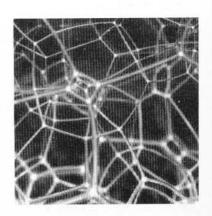


BUBBLES

When I arrived here yesterday Uncle William and Aunt Fanny met me at the door, Uncle William armed with a vessel of soap and glycerine prepared for blowing soap bubbles, and a tray with a number of mathematical figures made of wire. These he dips into the soap mixture and a film forms or adheres to the wires very beautifully and perfectly regularly. With some scientific end in view he is studying these films.

Agnes G. King, niece of Lord Kelvin



am quite sure that a fascination with patterns in nature is as old as civilization. When the Egyptians began to keep bees in clay pipes 5000 years ago, they cannot have failed to notice the astonishing hexagonal pattern of the honeybee's dwelling (Fig. 2.1). Charles Darwin declared it 'absolutely perfect in economising labour and wax', and marvelled at the bees' instincts for producing such a masterpiece of engineering.

If you want to fill up a plane space with identical, equal-sided and equalangled cells, there are only three choices: triangles, squares or hexagons. Only these regular polygons can be packed together to fill space without leaving gaps. Pentagons, for example, will not work, and neither will octagons (Fig. 2.2). Bees making a pentagonal honeycomb would be constantly leaving gaps, and it is not hard to see why these aberrant bees would not be very successful in the Darwinian struggle for survival. The same is true for circular cells.

But why do bees not make square or triangular cells instead of hexagonal? The ancient Greeks suspected that the bees possessed 'a certain geometrical forethought' by which they deduced that hexagonal cells could hold more honey; but the Frenchman R.A.F. de Réaumur

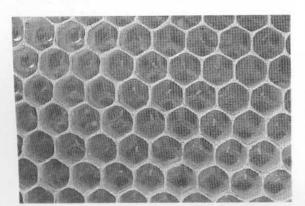


Fig. 2.1 The hexagonal honeycomb of the honey bee was surely one of the first recognized examples of geometrical pattern in the natural world. (Photo: Scott Camazine, Pennsylvania State University.)

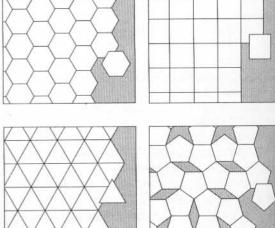


Fig. 2.2 There are just three types of regular polygon (with equal sides and angles) that will tile a plane without leaving gaps: equilateral triangles, squares and hexagons. Pentagons will not fit. But, as we will see, nature nevertheless has plenty of uses for fivefold symmetry!



proposed in the eighteenth century that it is the area of the walls, not the volume of the cavities, that matters. The total length of the cell walls for hexagonal cells filling a given area is less than that of square or triangular cells enclosing the same area. In other words, it takes less material to make hexagonal walls. It is this drive towards economy that leads bees to make hexagonal honeycombs. Why bees should be economy-conscious was not obvious at that time, however, and Réaumur's contemporaries decided that the bees were guided by mathematical principles according to 'divine guidance and command'. Darwin, of course, removed any residual need for the hand of God in nature's minutiae: he showed that competition and natural selection are the principles that favour organisms who minimize their metabolic costs.

End of story? Hardly. For this was just the kind of Darwinian fable that made D'Arcy Thompson reach for his hammer.

Water's skin

It sounds very neat, but when you start to think about what this explanation requires, it gets uncomfortably elaborate. We must assume that bees and their ancestors have tried out just about every honeycomb pattern a tiler could imagine, before gradually conceding that, yes, hexagons really did leave you less tired and more able to go out foraging. And then they would have had to acquire some kind of sophisticated instinct that allowed them to construct perfect hexagons without the assistance of set-squares, protractors, compasses or any trigonometric know-how.

Why accept this concoction of untested suppositions, asked Thompson, when one could see quite clearly that



Fig. 2.3 A bubble raft of equal-sized bubbles adopts the hexagonal pattern of a honeycomb. Coincidence? (Photo: B.R. Miller.)

the hexagonal honeycomb was an inevitable result of purely physical forces? For everyone knows that a layer of bubbles packs together in just this hexagonal arrangement (Fig. 2.3). If the wax of the comb is made soft enough by the body heat of the bees, suggested Thompson, then it is reasonable to think of the compartments as bubbles surrounded by a sluggish fluid, and so they will be pulled into a perfectly hexagonal array by the same forces of surface tension that organize bubbles into hexagonally packed rafts. In other words, the pattern would form spontaneously, without any great skill on the part of the bees and without the guiding hand of natural selection.

That all sounds plausible enough, perhaps, but it doesn't really explain the hexagonal pattern in any fundamental way-it simply says that the honeycomb is like a bubble-raft, and bubble-rafts make hexagonal arrays. Why hexagons, though? If cellular packings like bubble-rafts and honeycombs really are the product of blind physical forces, why should there be any requirement of equal sides, or of identical shapes, at all? Why not a crazy-paving mosaic of random polygons? At this point we are going to need to know a little more about what a bubble really is, and what controls its shape.

Bubbles are structures made from liquids. We don't often think of liquids as having characteristic shapes—a liquid is fluid, it takes on the shape of the vessel that contains it. But liquids most certainly can have shapes of their own, though these are acutely sensitive to forces such as gravity. In a mist, tiny droplets of water small enough to be buoyed against gravity's tug by the buffeting of air molecules take on the form of near-perfect spheres. Raindrops too take this shape, slightly modified by the frictional forces of their passage through the air and by the urgent pull of gravity.

A spherical droplet provides an illustration of that counter-intuitive aspect of symmetry mentioned in the first chapter: it is generally greatest in the presence of extreme randomness. Unlike crystals, in which the atoms are stacked into regular arrays like eggs in an eggbox, liquids have no ordering of their constituent particles over long distances. The position of one molecule of water bears no relation to the position of another a few millionths of a millimetre away-everything is a jumble. This means that the liquid looks the same in all directions—it is isotropic, and that is reflected in the 'perfect' spherical symmetry of a droplet. But there is something more to the spherical shape, because it is robust: a droplet returns to this shape if momentarily deformed. In other words, there



is some factor that *selects* a spherical form. That factor is surface tension.

Liquids and solids are held together by forces of attraction between the constituent molecules, which prevent them from flying apart into vapour. These forces can take many forms. In solids like diamond, strong chemical bonds bind the atoms into structures that can be disrupted only by very energetic processes. In a molecular liquid like water, these same strong bonds hold together two atoms of hydrogen with one of oxygen in each water molecule; but the molecules themselves are bound only by much weaker forces, which give the liquid some cohesion even though the individual molecules are free to move around. These forces of attraction are electrical in origin: regions of the water molecules that bear a slight positive charge (the hydrogen atoms) are electrically attracted to regions on other molecules with a slight negative charge (the oxygen atoms).

Deep within the bulk of the water, a molecule feels attractive forces from all directions. But molecules at the surface are attracted only by the molecules below it, since above is only air (and very diffuse water vapour). There is, therefore, a net inward force on the surface molecules, which we call surface tension. Since the attractive forces have the effect of lowering a molecule's energy (stabilizing the molecule), the surface molecules are more energetic than those deep in the bulk. So there is an excess energy at the surface. Surface tension and surface excess energy are two equivalent manifestations of the fact that surfaces are less stable than the interior of a substance. This means that surfaces cost energy.

As all physical systems like to reach their most energetically stable state (that is, their *equilibrium* state—see Box 2.1), they tend to minimize the area of their surfaces. For a mass of a substance with a certain volume, the shape that has the smallest surface area is a sphere. So a droplet of water forms a sphere to minimize its surface excess energy. It is a statement of the same thing to say that surface tension pulls at the surface of the droplet equally from all directions, so that it acquires spherical symmetry.

I might point out here that surface tension can play a crucial role in determining the forms of solid objects too, in particular those of crystals. Crystals grow by adding atoms to those already packed into regular arrays; but there are several alternatives for where the newly added atoms might sit, and the positioning of these determines the shape of the facetted object. Is it better to add atoms onto the face of an existing layer, or to add them on at the edges of the layer? In other words, which face of a facetted crystal will grow fastest?

Whereas in a liquid droplet the surface tension is the same in all directions, the different faces of a crystal have different surface tensions (because the arrangement of atoms is different on each). The face that grows the fastest will often be that with the greatest surface tension. These considerations determine whether, for example, a crystal like rock salt (sodium chloride) will grow as cubes or as octahedra. Either can be generated from the stacking arrangement of sodium and chlorine atoms, but the cubic shape is selected because of the way that certain facets grow faster than others.

Surface tension controls the shapes that droplets adopt when they sit on surfaces. If a droplet spreads, it increases its surface area and thus its surface excess energy; but on the other hand, it covers the surface below, which also has a surface excess energy. If the total surface excess energy is lower for a fully liquid-covered surface, the droplet will spread into a liquid film; if not, it remains a glistening bead (Fig. 2.4).

Thus, it is not hard to see how surface tension produces the spherical form of liquid droplets. Perhaps more surprisingly, it can also be responsible for regular patterns. In Fig. 2.5a I show a string of pearl-like beads of flycatching glue attached to the thread of a spider's web. The spider has not painstakingly placed all of these beads at regular intervals along the thread; they have formed spontaneously in a regular pattern through the action of surface tension. A thin, cylindrical column of liquid like the coating of glue on a spider's thread is unstable in the face of tiny disturbances: if the column develops a slight wavy unevenness (Fig. 2.5b), surface tension acts to accentuate the convex curving faces, pulling each undulation into a roughly spherical droplet. This 'pearling'

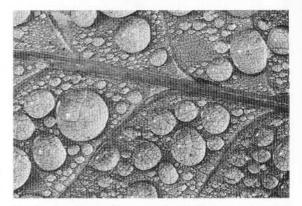


Fig. 2.4 Water droplets will not spread on the waxy surface of a leaf, but instead form an array of beads. (Photo: Christoph Burki, Tony Stone Images.)



phenomenon is called the Rayleigh instability, after Lord Rayleigh who studied it at the end of the nineteenth century. Although the instability acts for perturbations of all sizes, there is a certain wavelength of undulation that is the *most* unstable, and this determines the size and separation of the resulting string of pearl-like droplets. The Rayleigh instability also acts on a thin columnar jet of water, breaking it up into droplets (Fig. 2.5c).

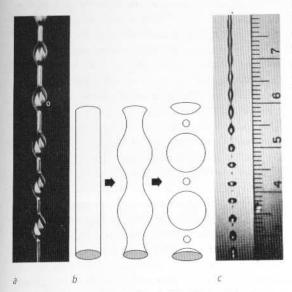


Fig. 2.5 A coating of glue on the threads of a spider's web breaks up spontaneously into a string of pearl-like beads (a). This beading process, called the Rayleigh instability, is a fundamental property of a narrow cylindrical column of liquid, and it selects a certain wavelength (b). It can be seen also in the break-up of a narrow jet of water (c) (From: Tritton 1988).

We will find throughout this book that pattern-forming processes are often initiated by abrupt instabilities. Generally an instability sets in suddenly when some critical parameter is surpassed. For instance, a person on a bicycle is potentially unstable to falling over (with an equal probability of tipping to the left or the right), but this instability sets in only when the speed falls below a certain threshold. Two common aspects of pattern-forming instabilities are that they involve symmetry-breaking (in the present case, the liquid film is initially uniform (symmetric) along the thread's axis, but the instability breaks this symmetry) and that they have a characteristic wavelength, so that the features of the pattern have a specific size.

Balloon games

A bubble seems to defy the exigencies of surface tension. It is spherical, sure enough—but what a surface area! The liquid is stretched into a thin film with a surface area far, far greater that that of a spherical droplet with the same volume of liquid. What has happened?

Everyone knows that, while it is well-nigh impossible to blow bubbles from pure water, they can be made in abundance from water to which a little soap or detergent has been added. Soaps contain molecules called surfactants, which have a tendency to migrate from the bulk of the liquid to the surface, where their presence greatly reduces the surface tension. This means that surfaces cost less, and a larger surface area can be sustained. Notice that, although our intuition tells us that bubbles have a 'stronger skin' than pure water, they can exist at all only because their surface tension is *lower*.

Box 2.1: Energy and equilibrium

Energy is a term that is put to many uses, but in science its meaning is precise: a system's energy is its capacity for doing mechanical work, for moving objects against forces. Every process—every movement, every change—in the real world involves a conversion of energy from one form to another. My muscle movements change chemical energy to kinetic energy (the energy of matter in motion), and also to heat. A light bulb changes electrical energy into heat and light energy.

Just about every energy conversion process that we encounter in everyday life produces some quantity of heat, which for our purposes is often 'wasted' energy (I don't need the heat from my ceiling light). With this in mind, there is a maximum amount of useful work that can be extracted from

any system or process, which is less than the total amount of energy converted—some is always squandered. This maximum amount of extractable work is called the *free energy*. The direction of spontaneous change is always that which results in a decrease in free energy. At equilibrium, the free energy is minimized and no further change takes place.

I shall say more about these concepts, which underpin the discipline of thermodynamics, in the next chapter. For now, you might like simply to imagine processes of change as being like a ball rolling down a hill—this entails the lowering of the ball/hill system's free energy. At equilibrium, the ball comes to rest in a valley at the foot of the hill—a static, unchanging state.

Surfactants are molecules that have a double nature: part of them is soluble in water, and part is not. In soaps the surfactants are salts of fatty acids, which have a compact, negatively charged 'head group' attached to a long, fatty tail (Fig. 2.6). The head group can interact strongly with the electrical charges on water molecules, and so is water-soluble. The tails do not interact strongly with water at all, although they do have an affinity for oily hydrocarbon liquids and greases, whose chemical structure resembles theirs. Molecules with this dual nature are called amphiphiles ('liking both'); the term surfactant (a condensation of 'surface-active agent') originated in the detergent industry and is often now synonymous with amphiphile, although in fact it has the rather more general meaning of a molecule that mediates surface interactions.

Although soap surfactants will dissolve in water, they prefer to position themselves at the water surface, where the water-insoluble tails can poke above the surface while the water-soluble heads remain in solution (Fig. 2.6). Surfactants will therefore form a film, just one molecule thick, at the surface of water. Because the surface layer of 'unsatisfied' water molecules becomes replaced with a layer of fatty tails that didn't want to be

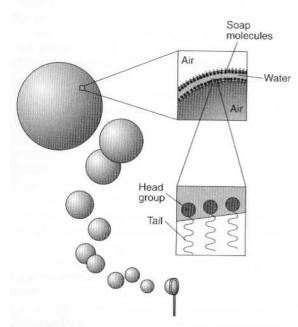


Fig. 2.6 The surface tension of the liquid in a soap bubble's skin is lowered by the presence of the soap molecules at the surface. These molecules, members of a class called surfactants, have a water-soluble head and a water-insoluble tail, which pokes out from the water surface.

in the water anyway, this film lowers the surface tension.

When you blow a bubble from a soap film, the hollow sphere is filled with air. The pressure inside the bubble is greater than that outside, by an amount that is proportional to the inverse of the bubble's radius: the smaller the bubble, the greater the pressure inside. Thomas Young and Pierre Laplace independently established this relationship in 1805. A bubble's size is determined by a balance between the force of surface tension, which acts to shrink the bubble and decrease its surface area, and the internal pressure, which opposes shrinkage by increasing as the bubble gets smaller. The spherical form, meanwhile, is a consequence of the fact that, of all shapes that can enclose a given volume of space, the sphere has the smallest surface area (and thus the smallest surface excess energy). Mathematically, it is called a minimal surface, about whose properties I shall have more to say later.

This minimization principle determines the shapes of all soap films: when confined between boundaries, the film adopts the shape that has the smallest surface area. Soap films stretched between wire frames take on elegant, smoothly curved shapes that have inspired architects such as the German Frei Otto. From the 1950s, Otto designed lightweight membrane structures in which sheets of translucent material form tent-like shapes whose curvature is calculated to minimize surface area (Fig. 2.7a). These structures experience almost exclusively tensile, rather than compressive, stressesjust as a soap film is moulded by surface tension. Otto made use of soap films draped across wire frames (Fig. 2.7b) to plan the curves of his buildings: these models provide an instant experimental solution to the mathematical problem of how to connect specified boundaries with the minimum of material.

A good head

When bubbles are packed together, the result is a foam. Foams are amongst nature's most complicated architectural structures, and it is safe to say that, while they have been studied for centuries, they are still not fully understood. Nature has learned to make use of foams—the spittle bug, for instance, blows a foamy froth to obscure its larvae on leaves, hiding them from predators. They are of great technological value too: foams are used to fight fires, by smothering them with a light but semirigid blanket. They will also damp the power of an explosion, absorbing most of its energy as the bubbles are converted to droplets, which then evaporate. Foams blown in plastics are used as insulation and packaging,



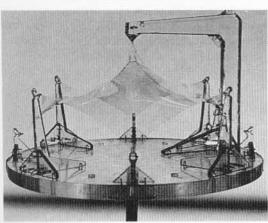


Fig. 2.7 The elegant areaminimizing shapes of soap films have inspired architects such as Frei Otto, whose design for the Olympic Swimming Arena in Munich is shown here (a). Otto used soap films stretched across wire frames to plan the curves of his membrane structures (b). (Photo (b): Michele Emmer, University of Rome 'La Sapienza'.)

while watery foams are used in mineral extraction and metal foams promise strong, lightweight engineering materials. And considerable effort goes into the creation of a good head of beer, although the value is purely aesthetic. So there are plenty of practical as well as academic reasons for wishing to understand the factors that govern foam structure.

But one difficulty is that we're shooting at a moving target. The structure of a foam depends on when you look. A freshly formed foam in water (an aqueous foam), such as that on a newly poured glass of beer, is heavy with water (it is called a wet foam), and the bub-

bles are mostly spherical (Fig. 2.8a). Later the walls become thinner and the bubbles take on a polyhedral shape with more or less flat faces (Fig. 2.8b). This is called a dry foam, as much of the liquid has drained from the walls between bubbles. Typically, a foam then begins a process of coarsening, whereby bubbles merge so that their average size increases with time. Eventually, coarsening and evaporation of the liquid leads to collapse.

A wet foam is rather like a box of marbles of different sizes—the spherical bubbles are jumbled together haphazardly, with smaller ones filling the spaces between