4 Capillary Forces

In the interactions between solid surfaces and liquids or between solid bodies in the presence of small amounts of liquids, the so called capillary forces play an important role. Capillary forces are responsible for the wetting of solids by liquids or the "repelling" of liquids. The transportation of water in all organs of plants is caused by capillary forces. They are behind the unwanted "spreading" of lubricating oil and its transportation to friction sites in the for-life lubrication of systems. Capillary forces are among the most important causes of "sticktion" between the small components in micro-technology. They can considerably influence frictional forces, especially that of static friction.

4.1 Surface Tension and Contact Angles

The most important physical parameters that influence capillary forces in various situations are the surface tension and the contact angle. In order to clarify the concept of surface tension of a liquid, we visualize a soap film stretched within a

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square-shaped wire frame. If we pull on a movable side of the frame, the area of the film gets larger. Consequently, the surface energy rises. With a displacement of Δx the energy rises by the amount $\Delta E = 2\gamma l \Delta x$, where γ is the surface energy density of the liquid, often referred to simply as "surface energy"; the factor of 2 accounts for the fact that the film has two sides. According to the principle of virtual work, this change in energy must be equal to the work performed by the external force $W = F\Delta x = 2\gamma l \Delta x$. Thus, $F = 2\gamma l$. That means that a uniform load of $f = F / l = 2\gamma$ acts on the edge of the frame. Due to the fact that the film has two identical sides, both are acted on by a uniform load of γ, which is simply equal to the surface energy. Therefore, every free surface is in "tension", from where the term "surface tension" for surface energy originates.

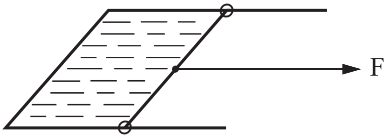

Fig. 4.1 An experiment with a soap film, in order to explain the notion of surface tension.

If a droplet of liquid is at rest on a solid surface, the surface of the liquid forms a specific angle θ (Fig. 4.2), which, in equilibrium, only depends on the thermodynamic properties of the system. This angle is called the *contact angle* and affects most of the important properties dealing with the contact between solid bodies and liquids.

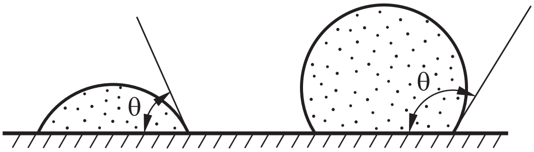

Abb. 4.2 Drop of liquid on a solid surface.

In the boundary line of the droplet, three interfaces meet each other (Fig. 4.3 a). In every interface, a corresponding surface tension acts. In equilibrium,

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta \tag{4.1}$$

is valid, in which γ_{sv} is the relative surface energy of the interface between the solid body and the vapor, γ_{sl} is the relative surface energy between the solid body and the liquid, and γ_{lv} is the relative surface energy between the liquid and the vapor. The angle θ can assume any value between 0 and π depending on the relationships of the three relevant surface energies. If the contact angle is smaller than $\pi / 2$, it is said that the liquid *wets* the given surface. At contact angles larger than $\pi / 2$ we then talk about "*repelling*" surfaces. When dealing with water, surfaces with a contact angle smaller than $\pi / 2$ are called *hydrophilic*, while surfaces with a contact angle larger than $\pi / 2$ are called *hydrophobic.* The meaning of the differentiating between contact angles larger and smaller than $\pi / 2$ is first clarified through the investigation of capillary bridges. At a contact angle of zero it is said that complete wetting takes place. In this case, the droplet would completely disperse and form an infinitely thin film (as seen macroscopically). Complete wetting exists when the condition

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \tag{4.2}$$

is met. For $\gamma_{lv} < \gamma_{sv} - \gamma_{sl}$, the liquid spreads out until it forms a film with a thickness of a few molecular diameters. The dispersion of thin liquid films is known as “creep.” The driving force for this process is given by the difference

$$\gamma_{creep} = \gamma_{sv} - \gamma_{sl} - \gamma_{lv} \,. \tag{4.3}$$

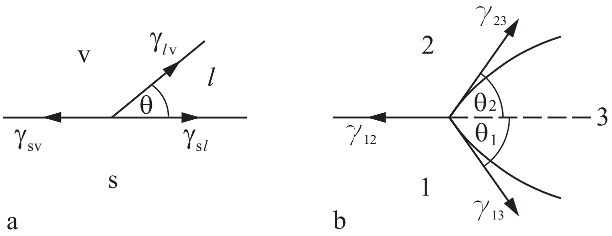

Fig. 4.3 Calculating the equilibrium of the contact line: (a) between a liquid and a solid body, (b) between two liquids.

In the equilibrium equation (4.1) we have accounted for only the force equilibrium in the horizontal direction. The surface tension component in the vertical direction is in equilibrium with the reaction force from the rigid body**.** If we are dealing with the contact between two liquids (or between two solid bodies in thermodynamic equilibrium, for example, after an extended exposure to high temperatures), then both components must be taken into account (Fig 4.3 b). Hence, two characteristic contact angles can be provided from the equations

$$\gamma_{12} = \gamma_{13} \cos\theta_1 + \gamma_{23} \cos\theta_2 \quad \text{and} \quad \gamma_{13} \sin\theta_1 = \gamma_{23} \sin\theta_2 \,. \tag{4.4}$$

Whether or not a liquid completely wets a surface, is dependent on the three surface energies of the three interfaces. It has been empirically shown, however, that the wettability is already for the most part defined by the relationship between the surface energies of the solid body and the liquid. If the surfaces can only interact through van der Waals forces, then the surface energies at the interfaces of both substances can be estimated as[1]

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[1] F.M. Fowkes, Dispersion Force Contributions to Surface and Interfacial Tensions, Contact Angles and Heats of Immersion. In Contact Angle, Wettability and Adhesion, American Chemical Society, 1964, pp.99-111.

$$\gamma_{sl} \approx \gamma_s + \gamma_l - 2\sqrt{\gamma_s \gamma_l}\ . \tag{4.5}$$

It can be noted that this estimation differs from the estimation of the surface energy of solid bodies (3.16), where the physical origins of the surface energy is different (for solids it is the force that is required to separate the bodies, while for liquids it is the force required to reconstruct them during stretching). The energy (4.5) vanishes in contact between identical liquids.

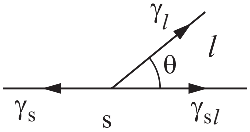

Fig. 4.4 Estimation of contact angles for known surface energies between a liquid and a solid body.

From the force equilibrium of the boundary (see Fig. 4.4) observing (4.5) we get

$$\gamma_s = \gamma_l + \gamma_s - 2\sqrt{\gamma_l \gamma_s} + \gamma_l \cos\theta\ . \tag{4.6}$$

From which we can then calculate the contact angle

$$\cos\theta = 2\sqrt{\frac{\gamma_s}{\gamma_l}} - 1\ . \tag{4.7}$$

The right side of this equation assumes the value 1 (contact angle $\theta = 0$, complete wetting) at $\gamma_s \approx \gamma_l$. The value -1 ($\theta = \pi$, complete repelling) is never reached. The contact angle is equal to $\pi/2$ for $\gamma_l \approx 4\gamma_s$. The driving force for creep (4.3) is given by $\gamma_K = \gamma_s - \gamma_{ls} - \gamma_l = -2\gamma_l + 2\sqrt{\gamma_l \gamma_s} = 2\left(\sqrt{\gamma_l \gamma_s} - \gamma_l\right)$. It reaches a maximum at $\gamma_l \approx \gamma_s / 4$.

Oils with very small surface energies (e.g. silicon oil with $\gamma_l \approx 2{,}1 \cdot 10^{-2}$ J/m^2) wet all solid surfaces (with the exception of Teflon, see Table 3.1). They can inconspicuously contaminate manufacturing plants. The spreading of lubricants can lead to disturbances in parts of machines and loss of function, because they can flow out of friction sites where lubrication is needed. This unwanted spreading can be impeded through the epilamization process. During epilamization, the surface tension of the machine part is reduced by the application of a film which makes the solid surface repellent.

4.2 Hysteresis of Contact Angles

We have so far assumed that no forces other than the surface tension act on the line of contact. If the contact is between a liquid and a solid body, *frictional forces* can also appear in the line of contact. The equilibrium condition (4.1) then changes to

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta \pm f_R , \tag{4.8}$$

where f_R is the frictional force per unit length of the line of contact. The sign of the frictional force is dependent on the direction of the movement of the droplet. Therefore, the actual contact angle will depend on the direction of motion. This phenomenon is called the *hysteresis of the contact angle.* From the hysteresis, the frictional force can be defined. This force is responsible for droplets sticking on macroscopically smooth, sloped surfaces. It is of interest for many technical applications.

The frictional force in the line of contact can be caused by the roughness of the solid surface, its heterogeneity, or the atomic structure of the solid body. These factors lead to the fact that the energy of a droplet is dependent on its position on the solid surface. Thus, static friction is made possible.

4.3 Pressure and the Radius of Curvature

If the surface of a droplet of liquid is curved, then there is a pressure difference between the "outside" and "inside" of the droplet. For a spherical droplet (Fig. 4.5 a), this pressure difference is easy to calculate. If a definite amount of liquid is "pumped" into the droplet, the radius would grow by an amount dR. Thereby, the surface changes by $dA = 8\pi R dR$. The work $dW = (p_1 - p_2) dV = (p_1 - p_2) 4\pi R^2 dR$, which is performed through the difference in pressure, must be equal to the change in the surface energy[2] $\gamma_l dA = \gamma_l 8\pi R dR$. From which:

$$\Delta p = (p_1 - p_2) = \frac{2\gamma_l}{R} . \tag{4.9}$$

If the force of gravity is neglected, then the pressure is constant everywhere inside of the droplet. Therefore, the radius of curvature must also be constant: *A droplet takes the form of a sphere.* On flat solid surfaces, it is always a portion of a sphere (Fig. 4.2).

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[2] We denote the surface tension of the vapor-liquid interface, which is normally simply referred to as the surface tension of the liquid, as $\gamma_l = \gamma_{lv}$.

For non-spherical surfaces it is generally true that

$$\Delta p = \gamma_l \left(\frac{1}{R_1} + \frac{1}{R_2} \right), \tag{4.10}$$

where R_1 and R_2 are the *principal radii of curvature*. Here, we would like to stress that in Equation (4.10), the radii of curvature can also be negative. The sign of the radius of curvature is defined by whether the center of the curve lies on the positive or negative side of the surface of the liquid. The radii of curvature have different signs for saddle-shaped surfaces (Fig. 4.5 c).

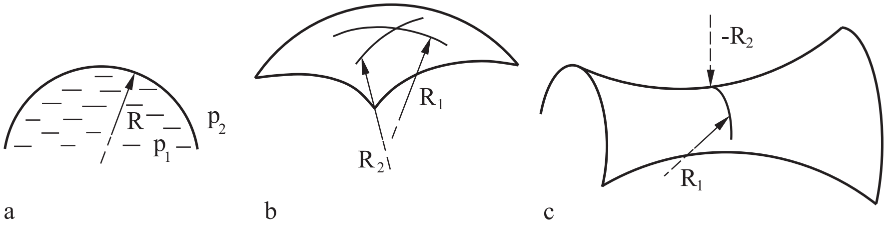


Fig. 4.5 Curved surfaces with different ratios of the principal radii of curvature.

4.4 Capillary Bridges

We observe a rigid cylinder near a solid surface with a small amount of liquid in between. For the sake of simplicity, we assume that both of the "contact partners" are composed of the same material.

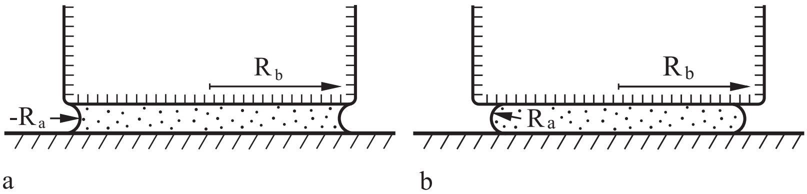


Fig. 4.6 Capillary bridges at a contact angle (a) smaller than $\pi/2$, (b) larger than $\pi/2$.

In equilibrium, the liquid forms a capillary bridge, which has two radii of curvature. The largest radius R_b is always positive. The sign of the smaller radius depends on if the contact angle is larger or smaller than $\pi/2$. For small contact angles, in the case of wetting of the surface, R_a is negative. There is a reduced pressure in the liquid, which leads to a force that we call *capillary force*. In order to keep the system in equilibrium, an opposing reaction force must be applied. The capillary force is calculated by multiplying the pressure difference by the area of the capillary bridge:

$$F_{cap} = A\gamma_l \left(\frac{1}{R_b} - \frac{1}{R_a} \right) \approx -A\gamma_l \frac{1}{R_a}, \tag{4.11}$$

where $|R_a| \ll |R_b|$ is assumed. However, if the surface is not wettable by a given liquid (contact angle larger than $\pi/2$), then the contact partners repel each other. This property explains the origin of the distinction between "wettable" and "repelling" surfaces (or hydrophilic and hydrophobic surfaces in the case of water) depending on if the contact angle is larger or smaller than $\pi/2$.

4.5 Capillary Force between a Rigid Plane and a Rigid Sphere

We consider a capillary bridge between a rigid sphere and a rigid plane of the same material, for which the contact angle is zero (complete wetting), Fig. 4.7. Let the radius of the bridge be *r* and the radius of the sphere *R*. The height of the capillary bridge is $h \approx r^2 / 2R$ and the surface $A = \pi r^2$. The (small) radius of curvature is clearly $r_0 = h/2$. For $|r_0| << |r|$, the resulting pressure difference in the liquid is

$$\Delta p = -\frac{\gamma_l}{r_0} = -\frac{2\gamma_l}{h} = -\frac{4\gamma_l R}{r^2}. \tag{4.12}$$

The capillary force is, therefore,

$$F_{cap} = A\Delta p = -\pi r^2 \frac{4\gamma_l R}{r^2} = -4\pi\gamma_l R. \tag{4.13}$$

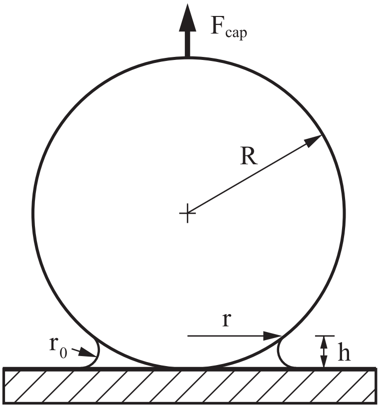


Fig. 4.7 A capillary bridge between a rigid plane and a rigid sphere.

It is proportional to the radius of curvature of the sphere and independent from the amount of liquid. The force, F_{cap}, which is required to pull the sphere from the surface has the same magnitude.

4.6 Liquids on Rough Surfaces

Up to now, we have assumed that the solid surface is ideally smooth and even. That is almost never the case in reality. Roughness leads to a macroscopically observable change in the contact angle. Depending on the type of roughness, a variety of situations can occur. If the level of roughness is small, then the liquid will remain in complete contact with the solid body over the entire area (in Fig. 4.8, to the right of the boundary of the droplet). If there is no pressure difference between the atmosphere and the liquid, then the sum of the radii of curvature for every point of the surface must be zero.

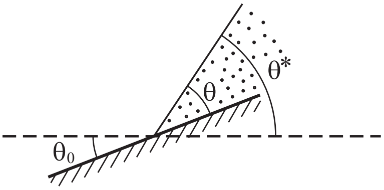


Fig. 4.8 Surface of a liquid in contact with an inclined solid surface.

Because of this, the surface on average, is flat and at a small distance from the contact line inclined at an angle θ^* from the horizontal (Fig. 4.8). The horizontal component of the uniform load in the contact is

$$\gamma_{sv}\cos\theta_0 - \gamma_{sl}\cos\theta_0 - \gamma_{lv}\cos\theta^* . \tag{4.14}$$

In order for the boundary line to remain in equilibrium, the average linear force must be zero:

$$\left(\gamma_{sv} - \gamma_{sl}\right)\left\langle\cos\theta_0\right\rangle - \gamma_{lv}\cos\theta^* = 0 . \tag{4.15}$$

Observing equation (4.1) it follows that

$$\cos\theta^* = \left\langle\cos\theta_0\right\rangle \cdot \cos\theta \tag{4.16}$$

(R.N. Wenzel, 1936). Because $\left\langle\cos\theta_0\right\rangle$ is always smaller than 1, the visible contact angle for hydrophilic surfaces is always larger than the “real” contact angle, while for hydrophobic, it is always smaller. This equation can also be derived purely from thermodynamic reasoning.

If the gradient of the roughness profile is large, then the liquid can remain on the peaks of the roughness (Fig. 4.9). If the surface has a form as is shown in

Fig. 4.9 a, then the liquid remains atop the peaks only if the contact angle is larger than $\pi - \theta_{\max}$, where $\theta_{\max}$ is the maximum angle of elevation of the surface. If the liquid were then to be acted on by some additional pressure, its surface would curve and it would press deeper into the recesses of the roughness until it reaches an instability point and the entire surface is wet. This can, however, be hindered by air trapped in the recesses. If the surface roughness has the form as in Fig. 4.9 c, then fluids with a contact angle of less than $\pi / 2$ can remain hanging without coming into complete contact with the surface.

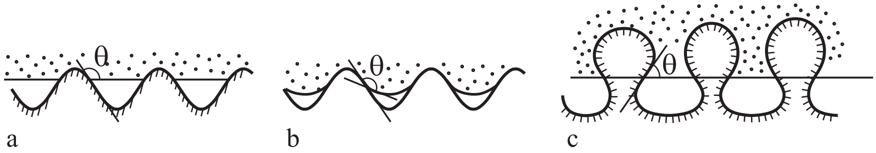


Fig. 4.9 Sheet of fluid on a rough surface.

4.7 Capillary Forces and Tribology

There are several situations in which the capillary forces promote the movement of liquids. If a droplet is at rest on a curved surface, then its energy grows with the curvature. Therefore, the droplet is repelled by areas of high curvature, especially at edges or sharp points (Fig. 4.10, see also Problem 2 in this chapter). If a liquid is in a capillary or crevice of varying width, then capillary forces cause it to move in the direction of the smaller crevice width or capillary diameter.

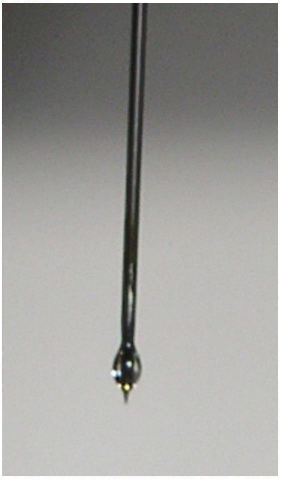


Fig. 4.10 Droplet is repelled from a sharp point.

This effect can be used to keep lubricants in place. In narrow joints, these forces are so large that they allow for life-long lubrication without reapplication. Such examples can be found in clockwork, measurement instruments, electricity meters, etc. If oil is wanted to reach such an area, the described effect can be used in the design of the joint so that the oil moves in the direction of the narrowest point.

Problems

Problem 1: Determine the total surface energy of a drop of liquid resting on a solid surface.

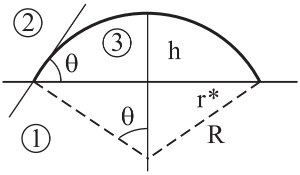


Fig. 4.11 Droplet of liquid on a flat, solid surface.

Solution: Using the notation defined in (Fig. 4.11), we obtain the following equations for A as the surface area of the droplet, V as its volume, θ as the contact angle, and r^* as the "contact radius":

$$A = 2\pi R h, \quad V = \frac{\pi h^2 (3R - h)}{3}, \quad \cos\theta = \frac{R-h}{R}, \quad r^{*2} = 2Rh - h^2 .$$

The surface energies are related through the equation

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} .$$

For both geometric values R and h, which are completely determined by the configuration of the droplet, we have

$$R^3 = \frac{3V}{\pi (1-\cos\theta)^2 (2+\cos\theta)}, \quad h = R(1-\cos\theta) .$$

Therefore, we obtain the following expression for the sum of all of the surface energies:

$$E = (\gamma_{sl} - \gamma_{sv}) \pi r^{*2} + \gamma_{lv} A = \frac{3\gamma_{lv} V}{R} = \gamma_{lv} \left(9V^2 \pi (1-\cos\theta)^2 (2+\cos\theta)\right)^{1/3} .$$

For a constant surface tension γ_{lv} of the liquid, it is a monotonically increasing function of the contact angle. For a heterogeneous surface, the droplet would be *repelled from areas with larger contact angles*.

Problem 2: Determine the total surface energy of a drop of liquid resting on a slightly curved surface (radius of curvature R_0). Let the contact angle be $\pi/2$ (Fig. 4.12).

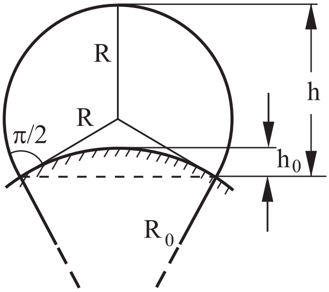


Fig. 4.12 Droplet of liquid on a curved surface. The contact angle is equal to $\pi/2$.

Solution: The contact angle is $\pi/2$ when $\gamma_{sv} = \gamma_{sl}$. In this special case, the surface energy is reduced to $E = \gamma_{lv} A$. Through geometric reasoning we obtain

$$h = R + \frac{R^2}{\sqrt{R_0^2 + R^2}}, \qquad h_0 = \frac{R^2}{\sqrt{R_0^2 + R^2}} + R_0 - \sqrt{R_0^2 + R^2}\,.$$

The volume, $V_T = \frac{\pi}{3}\left(h^2(3R - h) - h_0^2(3R_0 - h_0)\right)$, and surface area of the droplet, $A = 2\pi Rh$, are calculated using the terms up to the first-order of the curvature $\kappa = 1/R_0$:

$$V_T = \frac{2\pi R^3}{3} + \frac{3\pi R^4}{4}\kappa, \qquad A = 2\pi R^2 + 2\pi R^3 \kappa\,.$$

For a small change in the radius R and the curvature κ (from the value $\kappa = 0$), the volume and surface change as follows:

$$dV_T = 2\pi R^2 dR + \frac{3\pi R^4}{4} d\kappa, \qquad dA = 4\pi R dR + 2\pi R^3 d\kappa\,.$$

If we maintain a constant volume, then $dR = -\frac{3}{8} R^2 d\kappa$. The change in the surface is then $dA = \frac{1}{2}\pi R^3 d\kappa$. The "extra energy," which is related to the curvature, is therefore,

$$\Delta E \approx \frac{\pi \gamma_{lv} R^3}{2R_0} = \frac{3V_T \gamma_{lv}}{4R_0}.$$

The surface energy increases with the curvature of the base surface. Hence, the droplet is *repelled from areas with a larger curvature.*

Problem 3: Determine the capillary force between a curved surface with the Gaussian radii of curvature R_1 and R_2 and a plane. The surfaces of both bodies are assumed to be completely wettable.

Solution: Because the pressure in the liquid is overall constant, the radius of curvature and the height $h = 2r_0$ must also remain constant. The form of the contact area is determined by the constraint

$$\frac{x^2}{2R_1} + \frac{y^2}{2R_2} = h.$$

The semi-axes of this ellipse are equal to $\sqrt{2R_1 h}$ and $\sqrt{2R_2 h}$, and its area is $A = 2\pi h \sqrt{R_1 R_2}$. Thus, the capillary force is calculated as

$$|F| = \frac{\gamma}{r_0} A = 4\pi\gamma\sqrt{R_1 R_2}.$$

Problem 4: Determine the capillary force between a sphere and a plane. The contact angles are θ_1 and θ_2.

Solution: $F = 2\pi R\gamma(\cos\theta_1 + \cos\theta_2)$.

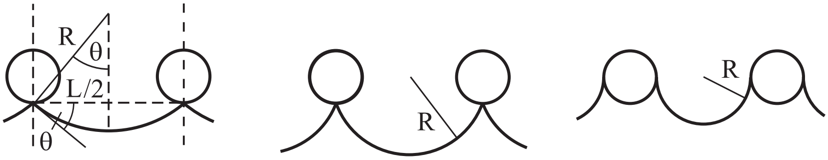
Problem 5: Determine the overhead pressure that is necessary to force a liquid through a lattice of round, parallel rods (Fig. 4.13). Let the distance between the rods be L.

Solution: If the overhead pressure on the liquid is Δp, then it forms a uniformly curved surface with a radius of curvature of R (Fig. 4.13):

$$\frac{1}{R} = \frac{\Delta p}{\gamma_{lv}}.$$

At the same time, the angle between the surfaces of the rod and the liquid must equal to the contact angle θ. If the pressure rises, then the liquid is pressed even farther between the rods, until a critical condition is met. For contact angles of $\theta \le \pi/2$, this critical condition is met when the contact points of the liquid come together from both sides of the rod (Fig. 4.14 a, b). For contact angles $\theta > \pi/2$ it is met sooner. In the case of a completely repellant surface, contact angle $\theta = \pi$, the critical condition is shown in Fig. 4.14 c.

Fig. 4.13 Liquid on a lattice of straight rods.



a b c

Fig. 4.14 Critical configurations for (a) $\theta < \pi / 2$, (b) $\theta \approx \pi / 2$, (c) $\theta \approx \pi$.

For wettable surfaces ($\theta < \pi / 2$) it follows, from Fig. 4.14 a, that in the critical condition $\frac{1}{R} = \frac{2}{L} \sin\theta$. For the maximum possible overhead pressure, we obtain

$$\Delta p = \frac{2}{L} \gamma_{lv} \sin\theta .$$

It reaches a maximum for rods with $\theta = \pi / 2$ and is equal to

$$\Delta p_{\max} = \frac{2}{L} \gamma_{lv} .$$

Problem 6: A cylindrical pin (mass m, length L) lays on the surface of water (Fig. 4.15). Determine the displacement of the pin beneath the undisturbed surface of the water and the maximum weight that the surface can hold, under the assumption that inclination of the surface of the water is small at every point.

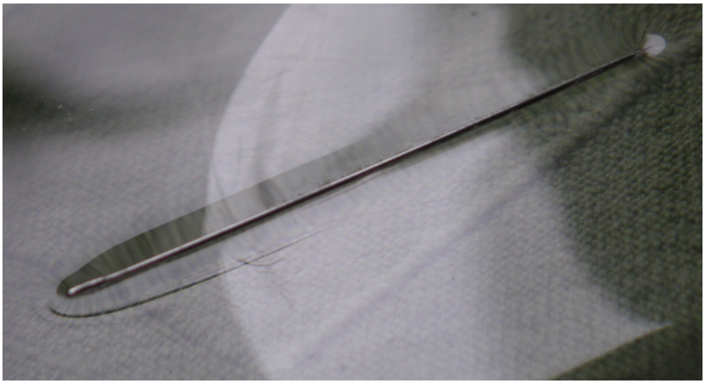


Fig. 4.15 A pin floating on the surface of the water.

Solution: In the solution, we will use the diagram in Fig. 4.16. The pressure difference at point (x, z) on the surface can be calculated either by using (4.10), or by calculating the hydrostatic pressure difference at a depth of z :

$$\Delta p = \gamma_{lv} / R = \gamma_{lv} z'' = \rho g z \ .$$

The solution of the differential equation with respect to $z(x)$ with the boundary condition of $z \to 0$ for $x \to \infty$ yields:

$$z = A \exp\left(-\left(\frac{\rho g}{\gamma_{lv}} \right)^{1/2} x \right).$$

The displaced water volume is equal to

$$V = 2L \int_0^\infty z(x) dx = 2AL \left(\frac{\gamma_{lv}}{\rho g} \right)^{1/2} .$$

In equilibrium, the weight is equal to the buoyancy force, according to Archimedes' buoyancy principle, thus, $\rho V = m$. For the depth that the pin has sunk, it follows that

$$z(0) = A = \frac{m}{2L} \left(\frac{g}{\rho \gamma_{lv}} \right)^{1/2} .$$

The angle of inclination of the surface at $x = 0$ is determined using

$$\tan \varphi = \frac{mg}{2L\gamma_{lv}} .$$

It is easy to see, geometrically, that the contact angle θ cannot be smaller than φ . The maximum weight that the surface can hold is, therefore, calculated as

$$mg = 2L\gamma_{lv} \tan \theta \ .$$

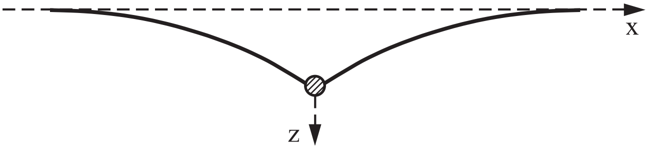


Fig. 4.16 A cylindrical pin supported by the surface of the water.