# Chapter 5
Water is wet

5-1. Surface tension

In the preceding chapter, we considered three types of forces, internal pressure, gravity and friction. Actually, there is a fourth type of force in fluids, but that one was omitted because it does not act inside the volume of a fluid; it acts only at the interface between a liquid and some other immiscible fluid[1]. It is called *surface tension*.

The nature of surface tension is rather complicated. In brief, molecules in a liquid almost always have an electrical polarization, and all is well when a molecule is completely surrounded by neighbors like itself; it is equally attracted from all sides. But this is not the case for molecules on the edge, which lack neighbors on one side; some of their electrical polarization is not balanced. These molecules compensate by being more attracted to their side neighbors. This is manifested at the macroscopic level as a tangential pull along the surface, as if the surface where an elastic membrane in slight tension. When the surface is straight the pull on the left is matched with the pull form the right, and nothing special happens. But when the water surface is curved (Figure 5-1) the pulling forces on the left and on the right have different angles, and although their size may be equal to each other, they do not equilibrate. This results in a net normal force onto the fluid, pulling in the direction of flattening the bump.
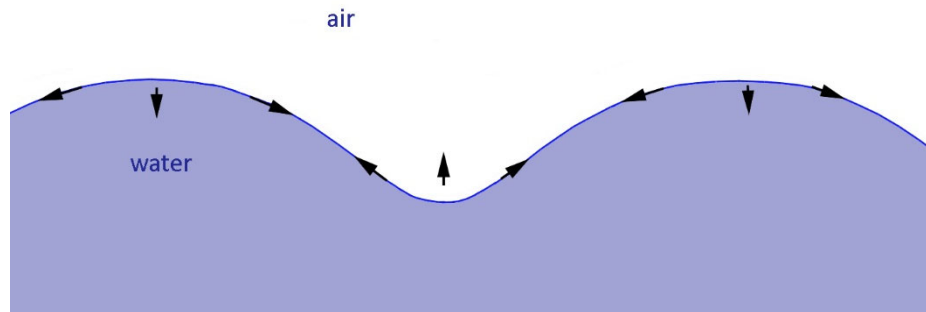
Figure 5-1. Surface tension forces on a bumpy surface of a liquid.

This normal force on the liquid surface generates an added pressure Δp in the liquid that, in first approximation, is proportional to the curvature of the surface. The formula is

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[1] Immiscible fluids are fluids that resist being mixed with each other. The most common occurrences are air with water and water with oil. These fluids separate from each other by gravity, forming a well defined interface.

$$\Delta p = \sigma \left(\frac{1}{R_x} + \frac{1}{R_y} \right),$$
(5-1)

in which the bracketed quantity is the total curvature of the surface, which may curve in one or both directions along the surface (R_x and R_y are the radii of curvature in the x- and y-directions, respectively), and σ is a coefficient of proportionality called the surface tension. Its units are N/m, and Table 5-1 provides values for common liquids.

Table 5-1. Values of the surface tension coefficient for common liquids. Note that values vary with temperature.

Liquid		Temperature T °C	Surface tension σ N/m
Water		10	0.0742
		20	0.0728
		30	0.0712
		40	0.0696
		50	0.0679
		60	0.0662
		70	0.0644
		80	0.0626
		90	0.0608
Soapy water		20	0.0250 – 0.0450
Benzene		20	0.0289
Ethylene glycol		20	0.0477
Glycerol		20	0.064
Mercury		20	0.425
Milk	38% cream	25	0.0314
	3.5% cream	25	0.0419
	skim	25	0.0473

An interesting case arises when the surface closes onto itself as it does when water forms droplets. When water flows slowly from a faucet (Figure 5-2), its stream can be fairly narrow, and as the water accelerates in free fall, the stream narrows further. At one point, surface tension becomes sufficient to pinch the water into droplets.

Figure 5-2. Water flowing from a faucet forming droplets when the water stream narrows. (*Photo credit*: ???)

We can calculate the pressure inside a water droplet that is in excess to the atmospheric pressure. Assuming a spherical drop, the two radii of curvature are each equal to the half the diameter D .and Equation (5-1) yields:

$$\Delta p = \frac{4\sigma}{D} \, .$$
(5-2)

Table 5-2 below shows how the pressure inside a water droplets increases with decreasing size. Note how it quickly rises as the droplet becomes smaller.

Table 5-2. Gage pressure inside a water droplet caused by surface tension at 15°C, as a function of the diameter of the droplet.

Droplet diameter	1 mm	0.1 mm	10 μm	1 μm
Δp	294 Pa	2.94 kPa	29.4 kPa	294 kPa
	0.0029 atm	0.029 atm	0.290 atm	2.90 atm

Water also coalesces into droplets during rain and in waterfalls (Figure 5-3). The refraction of sunlight gives each droplet a white color, making clouds and cascades appear bright white, a pleasant sight to the eye. The splashing of droplets in the water pool below a waterfall also generates a soothing sound, which would be quite different if the falling water were coming down as a sheet instead of droplets.
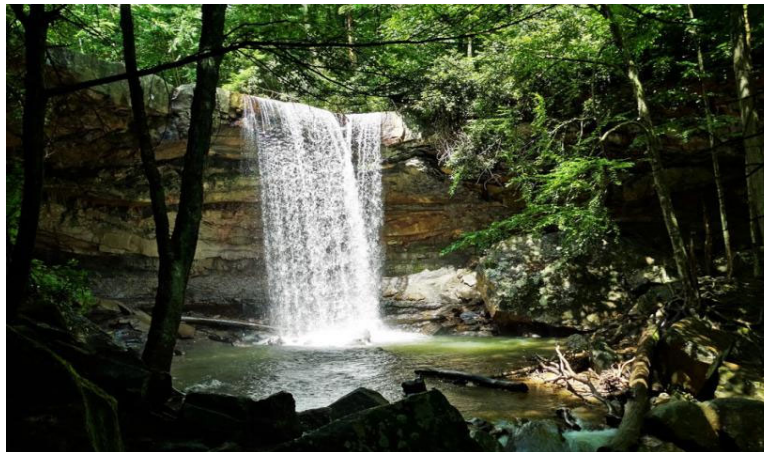
Figure 5-3. Water flow breaking into droplets at Cucumber Falls in Pennsylvania, USA . (*Photo credit*: The Grass Outlet)

When a liquid such as water or milk not in the form of small droplets hits a surface or sloshes over the rim of a container, it creates a *splash*, the complexity of which is controlled by surface tension seeking to coalesce pieces and parcels of the liquid into clumps. Figure 5-4 shows a couple of examples.
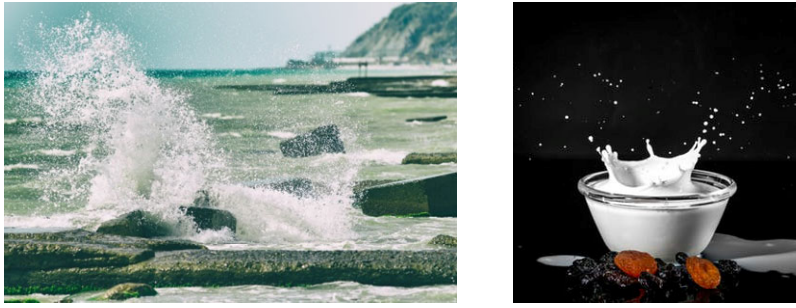
Figure 5-4. A couple of situations illustrating the formation of droplets by surface tension in a splashing liquid. (*Sources*: Seascape by Stanislav Kondratiev, milk splash captured by George Desipris)

5-2. Wetness

The situation becomes even more interesting where the interface between the two fluids meets a solid boundary because then the surface tension has to end on that boundary. The properties of the material surface come into play. An example is the case of water droplets resting on a solid surface, as illustrated in Figure 5-5. The boundary can either have a repulsion or an affinity for the liquid. In the case of water, we say that the surface is either *hydrophilic* or *hydrophobic* depending on whether it likes water or not (Figure 5-6). In the hydrophilic case, the affinity of the material surface for the water causes it to spread, and the contact angle is less than 90° and often much smaller; we call this *wetness.* In the hydrophobic case, the surface resists the water and prevents it from spreading; the contact angle is larger than 90° causing the water to form a bulge, which we call a *drop*. The grass blade seen in Figure 5-5 appears to be hydrophobic.

Figure 5-5. Water on a blade of grass separating itself into distinct droplets. (*Photo credit*: The Grass Outlet)
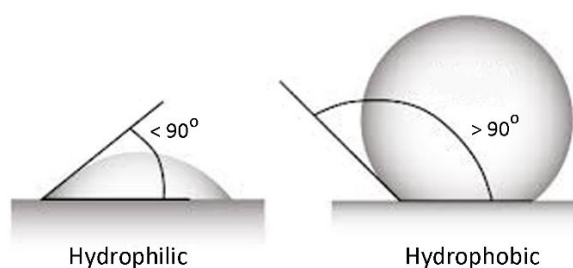
Figure 5-6. The difference between a hydrophilic (water loving) and hydrophobic (water repellent) surface. The angle between the solid boundary and the liquid surface is determined by the chemistries of both.

Wax is a famously hydrophilic material. Before Dupont™ invented Teflon® and other water repellents, people used to coat fabrics with wax to make them impermeable.

Table 5-3. Contact angles between liquids and solid surfaces. (*Source*: Young & Freedman, 2011)

Liquid		Solid	Contact angle
Water			
Acetic acid (vinegar)			
Carbon tetrachloride		soda-lime glass lead glass fused quartz	0°
Diethyl ether			
Ethanol			
Glycerol			
Water		paraffin wax	107°
		silver	90°
Methyl iodide		soda-lime glass	29°
		lead glass	30°
		fused quartz	33°
Mercury		soda-lime glass	140°

A word of caution when you go out camping: Don't touch the tent when it's wet! Common tent materials are made rainproof with finely woven hydrophobic fabrics so that the surface tension of water can bridge the pores in material and not seep through. But if you touch the tent with your finger, you can break the surface tension (like popping a bubble), and the rain will drip through.

5-3. Walking on water

Hydrophilic/hydrophobic behavior has been exploited by nature in numerous circumstances. Perhaps the most evident is the walking of insects on water. This is possible because their light weight is not enough to overcome the surface tension on their hydrophobic feet.

Consider the water strider (Figure 5-7). Its weight is mg, and each of its six legs are like little cylinders that contact the water over a length ℓ. If the wetting angle is θ, as defined in Figure 5-7b, the upward force on each leg, counting both sides of the cylindrical legs, is

$$F_{leg} = 2\sigma\ell\cos\theta \,, \qquad\qquad\qquad (5\text{-}2)$$

and the balance of forces $mg = 6F_{leg}$ tells how long the water strider's legs need to be to enable it to walk on water:

$$\ell = \frac{mg}{12\sigma\cos\theta} \,. \qquad\qquad\qquad (5\text{-}3)$$

Figure 5-7. How surface tension allows insects, such as the water strider, to walk on water. (*Photo credit:* Chegg.com/homework-help, modified)

(a)   (b)
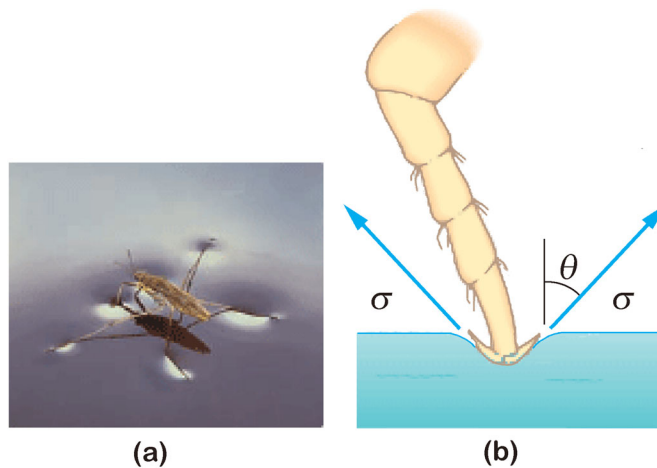
Let us see if this is realistic. A water strider weighs about 10 mg, the angle θ is 180° minus the wetting angle about 107°, and the surface tension at 10°C is 0.0742 N/m. This yields:

$$\ell = \frac{(10\times10^{-6}\text{ kg})(9.81\text{ m/s}^2)}{(12)(0.0742\text{ N/m})\cos(180^0 - 107^0)} = 3.8\,\text{cm} \,.$$

This is approximate as it ignores the upward buoyancy of the partly submerged legs, which helps alleviate the need for surface tension, but it does show that the water strider absolutely needs all of six legs for support, should prefer cold water (for its higher surface tension), and can't catch too large of a prey lest it would sink with it. This little bug lives on the edge!

Figure 5-8. Surface tension allows a butter-coated metallic paper clip to float on water. (Photo by the author)

Likewise, a slightly buttered[2] paper clip carefully placed on the surface of water can be made to float even though steel is several times more dense than water (Figure 5-8). When the surface is agitated to break up the surface tension, the clip quickly sinks.

Plants and trees use a network of hydrophilic little tubes, called xylem, to bring water and nutrients from their roots up to their leaves. The material of these little tubes is wetted, effectively creating an angle of 180º between water and tube wall, which means that the surface tension is optimally directed in the vertical direction. If the inner diameter of a tube is d, the upward force on the periphery of the tube is $\pi d \sigma$ and should be able to hold water up to a height h such that:

$$\rho g h \frac{\pi d^2}{4} = \pi d \sigma \quad \rightarrow \quad h = \frac{4\sigma}{\rho g d}. \tag{5-4}$$

Thus, the narrower the tubes, the higher the water can rise. Most plants have d no greater than 40 μm, thus permitting a maximum rise of 76 cm. This is fine with most flowers and bushes, but what about trees that grow much taller? Their trick is to partially fill their xylem tubes with hydrophilic cells, thus reducing the effective passage width to about 10 nm, by a factor of around 4000. The corresponding h rises to 3 km! This is far higher than we observe trees to be, and we conclude that the height of trees must be limited by something else[3] than the surface tension pull in its xylem.

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[2] The buttering is essential to create a hydrophobic surface on the metal. Wax also works but is less available than butter in a kitchen.

[3] Research (Koch *et al.*, 2004) has shown that the limit is set by energy: The higher a tree grows, the more energy it needs to spend to send water to its top leaves; water and nutrient-deprived top leaves tend to be smaller and to produce less energy by photosynthesis. A tree may thus grow until the energy produced by its top leaves equals the energy that it takes to bring water up to them; beyond this height, top leaves are no longer assets but liabilities. The theoretical limit is between 120 and 133 m (400 to 426 ft). The tallest tree in the world, a California redwood, stands 116 m (379 feet) tall.

An interesting application is the clinical test for jaundice: Normal urine has a surface tension of about 0.066 N/m, but if bile is present (as is the case in jaundice), it drops to about 0.055 N/m. In the Hay test, powdered sulfur is sprinkled on the urine surface. It floats on normal urine, but sinks if the surface tension is lowered by the bile. Another medical application is in disinfection: Disinfectants are usually solutions of low surface tension, which allow them to spread out on the cell walls of bacteria and disrupt them.

5-4. Drops and puddles on a surface

The drop of rain on the grass blade (Figure 5-5) is a situation where surface tension can prevent a finite drop of a liquid from collapsing. It turns out that one can estimate the maximum thickness that a drop can have before it spreads as a more extended puddle. Figure 5-9 shows the balance of forces at the edge of a drop or puddle: The gravitational force created the hydrostatic pressure over thickness h of the liquid pushing from left to right,

$$F_p = \int_0^h \rho g (h-z) dz = \frac{1}{2} \rho g h^2 \qquad (5\text{-}5)$$

per unit width, is resisted by the surface tension σ pulling along the top where the surface is horizontal and by the surface tension at the bottom where the liquid surface meets the underlying solid surface, which is $\sigma \cos(\pi - \theta) = -\sigma \cos \theta$, with θ being the angle that the liquid forms with the solid surface as indicated in Figure 5-9.
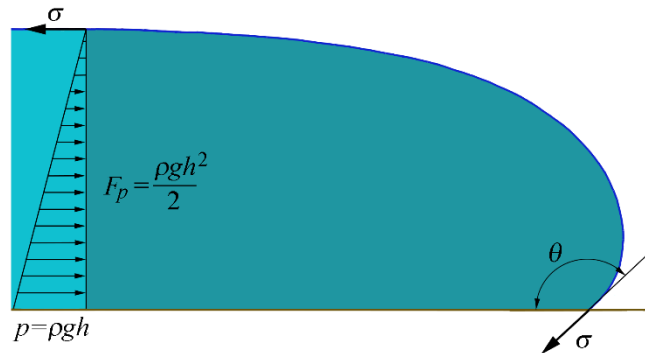
Figure 5-9. Balance between hydrostatic pressure force and surface tension forces at the edge of a drop or puddle.

The balance of forces is then:

$$\frac{1}{2} \rho g h^2 = \sigma - \sigma \cos \theta,$$

from which we deduce the thickness h that the puddle must be:

$$h = \sqrt{\frac{2\sigma\,(1-\cos\theta)}{\rho g}}\;.$$ (5-6)

Here, h = thickness of puddle (in m), σ = surface tension of the liquid (in N/m), θ = angle at which liquid attaches to the surface, ρ = liquid density (in kg/m³), and g = gravitational acceleration (= 9.81 m/s²). For water at 10°C on a hydrophobic surface, σ = 0.0742 N/m, $\theta \approx 180°$, ρ = 1000 kg/m³, leading to h = 5.5 mm, which is what we ordinarily observe.

5-5. Bubbles

When air finds itself under water, it breaks up into round bubbles. Why? Imagine a horizontal slab of air at some water depth. The buoyancy of air underwater makes the air want to rise to the surface, pushing against the water above it. This push against water creates a pressure that surface tension first attempts to resist. Surface tension can exert a push back onto the air only if the water-air interface is curved, but then curvature on the top demands continued curvature, and the net effect is a curved surface that closes into a sphere englobing the parcel of air. If the diameter of the bubble is D, the radii of curvature in each direction along the sphere are $R_x = R_y = D/2$, and formula (5-1) gives the pressure exerted by water onto the air, which is in addition to the hydrostatic pressure of water at the depth of the bubble:

$$\Delta p = \frac{4\sigma}{D}\;.$$ (5-7)

Because air is so much lighter than water, the pressure of air inside the bubble has virtually no hydrostatic gradient and is thus uniform. With a uniform internal pressure, the curvature of the containing surface must also be uniform, and this is why the spherical shape is the most common one assumed by bubbles. The toroidal shape is another that provides uniform pressure (Figure 5-10), but it is rather difficult to form and thus does not arise naturally.

Figure 5-10. Toroidal air bubbles produced by the breathing of a person at the bottom of a swimming pool. (*Source*: SwimSwam, Best underwater swimming photos of 2018)

Bubbles are buoyant and rise. The larger ones have more buoyancy and rise faster than the smaller ones, catching up with them and merging with them. The result is that the bubble size increases with height. Sometimes large bubble caps form (Figure 5-11). The reason why large bubbles break into caps is complicated. It has to do with the flow of water that has to go around as the bubble progresses upward, like a ship hull that needs to push water aside to make its way through it.

Figure 5-11. After repeated capture of smaller bubbles, large underwater bubbles degenerate into spherical caps. (*Source*: Alamy stock photo)

5-6. Surfactants and foam

A surfactant[4] is a chemical that reduces the surface tension of a liquid in which it is dissolved. It makes the liquid wetter. Common examples are soaps and detergents, with the difference that soaps are made from natural ingredients, such as plant oils or acids derived from animal fat, whereas detergents are synthetic. They all derive their chemical action from their ambivalence: They are long molecules with a water-loving (hydrophilic) head and a water-repellent (hydrophobic, oil-soluble) tail, as depicted in Figure 5-12.

Figure 5-12. Sketch of a surfactant molecule showing its water-loving head and water-repelling tail.

Inside water, the surfactant molecules come together to form so-called *micelles*, which are bunches of surfactant molecules with their heads forming an outward skin facing the water and their water-repelling tails enclosed inside to avoid contact with water, as shown in Figure 5-13a. This arrangement necessitates the collocation of a fairly large number of surfactant molecules, and, so, when stirring or any other flow disturbance occurs, the micelles are disrupted, and their pieces look for the next most favorable location, which is along the surface of the water. There, they orientate themselves with heads dipped into the water and tails sticking out away from water, as shown in Figure 5-13b. The latter configuration significantly lowers the surface tension of the water.
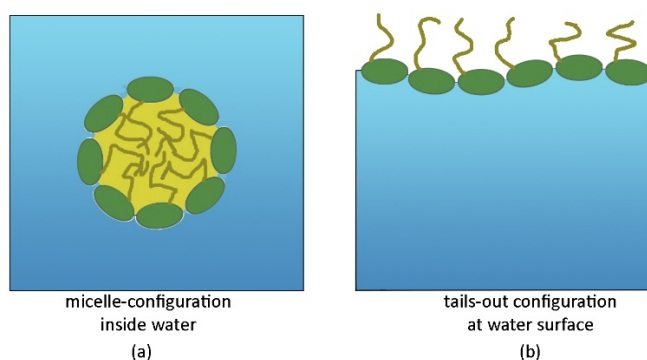
Figure 5-13. Arrangements of surfactant molecules: (a) micelle-configuration inside water, and (b) tails-out at the surface of water.

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[4] The word surfactant is a portmanteau for surface-active agent.

A major application is the spraying of surfactants on oil spills above water to accelerate the dispersion of the oil under wind and waves. A thinner oil film biodegrades more quickly into harmless products than a thicker oil film. If the remedial action is to suck the oil from the water surface with a vacuum-type of device, a surfactant is not used to keep the oil film as thick as possible.

In the washing of clothes, the constant agitation of the water disrupts both micelles and surface alignment, leaving surfactant molecules looking around for other desirable spots. When the detergent tails find grease and dirt on clothing, they go stick there making detergent molecules act as grease hooks, but the attractive force between the heads and the water is so strong that the grease is pulled away from the clothes. The pieces of grease become completely wrapped by detergent molecules (as in Figure 5-13a but with a piece of grease in the middle, like prisoners in the midst of guards, and float away in the water. Voilà! The clothes have become cleaned.

Foam is created by a large accumulation of gas bubbles that have reached the surface of a liquid, assisted by the presence of a soap, detergent, or other surfactant. The ambivalent hydrophilic-hydrophobic property of the surfactant helps spread water into very thin layers that then enclose gas pockets. Although it consists of gas pockets (~95% by volume) enclosed in liquid shells (~5%), the whole behaves rather like a solid, admittedly a very soft solid, but a solid nonetheless. In a bubble bath, you can scoop *suds* with your hands, shaving cream can be applied to the skin without running down like water would, and you may acquire a foam mustache when drinking beer from a glass with a generous layer of foam on top. Whipped cream exhibits solid-like properties because milk fat has excellent hydrophobic properties. Foams are so commonplace that they go by different names depending on the circumstances, froth, lather, mousse, scum, spume (foam on water waves), and suds, but they are all essentially the same.

The key aspect of this solid-like behavior resides in the way bubbles are able to stick to their neighbors or slip past one another. There is a critical point (Durian & Raghavan, 2010), usually around 37% liquid per volume, at which the foam consists of closely packed spherical bubbles of various sizes that touch one another at points, like solid spheres would, with liquid in the many interstices (Figure 10-14, left panel). Below that critical point, many bubbles don't touch their neighbors; any deformation of the foam simply causes bubbles to roll on one another, and the foam behaves as a liquid. But, this subcritical state does not persist, at least on earth. Gravity drains much of the liquid downward and away, collapsing the interstices, and pressing the bubbles against one another. After draining, bubbles touch their neighbors along finite surfaces, called plateau borders (Figure 10-14, right panel). At this stage, the foam resists spatial distortion because distortion of the tight packing demands significant re-arrangement and deformation of the bubbles; the foam has acquired a solid-like consistency.
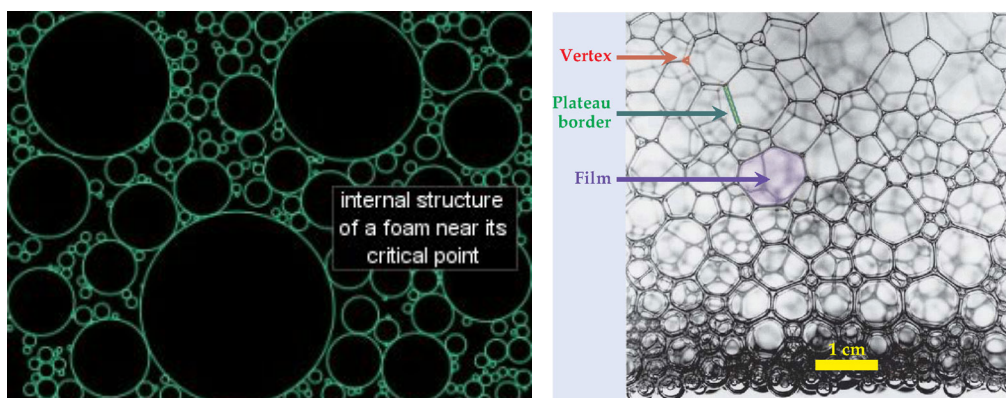
Figure 5-14. Close-ups of two foams showing different distributions in bubble packing. *Left panel*: Foam at its critical point, with closely packed spherical bubbles touching one another tangentially. *Right panel*: Stable foam with bubbles more closely packed than at the critical point; most bubbles touch neighbors along finite surfaces and have polygonal shapes. The close packing seen in the right panel occurs after gravity has drained away most of the liquid from the state shown in the left panel. (*Source*: Durian & Raghavan, 2010)

Foams have a number of practical applications, from bread making to fire-fighting. Perhaps the most common one is the spraying of polymer foam for thermal insulation in buildings. The polymer is chosen for two key properties, first its ability to form a foam and second its ability to dry into a solid[5]. A clever and environmentally friendly use is the *foam toilet*: In such a toilet, there is a soap dispenser in the water tank, and the act of flushing causes water to mix with soap to create a dense foam that acts as a solid plug to move the waste out and away. One flush of a foam toilet uses only about 0.09 L (3 oz.) of water compared to 13 L (3.5 gallons) in a regular toilet. For more on foams, their physics and applications, the reader is referred to Stevenson, 2012).

Thought problems

5-T-1. Imagine that surface tension did not exist. What would that change in our lives? Think about things we do and use every day, about vegetation, and about the weather.

5-T-2. The words capillary and capillarity were purposely avoided in the text simply because they are "big words." What happens to capillarity when a surfactant is added?

5-T-3. What is osmosis? How is it related to surface tension?

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[5] Note that the polymer is not the insulating material, the air pockets are. The polymer matrix merely prevents the movement of air that would otherwise allow convective motions and heat transfer.

5-T-4. If underwater bubbles need to be spherical or toroidal because air pressure within them has to be uniform, why can large soap bubbles in the air take on non-spherical shapes as depicted in Figure 5-15?

Figure 5-15. Large soap bubbles that are not spherical. (*Photo credit*: Ozgur Donmaz, Getty Images)

5-T-5. Why doesn't beer foam if the glass is greasy?

Quantitative exercises

5-Q-1. A soap bubble is like a bubble inside another bubble since the soapy water has two surfaces, one facing the outside and the other facing the inside. What is the pressure difference across the soapy film if the soap bubble is spherical with diameter D?

5-Q-2. A duck floats on water. What are the fractions of its weight that are supported by surface tension and by buoyancy? For simplicity, the duck's imprint in the water may be assimilated to a rectangular box 22 cm long, 12 cm wide, and 5 cm deep. The feathers are hydrophobic.

5-Q-3. Question

5-Q-4. Question