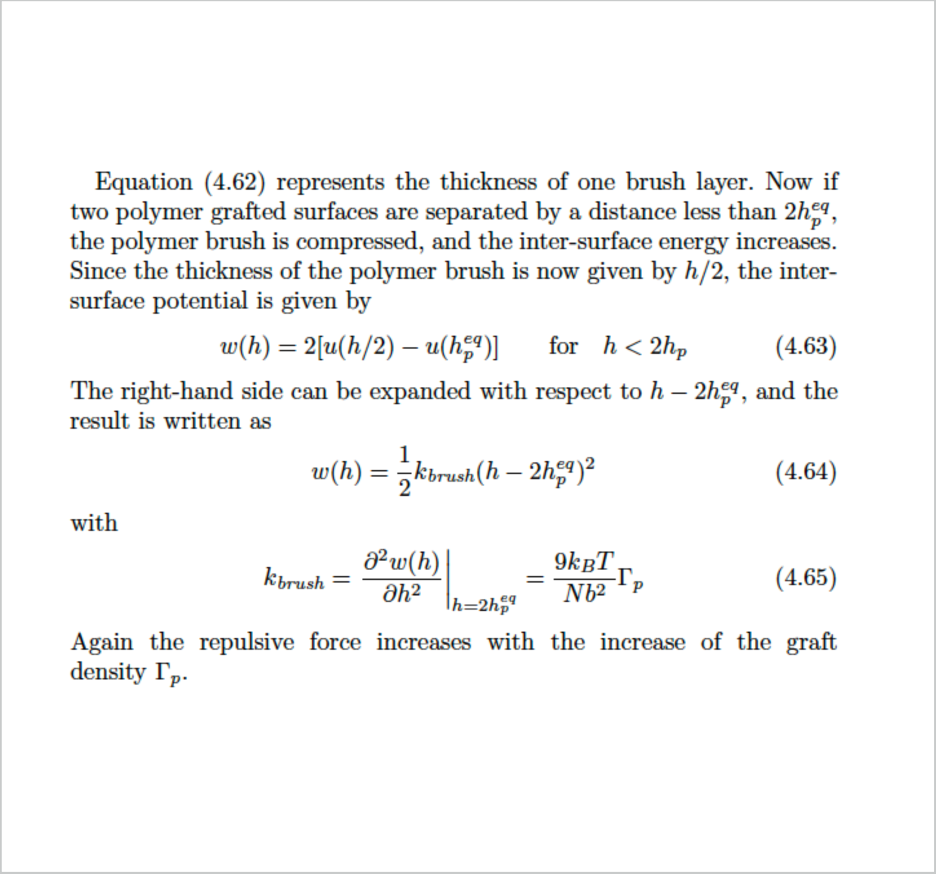
where we have expanded $f_{mix}(\phi)$ with respect to ϕ.

Minimizing eq. (4.60) with respect to h_p, we have the equilibrium thickness of the polymer brush

$$h_p^{eq} = N\Gamma_p^{1/3}\left[\frac{v_c b^2}{3}\left(\frac{1}{2}-\chi\right)\right]^{1/3} \tag{4.62}$$

The equilibrium thickness of the polymer brush is proportional to N. Therefore the polymer chains in the brush are strongly stretched relative to the natural state where the size is about $\sqrt{N}b$. The thickness of the brush layer increases with the increase of the grafting density Γ_p.

Repulsion from grafted polymers



Equation (4.62) represents the thickness of one brush layer. Now if two polymer grafted surfaces are separated by a distance less than $2h_p^{eq}$, the polymer brush is compressed, and the inter-surface energy increases. Since the thickness of the polymer brush is now given by $h/2$, the inter-surface potential is given by

$$w(h) = 2[u(h/2) - u(h_p^{eq})] \qquad \text{for} \quad h < 2h_p \tag{4.63}$$

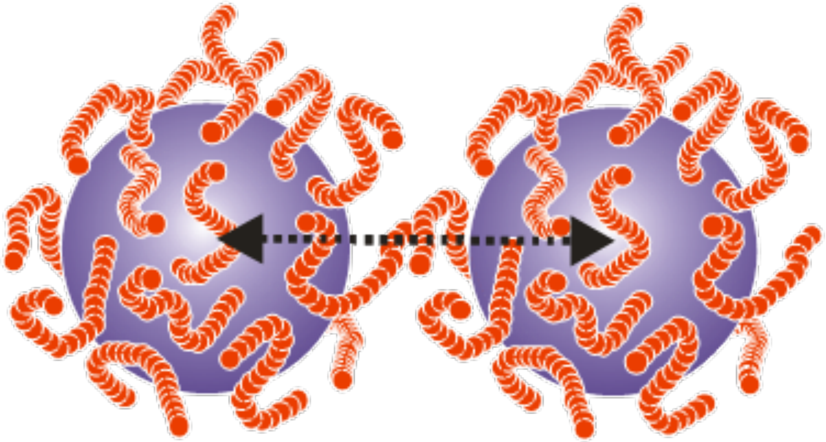
The right-hand side can be expanded with respect to $h - 2h_p^{eq}$, and the result is written as

$$w(h) = \frac{1}{2} k_{brush} (h - 2h_p^{eq})^2 \tag{4.64}$$

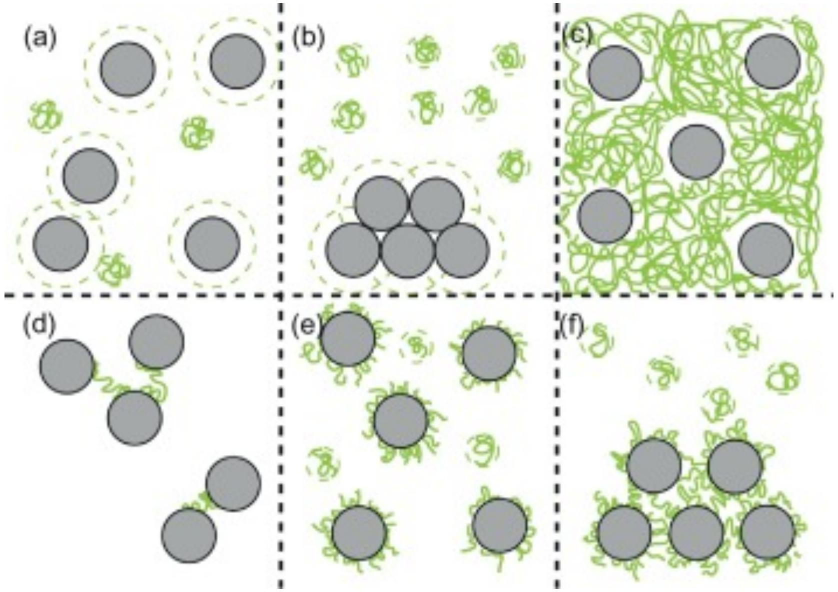
with

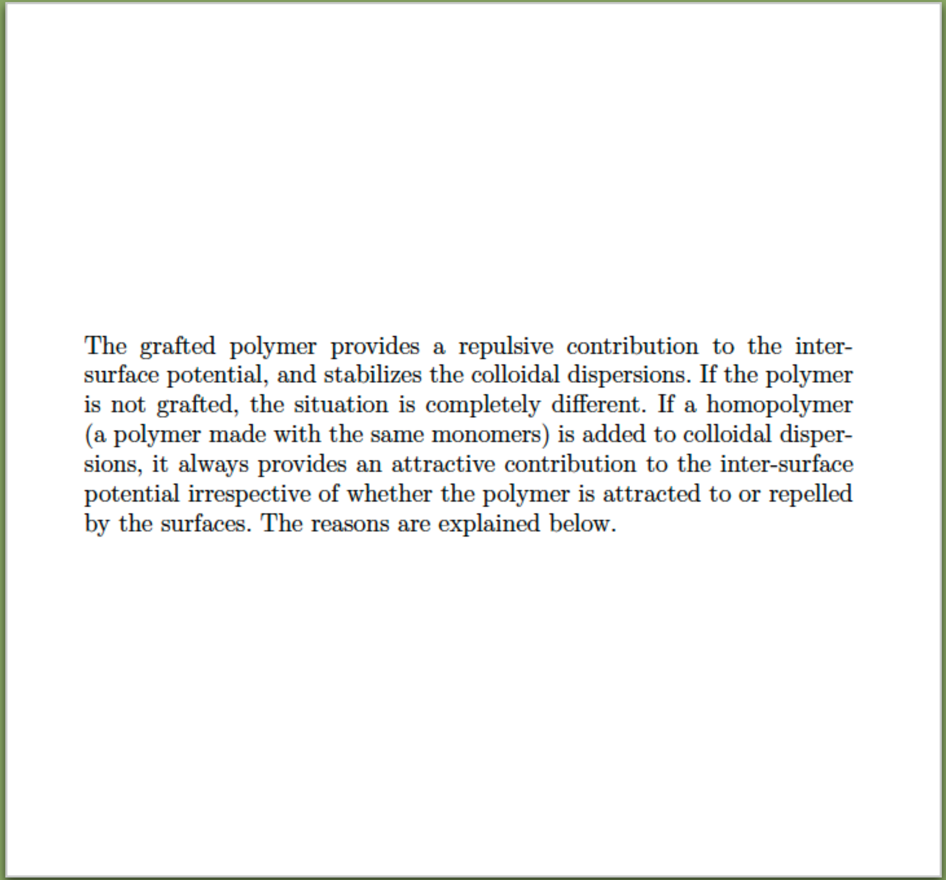
$$k_{brush} = \left. \frac{\partial^2 w(h)}{\partial h^2} \right|_{h=2h_p^{eq}} = \frac{9k_B T}{Nb^2} \Gamma_p \tag{4.65}$$

Again the repulsive force increases with the increase of the graft density Γ_p.



Attraction from non grafted polymers



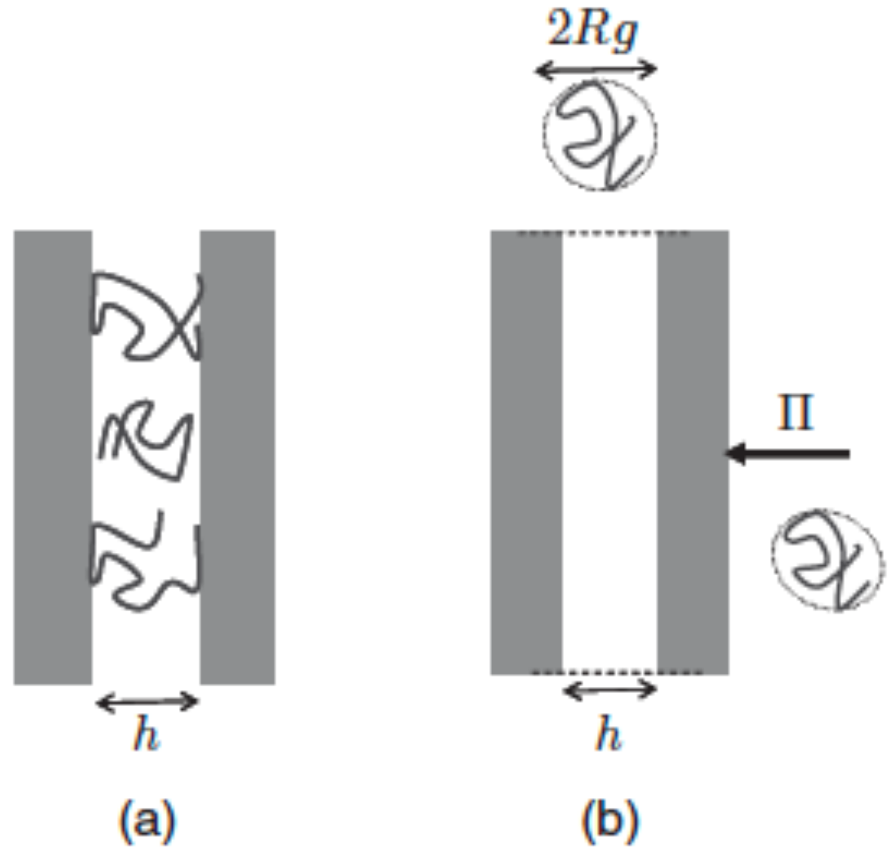


The grafted polymer provides a repulsive contribution to the inter-surface potential, and stabilizes the colloidal dispersions. If the polymer is not grafted, the situation is completely different. If a homopolymer (a polymer made with the same monomers) is added to colloidal dispersions, it always provides an attractive contribution to the inter-surface potential irrespective of whether the polymer is attracted to or repelled by the surfaces. The reasons are explained below.

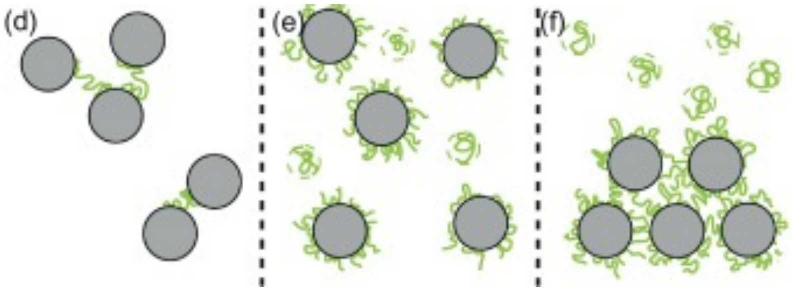
Attractive & repulsive polymers

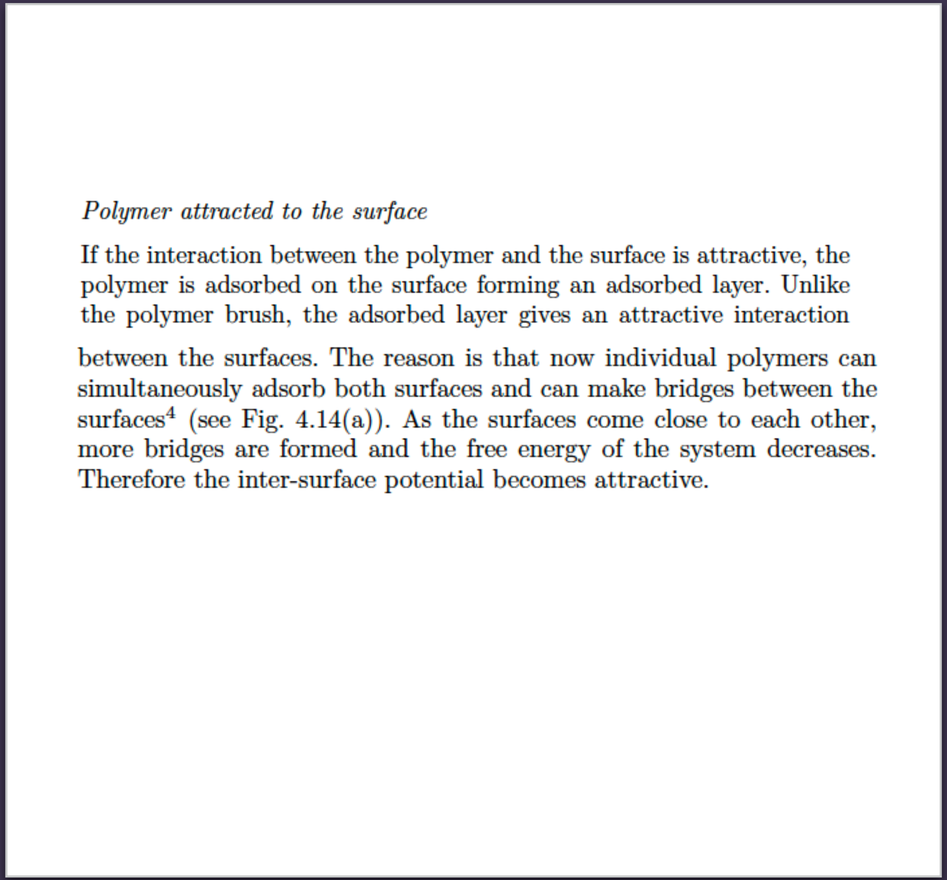
If the polymer is attracted to the surface, it creates bridges between the surfaces, and gives an attractive force between the surfaces.

If the polymer is repelled by the surface, it is excluded from the gap region between the surfaces. This effect also gives an attractive contribution to the inter-surface force.



Attraction from attractive polymers

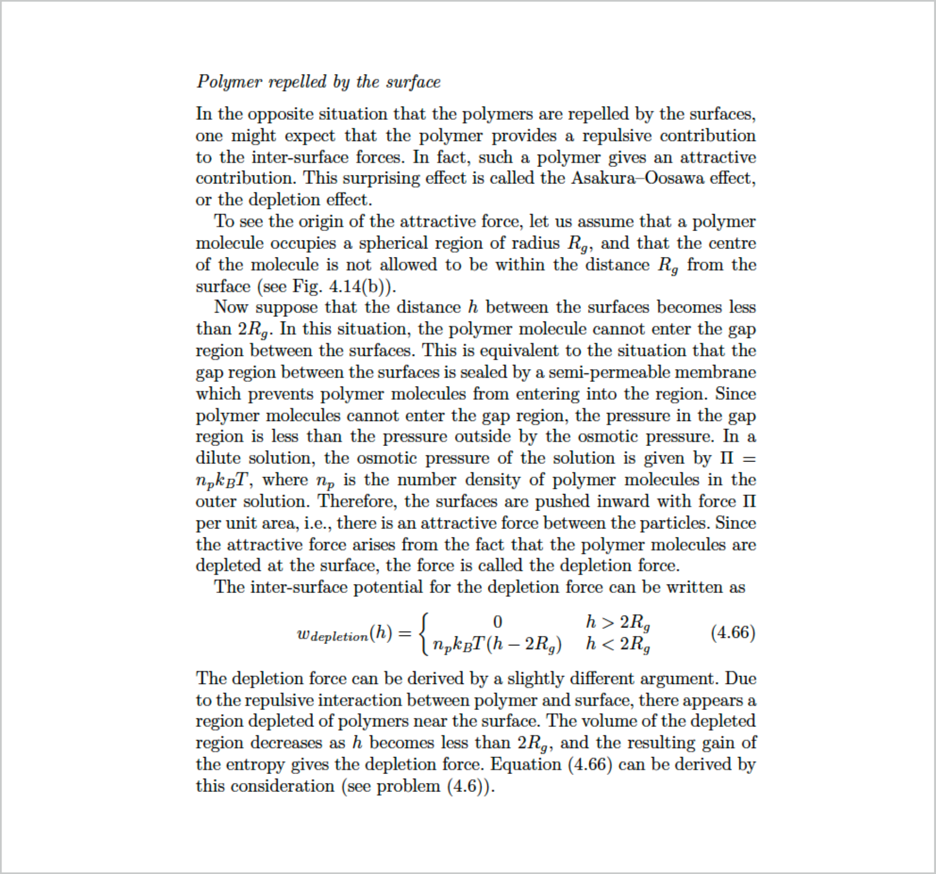




Polymer attracted to the surface

If the interaction between the polymer and the surface is attractive, the polymer is adsorbed on the surface forming an adsorbed layer. Unlike the polymer brush, the adsorbed layer gives an attractive interaction between the surfaces. The reason is that now individual polymers can simultaneously adsorb both surfaces and can make bridges between the surfaces[4] (see Fig. 4.14(a)). As the surfaces come close to each other, more bridges are formed and the free energy of the system decreases. Therefore the inter-surface potential becomes attractive.

Attraction from repulsive polymers



Polymer repelled by the surface

In the opposite situation that the polymers are repelled by the surfaces, one might expect that the polymer provides a repulsive contribution to the inter-surface forces. In fact, such a polymer gives an attractive contribution. This surprising effect is called the Asakura–Oosawa effect, or the depletion effect.

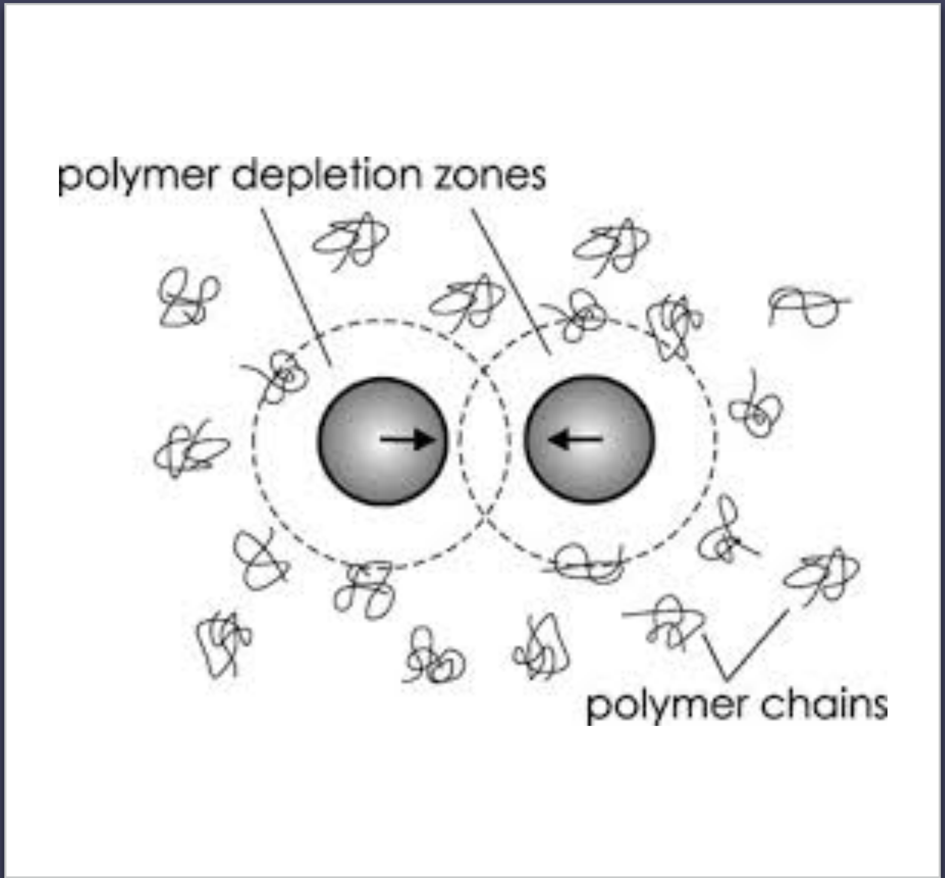
To see the origin of the attractive force, let us assume that a polymer molecule occupies a spherical region of radius R_g, and that the centre of the molecule is not allowed to be within the distance R_g from the surface (see Fig. 4.14(b)).

Now suppose that the distance h between the surfaces becomes less than $2R_g$. In this situation, the polymer molecule cannot enter the gap region between the surfaces. This is equivalent to the situation that the gap region between the surfaces is sealed by a semi-permeable membrane which prevents polymer molecules from entering into the region. Since polymer molecules cannot enter the gap region, the pressure in the gap region is less than the pressure outside by the osmotic pressure. In a dilute solution, the osmotic pressure of the solution is given by $\Pi = n_p k_B T$, where n_p is the number density of polymer molecules in the outer solution. Therefore, the surfaces are pushed inward with force Π per unit area, i.e., there is an attractive force between the particles. Since the attractive force arises from the fact that the polymer molecules are depleted at the surface, the force is called the depletion force.

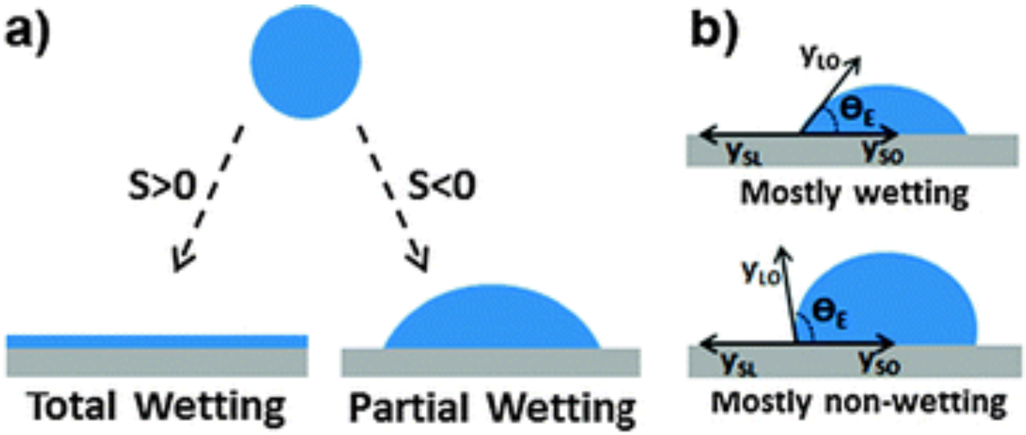
The inter-surface potential for the depletion force can be written as

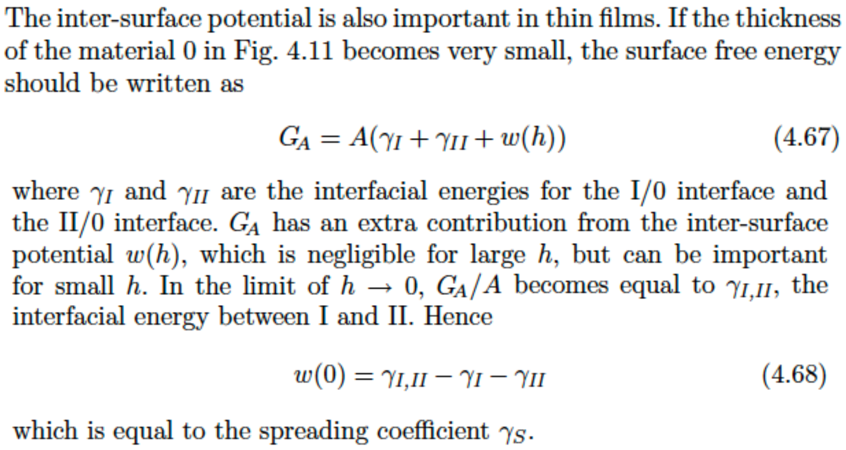
$$w_{depletion}(h) = \begin{cases} 0 & h > 2R_g \\ n_p k_B T(h - 2R_g) & h < 2R_g \end{cases} \tag{4.66}$$

The depletion force can be derived by a slightly different argument. Due to the repulsive interaction between polymer and surface, there appears a region depleted of polymers near the surface. The volume of the depleted region decreases as h becomes less than $2R_g$, and the resulting gain of the entropy gives the depletion force. Equation (4.66) can be derived by this consideration (see problem (4.6)).



Thin films



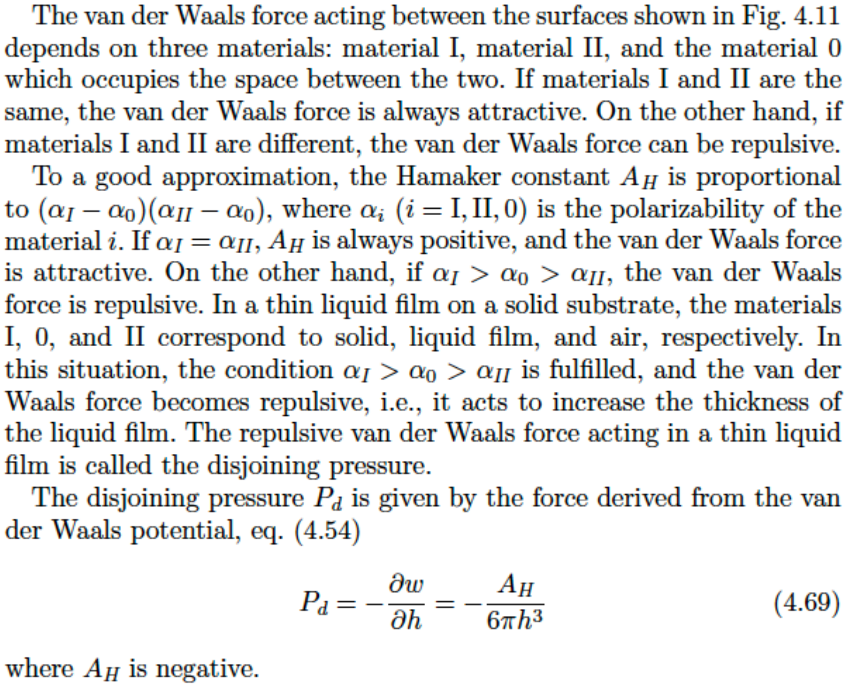

The inter-surface potential is also important in thin films. If the thickness of the material 0 in Fig. 4.11 becomes very small, the surface free energy should be written as

$$G_A = A(\gamma_I + \gamma_{II} + w(h)) \tag{4.67}$$

where γ_I and γ_{II} are the interfacial energies for the I/0 interface and the II/0 interface. G_A has an extra contribution from the inter-surface potential $w(h)$, which is negligible for large h, but can be important for small h. In the limit of $h \to 0$, G_A/A becomes equal to $\gamma_{I,II}$, the interfacial energy between I and II. Hence

$$w(0) = \gamma_{I,II} - \gamma_I - \gamma_{II} \tag{4.68}$$

which is equal to the spreading coefficient γ_S.


The van der Waals force acting between the surfaces shown in Fig. 4.11 depends on three materials: material I, material II, and the material 0 which occupies the space between the two. If materials I and II are the same, the van der Waals force is always attractive. On the other hand, if materials I and II are different, the van der Waals force can be repulsive.

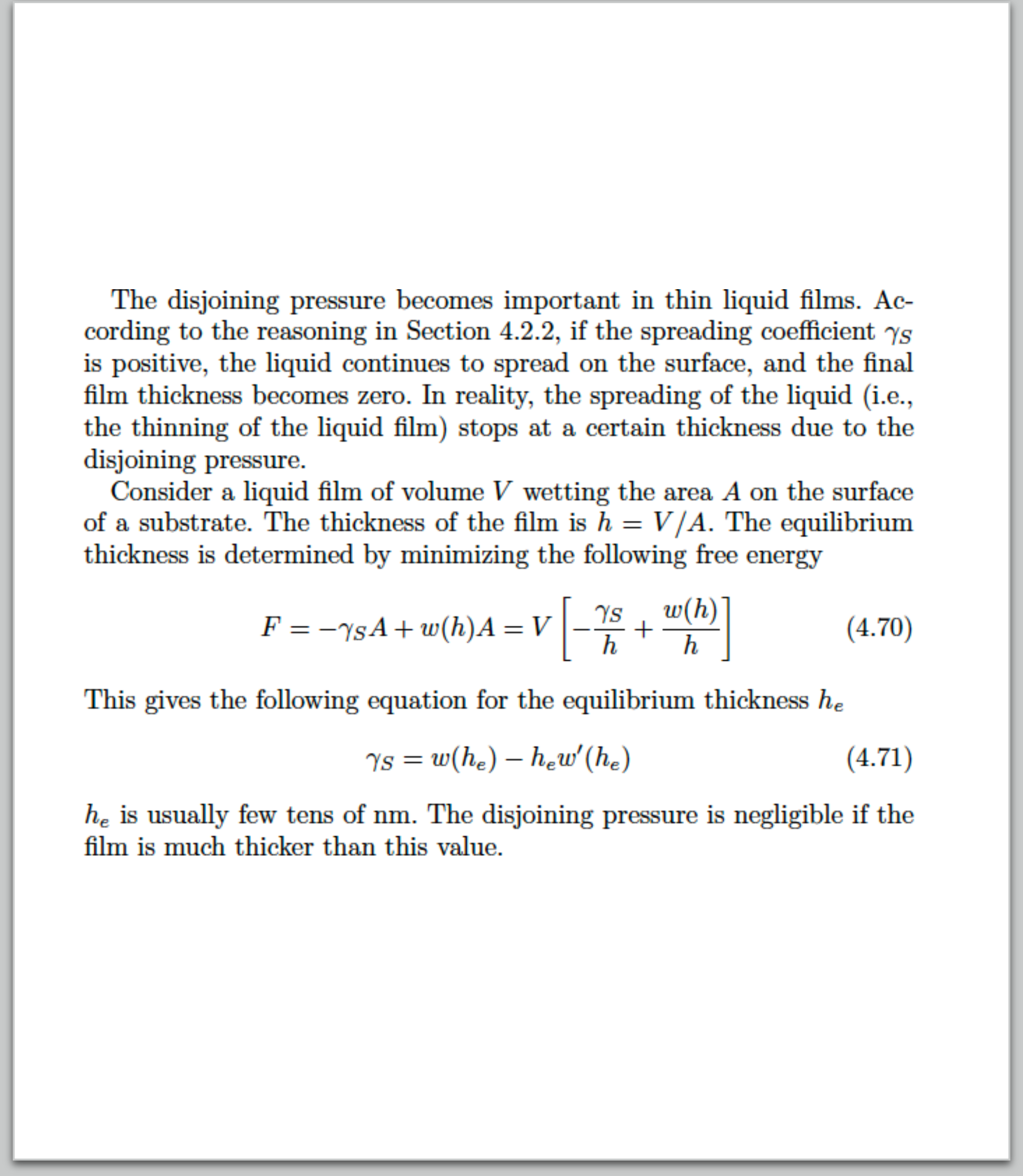
To a good approximation, the Hamaker constant A_H is proportional to $(\alpha_I - \alpha_0)(\alpha_{II} - \alpha_0)$, where α_i $(i = \mathrm{I}, \mathrm{II}, 0)$ is the polarizability of the material i. If $\alpha_I = \alpha_{II}$, A_H is always positive, and the van der Waals force is attractive. On the other hand, if $\alpha_I > \alpha_0 > \alpha_{II}$, the van der Waals force is repulsive. In a thin liquid film on a solid substrate, the materials I, 0, and II correspond to solid, liquid film, and air, respectively. In this situation, the condition $\alpha_I > \alpha_0 > \alpha_{II}$ is fulfilled, and the van der Waals force becomes repulsive, i.e., it acts to increase the thickness of the liquid film. The repulsive van der Waals force acting in a thin liquid film is called the disjoining pressure.

The disjoining pressure P_d is given by the force derived from the van der Waals potential, eq. (4.54)

$$P_d = -\frac{\partial w}{\partial h} = -\frac{A_H}{6\pi h^3} \tag{4.69}$$

where A_H is negative.

Disjoining pressure & film thickness



The disjoining pressure becomes important in thin liquid films. According to the reasoning in Section 4.2.2, if the spreading coefficient γ_S is positive, the liquid continues to spread on the surface, and the final film thickness becomes zero. In reality, the spreading of the liquid (i.e., the thinning of the liquid film) stops at a certain thickness due to the disjoining pressure.

Consider a liquid film of volume V wetting the area A on the surface of a substrate. The thickness of the film is $h = V/A$. The equilibrium thickness is determined by minimizing the following free energy

$$F = -\gamma_S A + w(h)A = V\left[-\frac{\gamma_S}{h} + \frac{w(h)}{h}\right] \tag{4.70}$$

This gives the following equation for the equilibrium thickness h_e

$$\gamma_S = w(h_e) - h_e w'(h_e) \tag{4.71}$$

h_e is usually few tens of nm. The disjoining pressure is negligible if the film is much thicker than this value.