Biophysics of water

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The two fluids which are by far the most important in biology are water and air, in that order. Biological fluids (blood, cytoplasm, sap etc) are very largely water: the total concentration of solutes may be half to a few kmol.m^{-3}, but the concentration of water is over 50 kmol.m^{-3}. So let's deal with water first.

Water is the major component of living organisms and its presence is essential for nearly all biochemical reactions. There are some tissues with very low water contents, say less than several percent. Dry seeds are one example, but the reactions that occur in very dry seeds are very slow (degradation by cosmic rays is an example). Some animals and plants (tardigrades, some nematodes, resurrection plants, seeds) can survive severe dehydration and rehydration, but the processes such as growth and replication — the reactions we recognise as characteristic of life — recommence only on the addition of water. Most (but not all) biochemical reactions occur in aqueous solution and their reagents and products move by diffusion or flow in water. Water molecules are an integral part of the active structures of many enzymes, and water is itself a substrate for the vital reactions of photosynthesis and phosphate hydrolysis.

As well as chemistry, the physics of water is biologically important. The large surface free energy of a water interface provides the thermodynamic stability of membranes and of other multi-molecular structures in the cell. On a larger scale, the bulk physical properties of water are also important to animals and plants: as the major component, water has a large influence on their mechanical structure and thermal properties. And on a still larger scale, the thermodynamic properties of water have a crucial role in the earth's climate and thus on conditions in the biosphere.

Animals and plants are sensitive to changes in their water content. Animals often have a range of strategies for controlling water content, including seeking and drinking. The water content of plants is sensitive to the concentration and distribution of water in their immediate environment. The study of the flow of water into, through and out of plants is therefore an important part of agronomy, as well as plant physiology. Water relations are somewhat less critical in animal physiology, except in pathological cases.

In this chapter we shall describe some properties of water. We shall first deal briefly with the chemistry of this peculiar but biologically ubiquitous solvent. Next, we shall discuss its thermal properties, properties which are in large part responsible for the mildness of weather on this planet. We then turn to the physical properties of bulk water: the surface tension and tensile strength that allow water to ascend the xylem vessels of tall trees, and the viscosity that determines the flow rate in such vessels. Although we shall give molecular explanations, we shall limit this chapter to discussion of bulk flow, and we shall leave discussion of independent motion of molecules (diffusion) till later. Finally, we discuss the hydrophobic effect, the property of water which is responsible for the structure of biological membranes.

Water — a tasteless, odourless, colourless liquid

The above description is less an observation about water than a statement about evolution on earth. Water as a liquid, solid or a vapour is omnipresent in the biosphere and so evolution has favoured sense organs to which water is transparent: eyes which could see the water in the air would have no selective advantage over eyes which could see through the air to the objects therein. So be not misled: water is by no means as bland as its taste. Water is in fact a complex and unusual substance: Felix Franks' monumental book, "Water: a Comprehensive Treatise" fills seven volumes. As we wish to investigate not only water but also life and the interaction of the two, we shall be less comprehensive.

Water is made from two relatively abundant elements and is moderately stable chemically (in bulk liquid water, one molecule in every 550 million is dissociated to H^+ and OH^-). It abounds on the earth's surface for three reasons. First, it is less dense than all other substantial components of the planet that exist in a condensed phase. Second, its molecules are sufficiently massive that, in a vapour at ordinary temperatures, they travel too slowly to escape the earth's gravitational field. Third, its boiling point is quite high[1], so it exists as a liquid at (currently prevailing) terrestrial temperatures.

Though the question is not yet settled, it seems likely that life began in the oceans or other bodies of water on the (relatively) young earth. Life which survives on land must withstand two processes which are much more severe than in the oceans: first, the water which is vital for the reasons listed above tends to evaporate away into the dry air. Second, the variations of temperatures which obtain on land are larger than those in the ocean because the water of the oceans has a large heat capacity. The survival of evaporation and temperature variation by terrestrial animals and especially plants is a major scientific topic (called water relations in plant physiology). Further, air is much less dense than water, so frail wet structures can be largely supported by buoyancy in aquatic environments; in air they must support themselves.

1 Properties of water

The water molecule as a whole is electrically neutral, however it has local regions of positive and negative charge (Figure 1). The shared electrons bonding the hydrogen atoms to the oxygen are more likely to be found near the oxygen, making the oxygen somewhat negative and the hydrogens positive. Along the axis of symmetry there is thus a separation of opposite charges — an electric dipole. Thus water molecules have a tendency to align in an electric field (this gives water the large dielectric constant of 78, i.e. a fixed charge in water causes an electric field that is 78 times smaller than it would be in vacuum). This tendency makes water a good solvent for ions: the water molecules near an ion tend to rotate and to polarise so as to reduce the electric field and thus reduce

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[1] Compare this with methane which has a similar molecular mass, but which is a gas at ordinary temperatures and pressures.

the energy of the electric field near the ion.

The slightly positive hydrogen atoms form hydrogen bonds[2] with the slightly negative oxygen of other water molecules (see Figure 1). Water also forms hydrogen bonds to many organic molecules. Molecules which have neither strong electric fields nor the capacity to form hydrogen bonds generally do not dissolve in large concentration in water. Indeed, the mutual attraction of water molecules is so strong that water appears to be repelled by neutral non-polar substances such as fats: this is known as the hydrophobic effect. ('phobic' or 'hating' suggests that hydrophobic materials repel water. This is not so, as we explain later, but their mutual attraction with water is less than the attraction of water for itself.)

The effect of hydrogen bonds on water structure is most dramatic in ice (see Figure 1) in which nearly every molecule is hydrogen-bonded to its neighbours in a regular lattice. It is sometimes helpful to imagine liquid water as ice with many defects in its crystalline structure. These defects move as bonds break and reform and molecules move relative to each other; nevertheless, at any instant most water molecules are hydrogen bonded to their neighbours. This makes water a peculiar liquid in many ways[3].

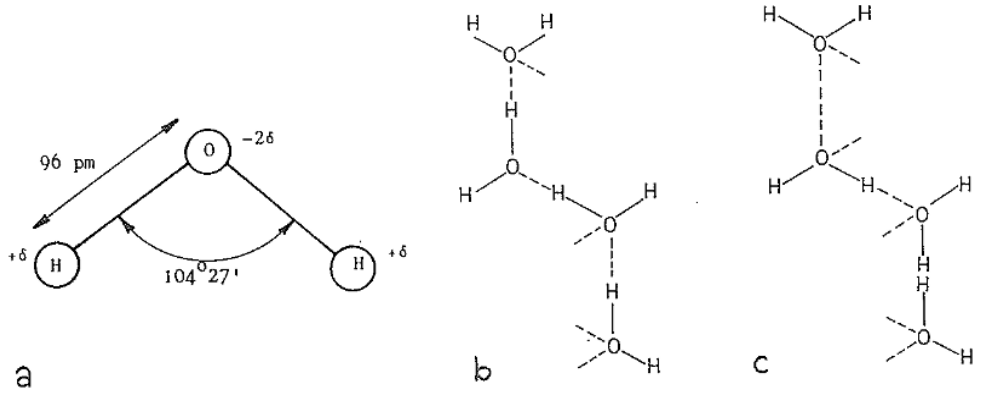

Figure 1: (a) shows the geometry of an isolated water molecule. (b) shows the normal lattice structure in ice with hydrogen bonds represented by dotted lines. (c) shows a Bjerrum defect: the effect of rotating the two middle molecules.

The molecules of most familiar liquids are held together by the van der Waals force[4]. This attractive force is often the same in all directions and so, while the atoms pack fairly closely together, the van der Waals force does not hinder their rotation and there is not such an organised structure as in water. Further, the attractive forces between water molecules are rather stronger than those in most liquids. The locally ordered structure and

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[2] Electrons of the two molecules are shared to some extent, so the hydrogen bond is partly electrostatic and partly covalent.

[3] In the 1960's, various researchers believed it possible that a previously unrecognized solid form of water (called "polywater") might be stable with respect to liquid water at room temperature. Kurt Vonnegut Jr., had already used this idea (which in turn came from the surface scientist Irving Langmuir) in his novel "Cat's Cradle" and, in this case, Life imitated Art to the extent that cold war paranoia provoked fears of a Doomsday Polywater Crystal that would solidify the oceans and make life impossible. The experimental observations concerning polywater are now attributed to impurities in the surface water. (See "Polywater" by F. Franks.)

[4] This is usually a force between transient dipoles, rather than permanent dipoles. A transient asymmetric distribution of electrons in a molecule causes a dipole whose field induces a dipole in nearby molecules, and the two dipoles attract.

strong intermolecular forces in water give it a large surface free energy and a tensile strength which is large for a liquid, and contribute to its large specific heat[5] and latent heat of evaporation. We shall look at these properties in turn in the following sections.

2 Specific heat and latent heat

When energy is added to a liquid, some of the energy goes to increase the kinetic energy of the molecules and the rest weakens the attractive bonds between the molecules (i.e. increases their potential energy). The increase in kinetic energy of the molecules is the microscopic change which corresponds to the macroscopic change we recognise as an increase in temperature.

The specific heat of a substance is the amount of heat energy (measured usually in joules) which must be added to raise the temperature of unit mass (e.g. 1 kg) of the substance by unit temperature (e.g. 1 K)[6]. Some of the heat energy added to water is stored in the strong attractive bonds, and so a relatively large addition of heat is required to increase its temperature a given amount — this contributes to its large specific heat (for liquid water, $Cp = 4.18\ J.kg^{-1}K^{-1}$. For steam and ice, the values are 1.96 and $2.09\ J.kg^{-1}K^{-1}$ respectively. For comparison, copper has $Cp = 0.130\ J.kg^{-1}K^{-1}$). (See Problem 1.)

If enough heat is added to an amount of water, its temperature will rise to a value at which the water boils (373 K or 100 °C at atmospheric pressure, higher at high pressure; lower at low). Further addition of heat does not raise the temperature, rather it causes some of the water to evaporate — to be transformed from liquid water at 373 K to water vapour at 373 K. Microscopically, this process corresponds to the transfer of molecules with a certain average translational kinetic energy from the interior of the liquid (where they are surrounded by and bonded to neighbouring molecules) to the vapour (where each molecule is remote from its neighbours). The heat required at the boiling point to evaporate a liquid is equal to the energy of the inter-molecular attraction in the liquid. The heat added to evaporate unit mass of liquid is the latent heat of vaporisation. For water, in which the attraction is strong and the molecules are light, the latent heat of vaporisation is large ($L_w = 2.26\ 10^6\ J.kg^{-1}$).

Water also evaporates at temperatures lower than the boiling point, unless the atmosphere above it is saturated with water vapour. This is due to the distribution of energies of molecules within the liquid: at any temperature some molecules will have sufficient energy to escape the bonds tending to retain them in the liquid. At saturation, these are replaced by molecules condensing from the vapour. Below saturation, there is a net loss: evaporation. The process of evaporation takes heat from the water and its neighbourhood, thereby lowering the temperature. Cooling by evaporation has a large and important effect on the physiological temperature of animals and plants on land. The large latent heat of vaporisation of water means that the loss of a small amount of water has the same cooling effect as would the loss of a larger amount of other familiar liquids.

3 Surface free energy and surface tension

Molecules at the surface of a liquid (at the air-water interface, for example) are in a physical condition different from that of the molecules in the bulk liquid: on one side

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[5] The small molecular mass of water is largely responsible for the large specific and latent heats: there are relatively many water molecules in a given mass.

[6] The kelvin, K, is the temperature unit of the Système International. The temperature in kelvin, T_K, is related to the Celsius temperature, T_C, by $T_K = T_C + 273.16$. Thus an interval of 1 K is the same as an interval of 1 °C.

there are no molecules with which to form hydrogen bonds. Imagine moving a molecule from the bulk to the surface. Initially the molecule is attracted equally in all directions (Figure 2) and so the net force needed to move it is zero. As it approaches the surface, the symmetry is lost and there are more attractive forces acting towards the bulk fluid. Work is done against these forces in bringing the molecule to the surface: it is, loosely speaking, the work done in breaking the bonds on one side. Another important point is this: if a molecule at the surface is hydrogen-bonded to other molecules, then some molecular orientations are forbidden. Thus molecules at the surface have a non-zero average orientation: they are more ordered (less random) and so the entropy associated with bringing molecules to the surface is negative. (This orientation also produces a strong, though very short range, electric field at any water interface.)

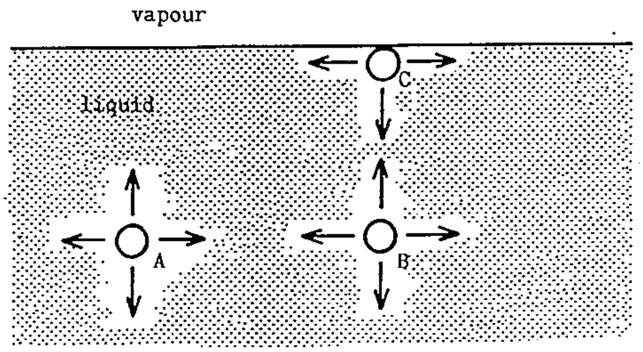

Figure 2 shows only the attractive forces acting on a molecule in a liquid. In the bulk, the net force is zero: to move a molecule from A to B requires no work. A molecule at the surface, however, is negligibly attracted in the direction of vapour whose density is much lower than that of the liquid. Thus there is a net attractive force towards the bulk. Work must be done against this force to move a molecule from B to C.

If the area of the water surface remains constant, then, for every molecule brought to the surface, one is transferred to the interior, and so there is no net energy change. If the area of the surface increases, work must be done to create the new area of surface molecules. The work per unit area of making a new surface is called the ***surface free energy***.

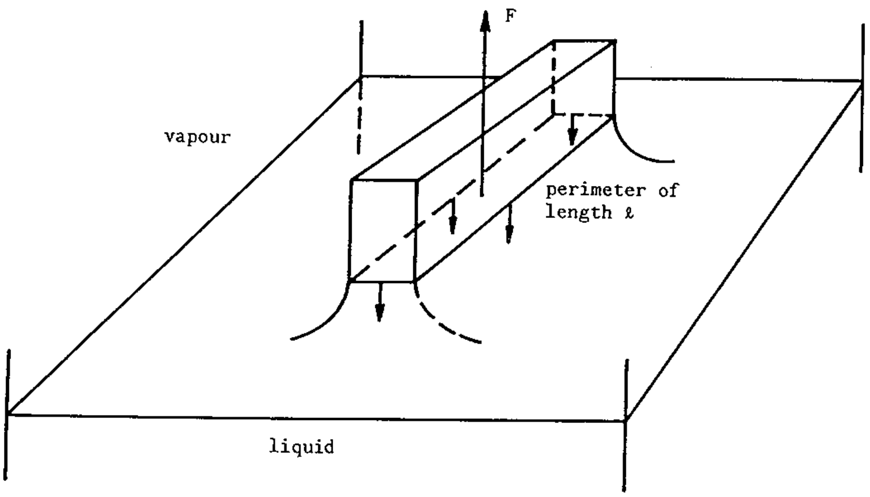

Figure 3: A barrier whose perimeter has length l can be moved to increase the area of liquid interface. Surface tension acts in the plane of the newly created interface.

Figure 3 shows an arrangement in which a barrier whose perimeter has length l is moved a distance dz to create a new water surface[7]. If dW is the work done by the barrier in creating this new surface, then there must be a force F exerted on the barrier by the surface, *in the plane of the surface*, and W = F.dz. This force exerted by the surface is proportional to the length of the line along the surface at which it acts. The force per unit length is called the surface tension γ so

$$\gamma = \frac{F}{l} \qquad (1).$$

Using the relation dW = F.dz, (1) becomes $\gamma = \frac{dW}{l.dz}$. Now (l.dz) is the new area dA of surface, so we have just shown that the surface tension is numerically equal to the work done per unit area of new surface:

$$\gamma = \frac{dW}{dA}.$$

Thus for pure liquids the surface tension is equal to the surface free energy. (This is not so for many mixtures and is most noticeably violated when surfactants such as soaps are present.) Because of its strong inter-molecular attraction and because of the negative entropy required to make a water surface, the surface tension of water is large: $\gamma_W = 73\ \mathrm{mN.m^{-1}}$ at 25 °C (for comparison, the surface tension of n-hexane is $18\ \mathrm{mN.m^{-1}}$). This has several important consequences in biophysics and physiology.

It is the surface tension of a fluid that causes a drop, in the absence of other forces, to become spherical. (For a given volume, a sphere has the smallest area and therefore a spherical drop has the lowest total surface free energy.) The surface tension tends to make the surface contract, but the volume can only contract a minuscule amount before it produces a hydrostatic pressure which resists further contraction (because of the low compressibility of liquids, changes in volume are usually immeasurably small — see section 5). Let us use this as an example: what is the pressure inside a drop of water?

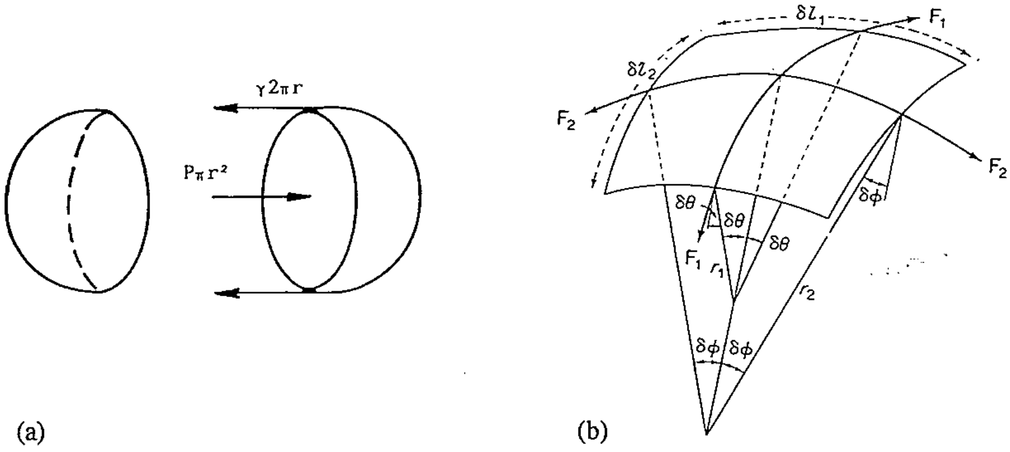

Figure 4: (a) shows a sphere divided into two halves. (b) shows a surface with unequal principal radii of curvature.

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[7] Raising the plate here also lifts a volume of water against gravity, which must be accounted for in a measurement of surface tension using this method.

Consider a sphere of radius r with a surface tension γ and a pressure which is greater inside than out by ΔP. (It could be a drop of water, a bubble, a rubber balloon or a spherical cell.) Let us conceptually divide it in two halves, as shown in Figure 4a. The right half is not accelerating, so the total force on it is zero. The force to the left is the tension γ acting along the perimeter of length $2\pi r$. The force to the right is the pressure difference ΔP acting on the area πr^2, i.e. $\Delta P.\pi r^2$. Thus $2.\pi r.\gamma = \Delta P.\pi r^2$ or

$$\Delta P = \frac{2\gamma}{r} \qquad (2).$$

This important equation is called the Young-Laplace equation. It can be applied to other curved surfaces. Of all the radii of curvature on a surface, the largest and least are called the *principal radii of curvature* (r_1 and r_2). Arcs with these radii intersect at right angles (see Figure 4b). Let r_1 and r_2 be measured in the direction of ΔP, and δl_1 and δl_2 are the lengths of their arcs defining a small area $\delta A \cong \delta l_1.\delta l_2$. On the edges of this surface, the surface tension forces are $F_1 = \gamma\delta l_1$ and $F_2 = \gamma\delta l_2$. They have components in the normal direction of $\gamma\delta l_1.\sin\delta\theta$ and $\gamma\delta l_2.\sin\delta\phi$. Making the small angle approximation and equating these components to the normal component of the pressure force $\Delta P\delta A$ gives

$$\Delta P\delta A = 2\gamma\left(\delta l_1.\delta\theta + \delta l_2.\delta\phi\right)$$

From the geometry of Figure 4b, $\delta\phi = \frac{\delta l_2}{2r_2}$, and $\delta\theta = \frac{\delta l_1}{2r_1}$ so

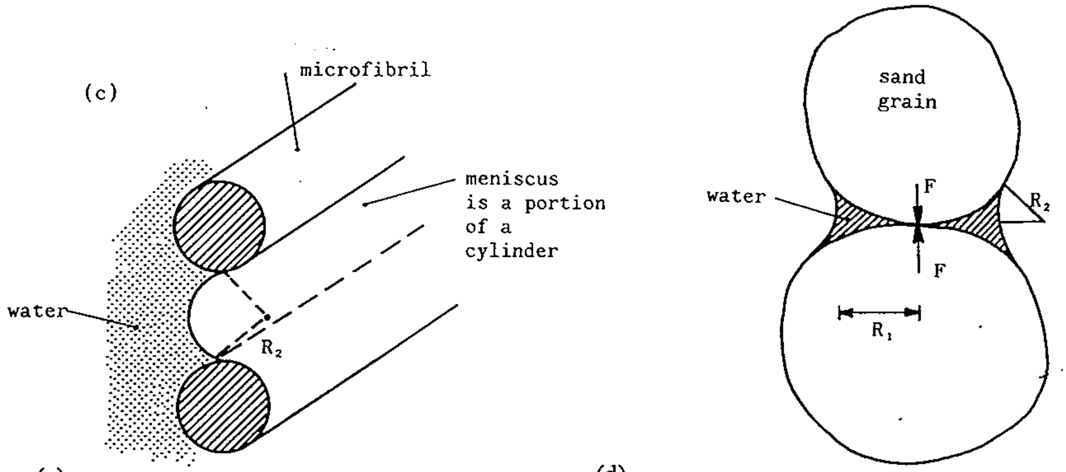
$$\Delta P = \frac{2\gamma}{\delta A}\left(\frac{\delta l_1.\delta l_2}{2r_1} + \frac{\delta l_1.\delta l_2}{2r_2}\right)$$

thus $$\Delta P = \gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \qquad (3)$$

called the generalised Young-Laplace equation, which of course reduces to the previous equation when $r_1 = r_2 = r$.

For a raindrop with $r = 1$ mm, ΔP would be 150 Pa (or about 0.15% of atmospheric pressure). For a tiny air bubble in pure water with radius 1 µm, ΔP is 150 kPa or about 1.5 atmospheres. The Young-Laplace equation becomes very important in the microscopic world, as we shall soon see. Note the sign convention: a positive surface tension gives a larger pressure on the convex side. The pressure would be higher inside a water droplet, and also higher inside a bubble of air in water.

Figure 4c shows an idealised sketch of another important case. Two wet microfibrils of cellulose (considered as very long cylinders) are joined by a meniscus of pure water with radius 10 nm. In this case the meniscus itself is also a section of a cylinder and so $r_1 = \infty$ and $r_2 = 10$ nm. Equation 3 gives $\Delta P = \gamma(0+1/10 \text{ nm})$, so $\Delta P = 7.3$ MPa, higher on the convex (air) side. Taking the air as the reference pressure the water is subjected to a negative pressure of about 73 atmospheres. There is an important point here: large suctions imply small radii of curvature and that usually implies a small volume of water. With a few exceptions mentioned previously, the tissues of animals and plants rarely survive such conditions. If the water pressure between the fibres of a towel is as low as that calculated, it is time to take it off the washing line.



(c) (d)

Figure 4: (c) (not to scale) shows two fibres at a tissue-air interface; (d) shows the meniscus joining two grains of sand in an atmosphere of finite humidity.

An example which is more directly important to plants than to animals is shown in Figure 4d. Two roughly spherical sand grains in the soil are joined by water (for this example, pure water) with the meniscus shown (see also Problem 2). In this case, the principal radii are in opposite directions and so have opposite sign. At the plane of symmetry[8], suppose that $r_1 = -2$ μm and $r_2 = +\ 0.1$ μm. Thus from Equation 3, the magnitude of the pressure difference is

$$\Delta P = \gamma(-1/2\mu\text{m} + 1/0.1\mu\text{m}) \cong 700 \text{ kPa}$$

Water is on the more convex side, so the water has a negative pressure (or suction, or tension) of about seven atmospheres. But wait a moment: seven atmospheres lower than atmospheric means six atmospheres lower than zero! How can a fluid have negative pressure? This is discussed later in the section on tensile strength.

4 Contact angles and capillaries

In the previous section we saw how the attraction of water to itself gives drops their rounded shape. If you look at the water surface in a clean glass beaker or tube you will observe that the water-air interface rises to meet the glass at the line of contact. Here the attraction between water and glass is greater than that between water and water. In a small tube (a capillary), this attraction can lift a small volume of water against gravity.

First, let's deal with one potential confusion: Water is attracted to all other substances, including oil and wax. Oil and wax are called hydrophobic (water hating). It's not that they 'hate' water, just that they don't 'love' water as much as water 'loves' itself: the water-water attraction is greater than the water-wax attraction. So let's discuss attractions.

Van der Waals forces are always present when molecules approach and, at close approach, they are always attractive. A charged or dipolar surface attracts water because the high dielectric constant of water lowers the energy in the electric field. Some surfaces form hydrogen bonds with water, which give another form of attraction. As we said above, water is attracted to all substances, including water itself.

We shall consider contact between a plane solid surface and a fluid (water) in the

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[8] For a pure liquid which is not accelerating, ΔP and γ are constant over all the surface. From the Young-Laplace equation, $(1/R_1+1/R_2)$ is constant. Subject to these boundary conditions, the surface with this property is a cosh of rotation.

presence of its vapour. For the solid-vapour interface (SV) we can define a surface free energy γ_{SV} just as we did for water (where it is possible to cut a molecularly smooth plane through the solid (as is possible for mica) the work done in making the *two* new surfaces is the surface free energy). The attraction between any two substances (in vacuum or atmosphere) can do work when they are brought together, so the work of formation of the interface is negative. The interfacial free energy γ_{SL} between a solid and a liquid is equal in magnitude to the work done in creating a surface of each substance and in bringing them together, but has the opposite sign (i.e. it is the work done in separating them less the energy of destroying that surface). This is most easily seen with an example. Suppose that you increase the are of solid-liquid interface by cutting a solid while it is immersed. First there is work to do to separate the two solid surfaces - this is the surface energy of the solid γ_S. Further one does to work to create the new liquid surface to cover the newly created solid surface - this is the surface energy of the liquid γ_L. Finally, because the fluid and solid attract each other, the work of bringing the new surfaces together is negative ($W_t < 0$, say). So the total work done, the interfacial free energy is $\gamma_S + \gamma_L + W_t$.

The contact angle[9] between a fluid and a solid (in contact at equilibrium) is the angle between the solid-fluid interface and the fluid-vapour interface (or, to be precise, the smallest angle between a line drawn in the solid-fluid interface and one drawn in the fluid-vapour interface). It is usually defined in the presence of a saturated vapour of the fluid.

(See Problem 3.)

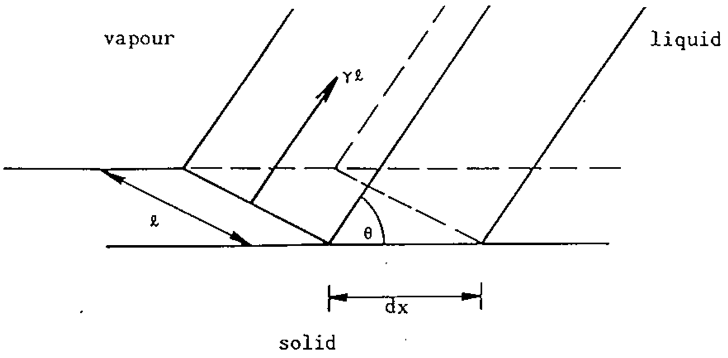

Figure 5: A portion of the line at the intersection of solid-vapour and liquid-vapour interfaces. This line of length l moves a distance dx; the force acting on it is γl and it acts at an angle θ to dx.

We shall derive an equation which relates the contact angle to the interfacial free energies by considering the work done in moving the line of contact at the edge of a drop on a surface (i.e. at the line where the edge of a drop meets the solid-vapour interface). A section with length *l* of the edge of the drop is shown in Figure 5. Suppose that it move a distance dx perpendicular to *l* along the surface of the solid. An area *l*.dx of solid-vapour interface has been exposed and the fluid solid interface has been reduced by *l*.dx. Thus the total change in free energy is $(\gamma_{SV} - \gamma_{SL}).l.dx$. Work is required to increase free

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[9] Contact angles are macroscopic. On scales of less than a nanometer the liquid-vapour interface is curved due to the finite range of van der Waals forces, and the angle of the asymptote of this curve is the macroscopic contact angle. This curvature near the line of contact can be explained by the local variation in surface tension: the surface molecules neat the line of contact are attracted, not by bulk liquid, but by a few molecular layers of liquid lying over the solid surface.

energy, and in this case the work is done by the liquid surface tension γ_{LV}. The horizontal component of the force exerted by this surface tension is $\gamma_{LV} \cos \theta$, and the line of application moves dx, so

$$(\gamma_{SV} - \gamma_{SL}) l \, dx = \gamma_{LV} \cos \theta \; l.dx,$$

so $\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta$ (4)

Thus the contact angle θ is determined by the relative magnitudes of the three surface free energies[10]. The forces between neutral substances are always attractive, so the γ are always positive[11]. There is no solution for θ when $\gamma_{SV} < \gamma_{SV} - \gamma_{SL}$. This corresponds to an attraction between solid and liquid which is stronger than the attraction between the liquid and itself: in this case the liquid spreads on the solid to form a very thin layer across the solid.

The attraction of water to many solids allows water to rise in thin capillaries made from those materials. It continues rising until the vertical component of the attractive force is balanced by the weight of the raised volume of water.

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[10] This is only a local equilibrium, though a very stable one. Over a *very* long time, the solid surface would deform to yield an angle at the three phase junction, thereby relaxing the vertical stress.

[11] As the attraction between molecules of a liquid goes to zero, the surface tension goes to zero and the liquid evaporates.

The phenomenon of capillary rise is represented in Figure 6. A capillary (a thin tube of radius a) made of a substance which has a contact angle θ with the enclosed fluid of density ρ stands vertically in a bath of fluid. The bath has a large surface area: this means that its surface curvature has a nearly infinite radius and so the pressure difference across that surface is zero (from the Young-Laplace equation 2). Since fluids at the same height in a stationary fluid have the same pressure, the pressures at points C and D are equal and the pressures at C, D and E are all equal to that of the atmosphere, P_{atm}.

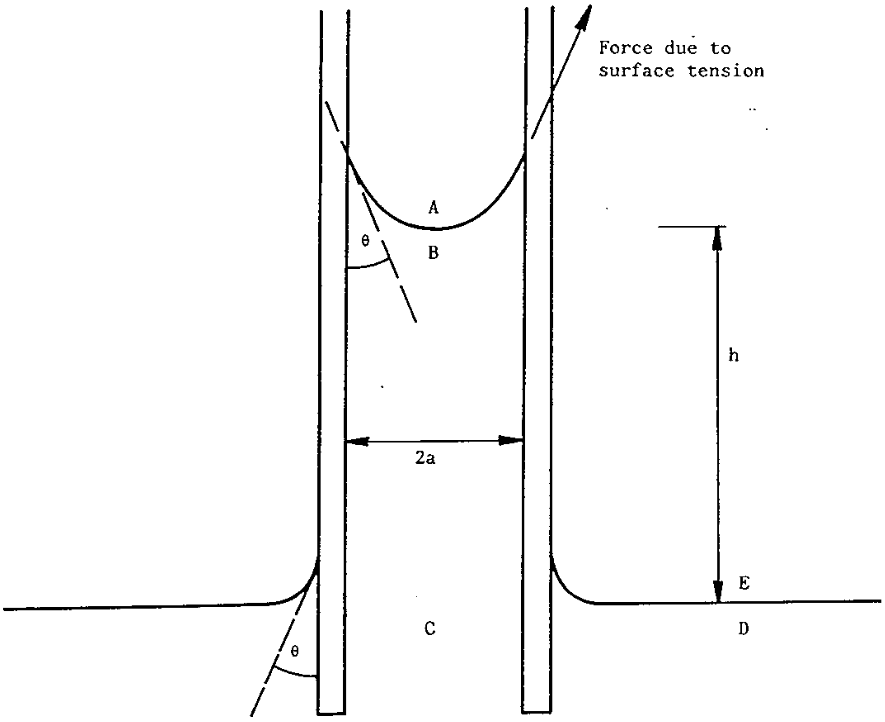

Figure 6: A capillary of radius 2a in a large bath of fluid. The vertical component of the force due to surface tension supports the pressure difference acting between B and A, and thus the column of liquid.

The vertical forces acting on the column of water of height h between A and C add up to zero if it is stationary. We've seen that the pressures at A and C are the same. The remaining forces are the weight of the column (approximately $\pi a^2 h.\rho.g$) and the vertical component of the force produced by its surface tension ($2\pi a \cos\theta$). The water is not accelerating, so these cancel. Thus

$$\pi a^2 h\rho g = 2\pi a\,\gamma\cos\theta$$

so $$h = \frac{2\gamma\cos\theta}{a\rho g} \qquad (5)$$

Note that h is negative if $\theta > 90°$, which is the case for mercury and glass. As expected from this equation, the surface of mercury in a glass capillary is depressed.

If the capillary radius is small, the surface in a capillary is shaped approximately like a spherical section, with a radius R. The geometry gives $\frac{a}{R} = \cos\theta$. From the Young-Laplace equation, the pressure P_B at B is

$$P_B = P_{atm} - \frac{2\gamma}{r} = P_{atm} - \frac{2\gamma\cos\theta}{a}$$

Since $P_B = P_{atm} - \rho gh$, we again derive equation 5. (The reason for doing this version of the derivation is to show that the shape of the water column is irrelevant to the result.)

Taking a contact angle of 60°, a radius of 1 mm gives a capillary height of 7 mm. Going microscopic, a capillary radius of 1 µm gives a column height of seven metres.

Going even smaller, we can see how tiny menisci — say those between the cellulose microfibrils in the leaves — can support substantial pressure differences and thus hold up tall columns of water.

But how tall? Consider a stationary column of water whose base is at atmospheric pressure. If it is taller than about ten metres, the absolute pressure just next to the meniscus must be negative i.e. more than one atmosphere less than atmospheric. Now if you try to produce such a pressure in a glass capillary (as did Torricelli), you will find that the water cavitates or breaks, and you end up with a column of water about ten metres high and a vacuum above it. So how does water get to the tops of tall trees, which may be many tens of metres above the water in the ground? We shall explain in the next section how water does indeed have quite a large tensile strength, and how pure water columns do not necessarily break at negative pressures. This is principally of interest to plants rather than to animals, except in pathological conditions.

5 Compressive and tensile strength

Water shares this property of fluids: it cannot resist static shear or bending stresses. In consequence, it takes negligible energy to change (slowly) the shape of a volume of water, except for work done in changing the area of its surface. Changing the volume, however, does require work to be done against the intermolecular forces[12]. Water is not quite incompressible (its compressibility is about $5\times10^{-10}\ \mathrm{Pa}^{-1}$), but extremely large pressures are required for even a small volume change (e.g. 2 MPa for 0.1%). We'll discuss later what happens under large suctions. For now, the following simplified argument will define and explain the effects associated with changes in volume.

It is conceptually convenient to divide intermolecular forces into an attractive component (van der Waals forces and hydrogen bonding) and a repulsive component[13]. Both components approach zero for molecules a long way apart, and get larger on approach. For all neutral molecules the total force is attractive at large separation. For all substances the total force becomes repulsive at small enough separation and this prevents molecules from occupying the same space. (There is a simple explanation for this: any substance which did not have repulsive forces that dominated at small separation would continue to

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[12] Intermolecular forces known as *conservative forces*. This means that, during a cycle in which molecules are moved and returned to their original positions, orientations and velocities, mechanical and electrical energy is conserved. It is thus possible to define a potential energy of interaction u between them in terms of the attractive and repulsive force components, F_a and F_r. At any given orientation this energy is the integral of force with respect to displacement from the position chosen as the zero of potential energy. The standard choice makes the interaction energy zero at large separation so, for example, we may write

$$u(x) = \int_{\infty}^{x} (F_a + F_r)\, dx' = \int_{\infty}^{x} F_a\, dx' + \int_{\infty}^{x} F_r\, dx' \qquad (6)$$

for approach along the x direction between two molecules. The attractive component contributes a negative integral to the interaction energy, and the repulsive force a positive integral. Intermolecular potential energies are sketched in Figure 7. For zero average force, $\frac{du}{dx} = 0$ at this separation (equation 6).

[13] Pushing molecules together brings their electrons closer together. This is opposed by electrostatic repulsion and also by a quantum mechanical effect called the Pauli exclusion principle.

shrink under the action of its attractive forces, until it formed a black hole. This would render its properties unavailable for discovery and investigation.)

When no external forces are acting on a volume of water, the total force between the molecules is, on average, zero, so the molecules are, on average, accelerating neither towards nor away from each other. The situation for a bulk fluid is rather more complicated than that for two isolated molecules, but the same principles apply. The average distance between molecules must be such that the total force on each molecule is on average zero, this is the condition of mechanical equilibrium. The condition for stable mechanical equilibrium is that the intermolecular potential u must be a local minimum (treated in more detail in Section 3.1) and so an average intermolecular spacing can be calculated from the position of the minimum in u (see Figure 7). Now any average separation between neighbouring molecules corresponds to a certain average volume per molecule, so we could similarly plot total interaction energy U against volume V for a given number of molecules. Again, when no external forces act U(V) is a minimum: at a volume V_0 say. Whereas the negative slope of the energy-distance curve, $-\frac{du}{dx}$, was the intermolecular force F, the negative slope of U(V), i.e. $-\frac{dU}{dV}$, is the bulk pressure P.

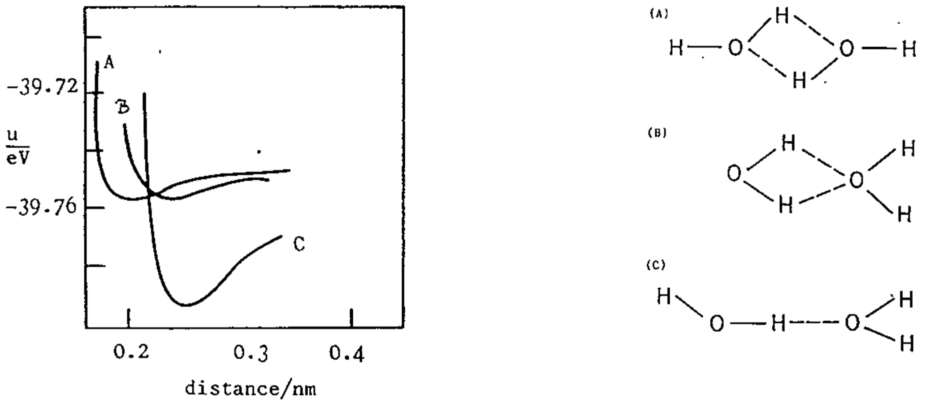

Figure 7: The intermolecular energy of a water dimer as a function of the O-O distance in the orientations shown (A,B,C) (Rao, 1972). The unit of energy commonly used in quantum chemistry is the electron Volt (1 eV = 1.60 10^{-19} J.

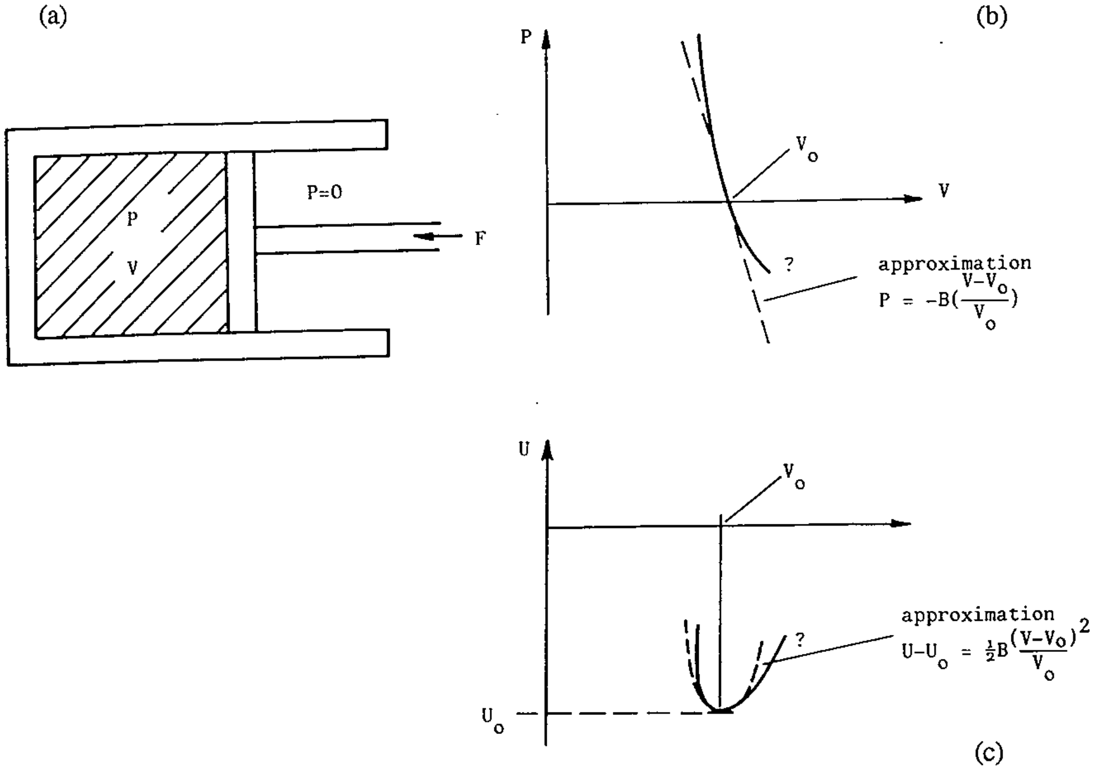

Figure 8: (a) represents a piston in a cylinder applying a pressure P to a volume V of a liquid. V = V_O when P = 0. (b) shows a sketch of P(V) for a volume of liquid. Near V_O it is approximated by a straight line (dashed). (c) shows the integral of (b). Near the minimum, U(V) is approximated by a parabola (dashed). The extent of the right hand side of these graphs is limited by cavitation, which we discuss later.

Now consider the arrangement shown in Figure 8 where a piston in an insulated cylinder confines a volume V of water. When no force is applied to the piston the pressure in the cylinder is zero and the volume of the water is V_O. When a pressure is applied with the piston, the molecules are compressed until the pressure produced by intermolecular repulsion equals the applied pressure. Very close to Vo, we can approximate P(V) as a straight line (see Figure 8)

$$P = -\text{ constant}\,.\,(V-V_O).$$

The constant chosen is scaled to the total volume, i.e.

$$P = -\frac{B}{V_o}(V - V_o) \qquad (7)$$

where B is called[14] the ***bulk modulus of the liquid***. B is just the ratio of the pressure applied to the proportional compression (V-Vo)/Vo produced. Integrating the previous equation gives

$$U - U_o = \frac{1}{2}\, B\, \frac{(V - V_o)^2}{V_o} \qquad (8)$$

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[14] Two different bulk moduli are commonly used. They correspond to two different experimental conditions and two different behaviours P(V). If the temperature is maintained constant, the *isothermal* bulk modulus is used. If there is no heat lost or gained (as is often the case in a rapid change in volume) the *adiabatic* bulk modulus is used.

That is, the internal energy is approximated by a parabola about its minimum. A large bulk modulus thus signifies a steep minimum in U and therefore intermolecular forces which vary strongly with average molecular spacing. For liquids, B is quite large (for water B = 2.04 10^9 Pa). We have already remarked that the strong intermolecular forces in water give it a steep energy minimum. That is, a pressure of 2 MPa or 20 atmospheres is required to reduce the volume by even 0.1%. For most practical purposes, water can be considered as being incompressible. (Franks notes, however, that gravitational compression of the water in the oceans lowers the sea level 40 m below the level it would have if water were completely incompressible.)

Cavitation. Now consider what happens when a tension (suction) is exerted by the piston in our hypothetical Fig 8 (i.e. when it is pulled rather than pushed). This time we move up the steep, attraction side of the energy parabola: the volume is increased very slightly from V_o until the attractive forces exceed the repulsive forces by an amount which matches the applied tension. ("Tension" or "bulk tension" here means negative pressure or suction and is measured in units of force per unit area. Do not confuse this with *surface* tension, measured in units of force per unit length.)

Suppose the pressure in the water starts at atmospheric pressure (P_A = 0.1 MPa). When its absolute pressure falls to zero, it has expanded only P_A/B = 0.005%. At approximately zero absolute pressure, a hole or bubble will usually be observed and further pulling on the piston just expands the bubble, not the liquid water.

The bubble will contain water vapour at low concentration. At temperatures well below 100°C, the pressure P_v of vapour in equilibrium with liquid water is very much lower than atmospheric, so the pressure inside the bubble is positive but $<< P_A$. Consider a small, spherical bubble of radius r in liquid water with pressure P. Remember that the surface tension acts to reduce the bubble's size, while the suction in the water acts to expand the bubble. The Young-Laplace equation gives the condition of balance: $P_v - P = 2\gamma/r$. If the absolute pressure in the water were 0.1 MPa, and neglecting P_v, the radius $r = 2\gamma/P$ = 1.4 µm[15]. Pressures more negative than $-2\gamma/r + P_v$ simply expand the bubble indefinitely. This is called cavitation. Smaller bubbles can close up and resist cavitation. (We discuss this from an energy perspective in an appendix.)

When and if the water in a plant cavitates, the result can be damaging. We should therefore look more closely at cavitation and how it is avoided.

Sufficiently small bubbles ($r<\sim 2\gamma/P$) spontaneously close up. Further, water is often strongly attracted to the walls of its container. So very pure water, completely filling the container and with no bubbles, can resist surprisingly large negative pressures. In practice, air trapped in microscopic fissures in the containing vessel can provide the nucleus for a cavitation bubble. Also, small bubbles may be present and stabilised by trace quantities of surfactant molecules — molecules that concentrate at the water surface (surfactants are discussed later in this chapter). Even a rather small number of surfactant molecules in a volume of fluid can produce enough surface for a microbubble, so even very clean water may have such microbubbles present. (The identity of these surfactant molecules is difficult to determine because the small number of molecules coating a submicroscopic bubble is difficult to analyse.)

So in usual cases, macroscopic containers of water, even with no visible bubbles, may have microbubbles or air in fissures with size comparable to that given by the Young-Laplace equation. Such microbubbles are said to **nucleate** the cavitation. It is usually

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[15] In this calculation, we've used the surface tension for pure water. More about this later.

impossible to produce a substantial tension in large volumes of water without elaborate experimental care.

An important exception is the water in plants: plant roots seem to filter out the nucleating microbubbles. The cell wall of most plants can be approximated as a mesh with holes that are smaller than a few nanometres. A microbubble cannot pass through such a hole because the Young-Laplace equation requires a very large pressure at such small curvature. Thus the water in xylem vessels of plants is unusual in that it can withstand suctions (sometimes many atmospheres) without cavitation. (The water in the soil, however, cavitates at much lower suction, with important consequences for soil wetting and de-wetting behaviour[16].)

6 The hydrophobic effect

We mentioned previously that charged or dipolar surfaces attract water strongly because of the high dielectric constant of water. When that attraction is stronger than that between water molecules (see equation 4) water forms an acute angle on that surface. Such a surface is called ***hydrophilic*** (etymologically "water loving"). Ions are strongly hydrophilic entities because their charge causes a large electric field.

Many organic substances (such as the alkanes) are uncharged and their molecules have negligible dipoles. Such substances are still attracted to water by the van der Waals force, but this attraction is weaker than the attraction between water molecules. If the attraction between a solid and water is small, then (4) gives an obtuse contact angle.

Substances that attract water only weakly are called ***hydrophobic***. This means "water fearing", which is an unfortunate name. Such substances do not "fear" water; they in fact "like" it a little, but the attraction is much less than the much stronger attraction of water for itself, not to mention the even stronger attraction between water and ionic substances. (4) shows that a hypothetical substance which actually repelled water would not have a contact angle at all, and indeed could be used to levitate water droplets. Hydrophobic substances (e.g. the oil, hexadecane) do not dissolve readily in water. Simplistically, this may be explained by noting that, to put a foreign molecule in water, a "hole" must first be made for it, and this means breaking bonds between water molecules, and reorienting the nearby water molecules. Unless the energy of attraction between the solute molecule and water is quite large, this process requires the addition of energy. Oil molecules introduced to water tend to aggregate so as to minimise the area of the oil-water interface, which has an interfacial tension of about 50 $\mathrm{mN.m^{-1}}$. This leads to the proverbial immiscibility of oil and water.

Surfactants

Ions and dipoles dissolve in water, oils do not. Consider the fate of a surfactant molecule, which has an oily (hydrophobic) portion and an ionic (hydrophilic) portion. (Fig 9.) First, the hydrophilic part does "dissolve" in the water while the hydrophobic part remains outside. Thus a layer of surfactant, one molecule thick, forms at the water surface. This is called a **monolayer** (Figure 12). Second, the molecules may aggregate in such a way that their hydrophilic sections are exposed to the water but their hydrophobic regions touch only the hydrophobic regions of other amphiphiles. Such a structure is called a **micelle**. These structures are represented schematically in Fig. 9.

Molecules forming a monolayer at the surface are said to be surface active, hence the

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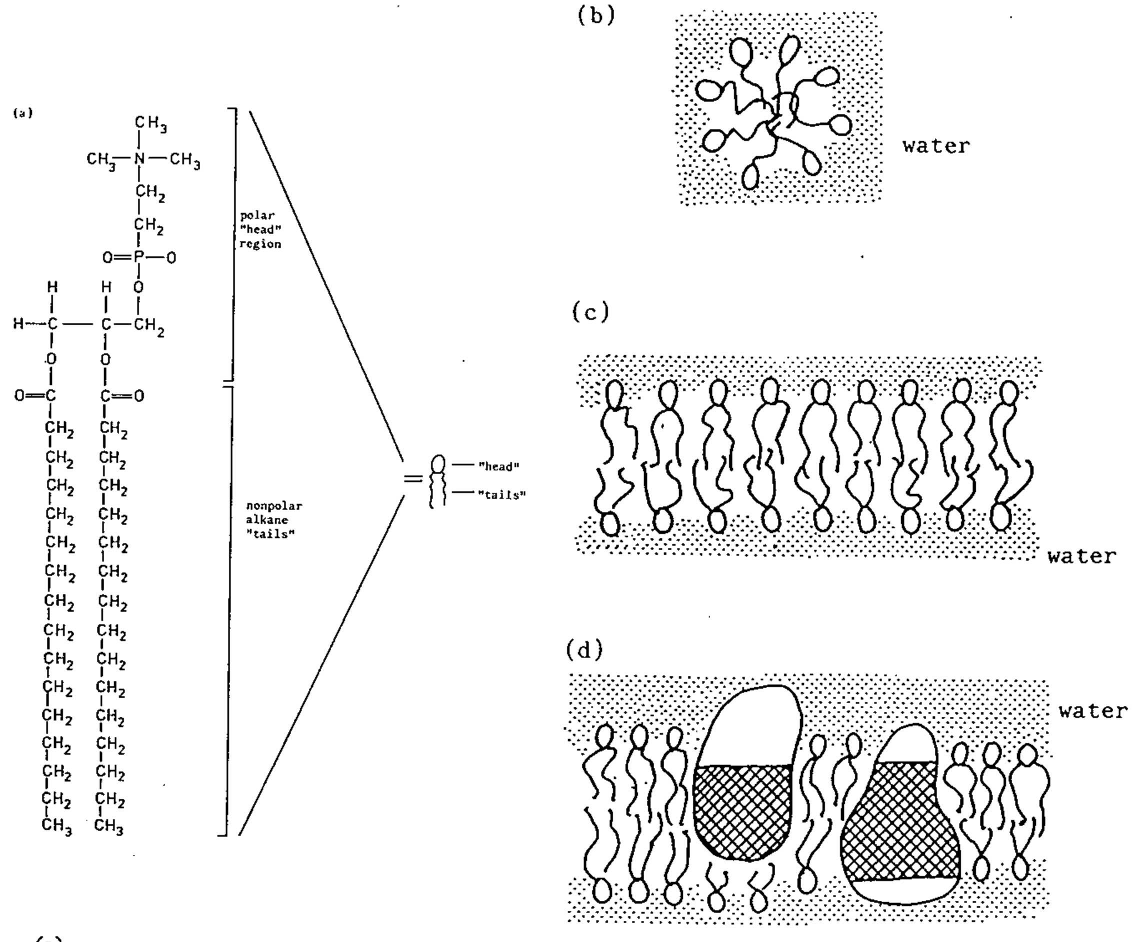
[16] It's tempting to speculate that the substances which nucleate cavitation and which are excluded by plant roots may thus be concentrated in the nearby soil water with possibly important effects on the local soil-water relations.

name **surfactant**. Detergents, fatty acids, lipids and some proteins are surfactants. When surfactants adsorb at an interface, they alter its surface free energy. Confined to their two-dimensional world, these molecules collide with and interact with each other, and can be considered to generate a two-dimensional pressure (a compressive force per unit length) just as collisions and interactions in a gas generate a three-dimensional pressure. This compressive force per unit length reduces the interfacial surface tension. The high surface tension of water opposes the formation of new air-water interfaces. Thus very pure water forms few bubbles when shaken. Water from a town supply may have some surfactants, and so a few bubbles will form and remain. Water with detergent[17] added forms many relatively stable bubbles. The very large interfacial area thereby produced is possible because its surface tension is small and so the energy cost of the interface is not large. The foam supported by a celebrated Irish stout, for instance, indicates a large surfactant concentration — though there are enough complicating effects such as thin layer viscosity and interfacial forces to justify an extended experimental study.



(a)

(a)

Figure 9: (a) shows the lipid phosphatidylcholine which comprises a hydrophilic "head" and two hydrophobic "tails". (b) shows a micelle formed by single tailed surfactants - a spherical aggregate which exposes only the hydrophilic portions of its component

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[17] Detergents dissolve oil in water because they adsorb at the oil-water interface, lowering the interfacial free energy. The energy required to make a droplet of oil in water is therefore much lower. This explains how detergents work to clean oily surfaces.

molecules to the water. (c) shows a lipid bilayer - the aggregate formed by many biologically important lipids. (d) shows a sketch of a biological membrane. The hydrophobic portions of the large protein molecules are shaded.

Of all the various aggregates formed by surfactants, the most important to our study is the bilayer membrane[18] (Fig. 9) which is formed by two planar layers of surfactants, such as lipids, oriented with their hydrophobic portions touching or intermingling and their hydrophilic portions facing the solution. We shall consider this and related structures next.

7 Membranes

The size and shape of micelles is governed by the geometry of the surfactants, the forces between them, and the principles of thermodynamics (see Israelachvili, Marcelja and Horn, 1980). Briefly, molecules which have a moderately large hydrophobic part (such as two long hydrocarbon chains) cannot form small round micelles without exposing a large area of hydrophobic surface to the water. The only way that they can pack together to keep the hydrocarbons away from the water is in the form of two monolayers with the hydrophobic sides touching, a structure called a lipid bilayer.

Biological lipids readily form bilayers in water when the mixture is agitated[19]. Proteins can "dissolve" in the bilayer if their tertiary configuration be suitable: they must have a hydrophobic portion to mix with the hydrocarbon "tails" of the lipids, and a hydrophilic portion to face the water. Biological membranes appear to be made from such a mix of proteins and lipids[20].

The importance of membranes in biology can hardly be overstated. The plasma membrane is the site of interaction between a cell and the outside world — its breakdown is usually regarded as the definition of death of the cell. Other membranes define and divide the specialised compartments of other organelles, and the thylakoid and mitochondrial membranes store electrical energy which is used to power vital reactions in respiration and photosynthesis and the transmission of electrical signals in nerves and muscles.

Biological membranes are selectively permeable. Very large differences in solute concentrations on either side produce very small flow of solutes across the membrane — membranes are poorly permeable to most solutes. They are much more permeable to water, and a small disequilibrium between the water on opposite sides of a membrane produces a relatively large flux. This is discussed in detail in the next chapter. The selective permeabilities of membranes are hard to explain in terms of a model such as that in Figure 9. To insert *either* an ion or a water molecule into the hydrophobic region from

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[18] The conclusion that the vital components of cells are held together by the surface tension of water may seem at first surprising because surface tension effects seem small in the macroscopic world. Surface tension forces, however, act on perimeters whereas weight, for example, acts on volume. Thus surface tension is proportionally more important in small bodies. The surface tension of water is unnoticed by a human swimmer, whereas it means life or death to an insect walking on the top of a pond. To a molecule, a surface tension of 50 $\mathrm{mN.m^{-1}}$ acting over an area of 1 $\mathrm{nm^2}$ (remembering the difficulty in applying a continuum concept to a molecule) represents an energy of $5\ 10^{-20}$ J. This is about twelve times larger than the thermal energy, k_BT, which is measure of the energy associated with a molecule's thermal motion.

[19] Perhaps the first cell was created by surface agitation of a pool of water with a surfactant monolayer at the surface. This produced a closed membrane with a few primitive organic molecules enclosed.

[20] The importance of a good diagram is exemplified by the fame of Singer and Nicholson, who were the first to draw a thee-dimensional picture of this model of the membrane which is now widely known as the Singer-Nicholson model.

the aqueous solution takes a large amount of energy, so only the most energetic molecules can do so. From this partitioning, one can calculate a permeability to ions and a hydraulic conductivity which are both far lower than those observed. Theories about this topic usually involve hydrophilic holes (channels or pores) through the membrane.

Mechanically, membranes can usually be treated as two dimensional fluids: they resist stretching but cannot sustain large shear stresses. (Evans and Skalak, 1979, give a comprehensive account.) The maximum surface tension[21] which plant plasma membranes can withstand is roughly 5 mN.m^{-1}.

In animals, the local differences in pressure are relatively small. In plants however, turgor pressures of tens of atmosphere may occur in the cytoplasm. How does the plasma membrane resist the large difference in pressure between that of the cytoplasm and that of the water in the cell wall? From the Young-Laplace equation, we can deduce that a membrane can only withstand a substantial pressure difference if its radii of curvature is very small. Take $\Delta P = 1.0$ MPa, a typical value for the turgor pressure in a plant cell. How curved would a free membrane have to be to support that pressure difference with a tension of $\gamma \sim 5.0$ mN.m^{-1}? Rearranging (3) gives the reciprocal of the curvature $(1/R_1 + 1/R_2)^{-1} = \gamma/\Delta P = 5$ nm. This is about the same size as the membrane thickness, so the concept of a purely two-dimensional surface tension is inappropriate. To analyse this problem properly we ought to consider the bending energies of plant membranes, and that is a subject about which little is known. Nevertheless, we can conclude that a plasma membrane dividing a cytoplasm and apoplasm whose pressures differ by a MPa or so will be pressed up against the cell wall and will thus adopt its shape except where its radii of curvature are similar to its thickness. It also follows that a cell wall cannot have holes in it which are larger than several nm, or else the plasma membrane will be extruded through it. This brings us to the mechanics of turgor and cellular water relations which we shall consider later.

Some further reading

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Kane J.W. and Sternheim, M.M. (1988) Physics. Wiley, NY.

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https://www.animations.physics.unsw.edu.au/jw/freezing-point-depression-boiling-point-elevation.htm

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[21] In this case, surface tension is not the same thing as surface free energy. A water surface has an equilibrium surface free energy because molecules at the surface are in equilibrium with those in the bulk water phase, which provides a reservoir of molecules to make new surface if the interface is increased in area. The plasma membrane also has a reservoir of membrane molecules and, under certain conditions, is in equilibrium with it when the membrane surface tension is of the order of 0.1 mN.m^{-1} (Steponkus and Wolfe, 1983).

Problems

P1 Calculate the energy required to “break” all the bonds in 1 kg of ice. The transitions from ice to water and water to steam effectively break all of these bonds. What fraction of the latent heats and specific heat is used in breaking hydrogen bonds? Where does the rest of the latent heat go? (The latent heats of fusion and vaporisation are $3.33\text{x}10^5$ and $2.26\text{x}10^6$ J.kg^{-1} respectively.)

P2 By considering the forces due to pressure and tension, calculate the forces exerted on each other by the sand grains in Figure 4 at the point of contact. What can you deduce about the mechanical properties of wet and dry sand? Approximate solutions for simple limits will do. Are the results surprising? Do they concur with your expericence from running on beaches?

P3 Suppose we waited for the final equilibrium referred to in Figure 5; that is until the solid bent at the contact line. What would be the relation between the contact angles and the interfacial energies?

P4 Suppose that a plasmodesma can be represented by an unobstructed cylinder of length 2 μm and radius 2 nm (this is an oversimplification). What flow would be produced through it by a pressure difference of 100 kPa? How many such plasmodesmata, connected in parallel, would be needed to conduct a total flow of 1 dm^3 in 1 day?

P5 A more realistic model of a plasmodesma is two concentric cylinders, with cytoplasmic flow through the annular cross-section, with radii $b > a$. By considering the viscous drag $2\pi\eta a l \frac{dv}{dr}$ acting at a, prove that the analogue of Poiseuille's equation which pertains to this system is

$$Q = \frac{P\pi}{8\eta l}\left(b^4 - a^4 - \frac{(b^2-a^2)^2}{ln\ (b/a)}\right)$$

(hint: first prove that the velocity distribution has the form:

$v = \text{constant}.r^2 + \text{constant}.ln\ r + \text{constant}.$)

P6 Find the root mean square velocity of molecules in air $\sqrt{\overline{v^2}} = \frac{3kT}{m}$ where m is the mass of a molecule and k is Boltzmann’s constant. Compare this to the escape velocity from the earth ($11\ \text{km.s}^{-1}$) and comment on the abundance of water, oxygen, nitrogen and hydrogen on the earth.

Appendix. Tension and cavitation from an energy perspective

In this appendix, consider tension from the energy perspective. First let us first assume that the water adheres strongly to the inside of the cylinder and that the water is a pure continuum (neither of these conditions are easily achieved on the molecular scale). Again, $-P = \frac{dU}{dV}$ (see Figure 8). Thus, if there were no cavitation and the expansion were uniform, the maximum tension which we might expect to be supported by a pure substance would be the steepest positive slope on the U(V) curve.

The amount of work dW required to expand a spherical cavity in a fluid under bulk tension has two terms: the (positive) work γdA done in expanding its area by dA against the surface tension γ and the work PdV done against the bulk pressure (which may be negative) on increasing the volume by dV. For a sphere whose radius changes from r to r + dr, $dA = 8\pi r.dr$ and $dV = 4\pi r^2 dr$. Thus

$$dW = \gamma.(8\pi r.dr) + P.(4\pi r^2 dr) = 4\pi r.(2\gamma + Pr).dr$$

If $dW > 0$, the cavity will tend to contract; if $dW < 0$ it will expand indefinitely. Since r is never negative, the cavity will expand indefinitely if P is more negative than $-2\gamma/r$. So, for any given tension, the cavity will expand indefinitely at a critical radius at which the tension becomes greater in magnitude than the pressure given by the Young-Laplace equation. (Actually, a tension slightly less than this can lead to cavitation because thermal fluctuations can expand the cavity and "push" it over the energy maximum in Figure A1. This makes cavitation probabilistic — the chance of cavitation depends not only on the tension but also on the time for which it is applied.) Similarly, a very small bubble will spontaneously close up due to surface tension: a cavity of molecular dimensions[22] — say r = 10 nm — will close against tensions less than 15 MPa.

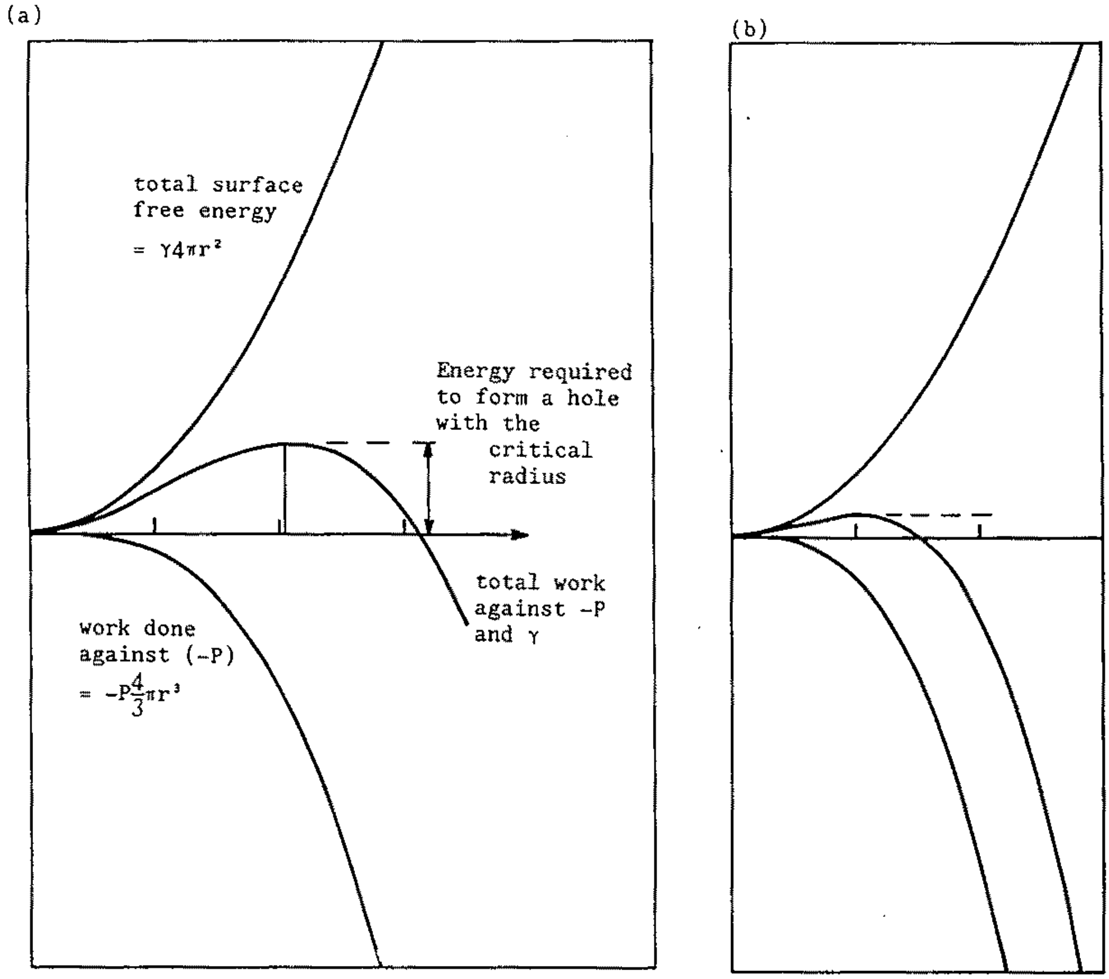

Figure A1: The two work terms - that done against surface tension and (bulk) negative pressure - are shown as solid lines. The total work to form a hole of radius r is shown: its maximum represents the minimum energy for cavitation. For pure water the surface term is constant so, at increasingly negative pressures, this energy barrier to cavitation becomes smaller. (b) shows the same three functions plotted with a more negative value

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[22] We should be cautious in applying continuum concepts, such as surface tension, on a molecular scale. Nevertheless, the Laplace-Young eqn. is found to apply to radii at least as small as 5 nm for water and 0.5 nm for simple organic liquids. (Fisher and Israelachvili, 1980.)

of pressure.

Thus small holes in water spontaneously close up and so water will cavitate at low tensions only if there exist stable cavities (microbubbles) with size comparable to that given by the Young-Laplace equation.