chapter five

Surface Tension

Intermolecular Forces

THE forces which exist between molecules can explain many of the bulk properties of solids, liquids and gases. These intermolecular forces arise from two main causes:

(1) The *potential energy* of the molecules, which is due to interactions with surrounding molecules (this is principally electrical, not gravitational, in origin).

(2) The *thermal energy* of the molecules—this is the kinetic energy of the molecules and depends on the temperature of the substance concerned.

We shall see later that the particular state or phase in which matter appears—that is, solid, liquid or gas—and the properties it then has, are determined by the relative magnitudes of these two energies.

Potential energy and Force

In bulk, matter consists of numerous molecules. To simplify the situation, Fig. 5.1 shows the variation of the potential energy V between two molecules at a distance r apart.

Along the part BCD of the curve, the potential energy V is negative. Along the part AB, the potential energy V is positive. The force between the molecules is always given by $F = -dV/dr = -$potential gradient. Along CD the force is *attractive* and it decreases with distance r according to an inverse-power of r. Along ABC, the force is *repulsive*. Fig. 5.1 shows the variation of F with r.

At C, the minimum potential energy point of the curve, the molecules would be at their normal distance apart in the absence of thermal energy. The equilibrium distance OM, r_0, is of the order 2 or 3×10^{-10} m (2 or 3 Å) for a solid. At this distance apart, the attractive and repulsive forces balance each other. If the molecules are closer, ($r < r_0$), they would repel each other. If they are further apart, ($r > r_0$), they attract each other.

Phases or States of Matter

The molecules in a *solid* are said to be in a 'condensed' phase or state. Their thermal energy is then relatively low compared with their potential energy V and the molecules are 'bound' to each other. They may now vibrate about C, the minimum of the curve in Fig. 5.1.

When the thermal energy increases by an amount corresponding to CC′ in Fig. 5.1, the molecule can then oscillate between the limits

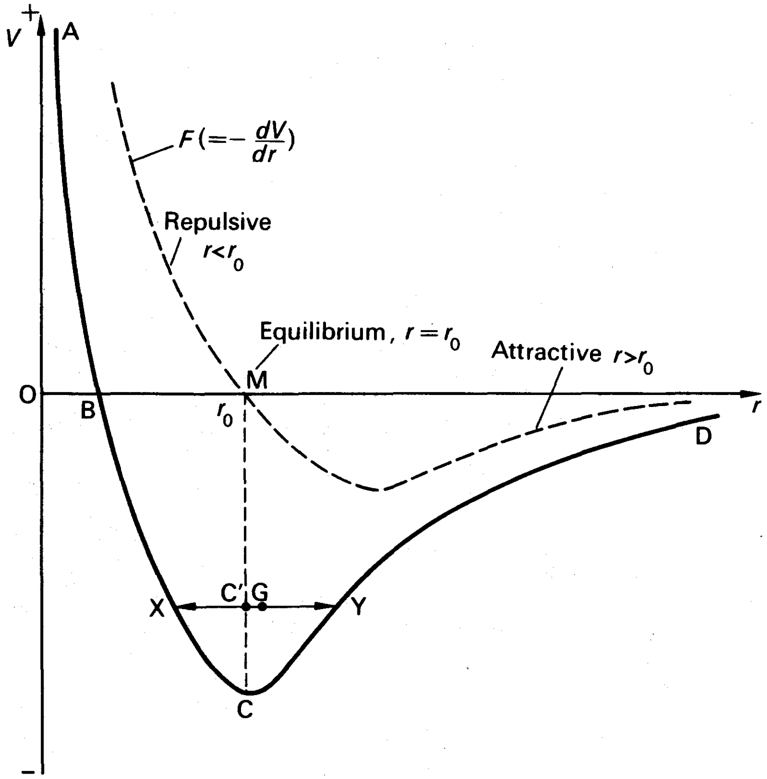


FIG. 5.1 Molecular potential energy and force

corresponding to X and Y. From the graph of force, F, it can be seen that when the molecule is on the left of C′ it experiences a greater force towards it than when on the right. Consequently the molecule returns quicker to C′. Thus the *mean position* G is on the right of C′. This corresponds to a mean separation of molecules which is *greater* than r_0. Thus the solid expands when its thermal energy is increased.

As the thermal energy increases further, at some particular temperature the molecules are able to move comparatively freely relative to neighbouring molecules. The solid then loses its rigid form and becomes a *liquid*. The molecules in the liquid constantly exchange places with other molecules, whereas in a solid the neighbours of a particular molecule remain unchanged. Further, the molecules of a liquid have translational as well as vibrational energy, that is, they move about constantly through the liquid, whereas molecules of a solid have vibrational energy only.

As the temperature of the liquid rises, the thermal energy of the molecules further increases. The average distance between the molecules then also increases and so their mean potential energy approaches zero, as can be seen from Fig. 5.1. At some stage the increased thermal energy enables the molecules to completely break the bonds of attraction which keep them in a liquid state. The molecules then have little or no interaction and now form a *gas*. At normal pressures the forces of attraction between the gas molecules are comparatively very small and the molecules move about freely inside the volume they occupy. Gas molecules which are monatomic such as helium have translational energy only. Gas molecules such as oxygen or carbon dioxide, with two or more atoms, have rotational and vibrational energies in addition to translational energy.

Gases

At normal pressure, permanent gases such as air or oxygen obey Boyle's law, pV = constant, to a very good approximation. Now in the absence of attractive forces between the molecules, and assuming their actual volume is negligibly small, the kinetic theory of gases shows that Boyle's law is obeyed by this ideal gas. Consequently, the attractive forces between the gas molecules at normal pressure are unimportant. They increase appreciably when the gas is at high pressure as the molecules are then on the average very much closer.

In the bulk of the gas, the resultant force of attraction between a particular molecule and those all round it is zero when averaged over a period. Molecules which strike the wall of the containing vessel, however, are retarded by an unbalanced force due to molecules behind them. The observed pressure p of a gas is thus *less* than the pressure in the ideal case, when the attractive forces due to molecules is zero.

Van der Waals derived an expression for this pressure 'defect'. He considered that it was proportional to the product of the number of molecules per second striking unit area of the wall and the number per unit volume behind them, since this is a measure of the force of attraction. For a given volume of gas, both these numbers are proportional to the *density* of the gas. Consequently the pressure defect, p_1 say, is proportional to $\rho \times \rho$ or ρ^2. For a fixed mass of gas, $\rho \propto 1/V$, where V is the volume. Thus $p_1 = a/V^2$, where a is a constant for the particular gas. Taking into account the attractive forces between the molecules, it follows that, if p is the observed pressure, the gas pressure in the bulk of the gas $= p+a/V^2$.

The attraction of the walls on the molecules arriving there is to increase their velocity from v say to $v+\Delta v$. Immediately after rebounding from the walls, however, the force of attraction decreases the velocity to v again. Thus the attraction of the walls has no net effect on the momentum change due to collision. Likewise, the increase in momentum of the walls due to their attraction by the molecules arriving is lost after the molecules rebound.

The effect of the volume actually occupied by all the molecules is represented by a constant b, so that the volume of the space in which they move is not V but $(V-b)$. The magnitude of b is not the actual volume of the molecules, as if they were swept into one corner of the space, since they are in constant motion. b has been estimated to be about four times the actual volume.

Surface Tension.

We now consider in detail a phenomenon of a liquid surface called *surface tension.* As we shall soon show, surface tension is due to intermolecular attraction.

It is a well-known fact that some insects, for example a water-carrier, are able to walk across a water surface; that a drop of water may remain suspended for some time from a tap before falling, as if the water particles were held together in a bag; that mercury gathers into small droplets when spilt; and that a dry steel needle may be made, with care, to float on water, Fig. 5.2. These observations suggest that *the surface of a liquid acts like an elastic skin covering the liquid or is in a state of tension.* Thus forces S in the liquid support the weight W of the needle, as shown in Fig. 5.2.

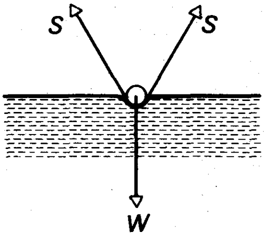


FIG. 5.2 Needle floating on water

Energy of Liquid Surface. Molecular theory

The fact that a liquid surface is in a state of tension can be explained by the intermolecular forces discussed on p. 125. In the bulk of the liquid, which begins only a few molecular diameters downwards from the surface, a particular molecule such as A is surrounded by an equal number of molecules on all sides. This can be seen by drawing a sphere round A. Fig. 5.3. The average distance apart of the molecules is such that the attractive forces balance the repulsive forces (p. 145). Thus the average intermolecular force between A and the surrounding molecules is zero. Fig. 5.3.

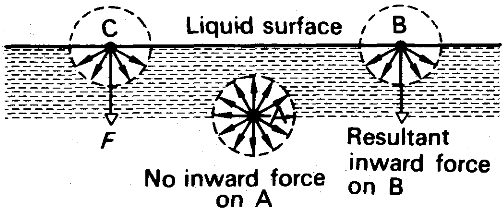


FIG. 5.3 Molecular forces in liquid

Consider now a molecule such as C or B in the surface of the liquid. There are very few molecules on the vapour side above C or B compared with the liquid below, as shown by drawing a sphere round C or B. Thus if C is displaced very slightly upward, a resultant attractive force F on C, due to the large number of molecules below C, now has to be overcome. It follows that if all the molecules in the surface were removed to infinity, a definite amount of work is needed. *Consequently molecules in the surface have potential energy.* A molecule in the bulk of the liquid forms bonds with more neighbours than one in the surface. Thus bonds must be broken, i.e. work must be done, to bring a molecule into the surface. Molecules in the surface of the liquid hence have more potential energy than those in the bulk.

Surface area. Shape of drop

The potential energy of any system in stable equilibrium is a minimum. Thus under surface tension forces, the area of a liquid surface will have the least number of molecules in it, that is, the surface area of a given volume of liquid is a minimum. Mathematically, it can be shown that the shape of a given volume of liquid with a minimum surface area is a *sphere.*

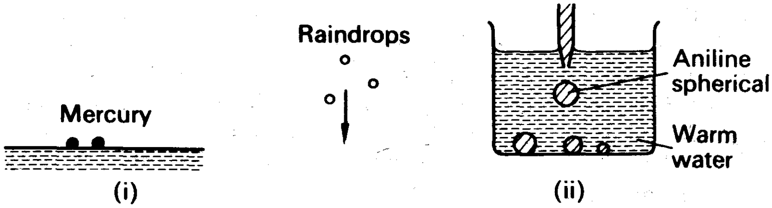


FIG. 5.4 Liquid drops

This is why raindrops, and small droplets of mercury, are approximately spherical in shape. Fig. 5.4 (i). To eliminate completely the effect of gravitational forces, Plateau placed a drop of oil in a mixture of alcohol and water of the same density. In this case the weight of the drop is counterbalanced by the upthrust of the surrounding liquid. He then observed that the drop was a perfect sphere. Plateau's 'spherule' experiment can be carried out by warming water in a beaker and then carefully introducing aniline with the aid of a pipette. Fig. 5.4 (ii). At room temperature the density of aniline is slightly greater than water. At a higher temperature the densities of the two liquids are roughly the same and the aniline is then seen to form *spheres,* which rise and fall in the liquid.

A soap bubble is spherical because its weight is extremely small and the liquid shape is then mainly due to surface tension forces. Although the density of mercury is high, small drops of mercury are spherical. The ratio of surface area ($4\pi r^2$) to weight (or volume, $4\pi r^3/3$) of a sphere is proportional to the ratio r^2/r^3, or to $1/r$. Thus the smaller the radius, the greater is the influence of surface tension forces compared to the weight. Large mercury drops, however, are flattened on top. This time the effect of gravity is relatively greater. The shape of the drop conforms to the principle that the sum of the gravitational potential energy and the surface energy must be a minimum, and so the centre of gravity moves down as much as possible.

Lead shot is manufactured by spraying lead from the top of a tall tower. As they fall, the small drops form spheres under the action of surface tension forces.

Surface tension definition. Units, dimensions

Since the surface of a liquid acts like an elastic skin, the surface is in a state of tension. A blown-up football bladder has a surface in a state of tension. This is a very rough analogy because the surface tension of a bladder increases as the surface area increases, whereas the surface tension of a liquid is independent of surface area. Any line in the bladder surface is then acted on by two equal and opposite forces, and if the bladder is cut with a knife the rubber is drawn away from the incision by the two forces present.

R. C. Brown and others have pointed out that molecules in the surface of a liquid have probably a less dense packing than those in the bulk of the liquid, as there are fewer molecules in the surface when its area is a minimum. The average separation between molecules in the surface are then slightly greater than those inside. On average, then, the force between neighbouring molecules in the surface are attractive (see p. 125). This would explain the existence of surface tension.

The *surface tension*, γ, of a liquid, sometimes called the *coefficient of surface tension*, is defined as *the force per unit length acting in the surface at right angles to one side of a line drawn in the surface*. In Fig. 5.5 AB represents a line 1 m long. The unit of γ is *newton metre*$^{-1}$ (N m^{-1}).

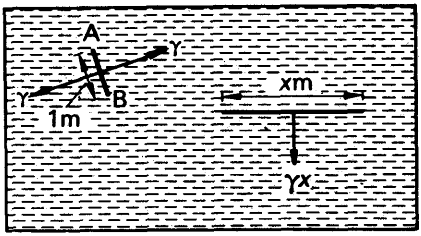


FIG. 5.5 Surface tension

The 'magnitude' of γ depends on the temperature of the liquid and on the medium on the other side of the surface. For water at 20°C in contact with air, $\gamma = 7{\cdot}26 \times 10^{-2}$ newton metre^{-1}. For mercury at 20°C in contact with air, $\gamma = 46{\cdot}5 \times 10^{-2}$ N m^{-1}. The surface tension of a water-oil (olive-oil) boundary is $2{\cdot}06 \times 10^{-2}$ N m^{-1}, and for a mercury-water boundary it is $42{\cdot}7 \times 10^{-2}$ N m^{-1}.

Since surface tension γ is a 'force per unit length', the dimensions of

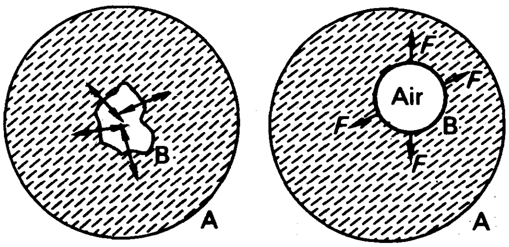
$$\text{surface tension} = \frac{\text{dimensions of force}}{\text{dimensions of length}} = \frac{\mathrm{MLT}^{-2}}{\mathrm{L}}$$
$$= \mathrm{MT}^{-2}.$$

We shall see later that surface tension can be defined also in terms of surface energy (p. 146).

Some surface tension phenomena

The effect of surface tension forces in a soap film can be demonstrated by placing a thread B carefully on a soap film formed in a metal ring A, Fig. 5.6 (i). The surface tension forces on both sides of the thread counterbalance, as shown in Fig. 5.6 (i). If the film enclosed by the thread is pierced, however, the thread is pulled out into a circle by the surface tension forces *F* at the junction of the air and soap-film, Fig. 5.6 (ii). Observe that the film has contracted to a minimum area.

Another demonstration of surface tension forces can be made by sprinkling light dust or lycopodium powder over the surface of water contained in a dish. If the middle of the water is touched with the end of a glass rod which had previously been dipped into soap solution, the powder is carried away to the sides by the water. The explanation lies in the fact that the surface tension of water is greater than that of a soap-film (p. 136). The resultant force at the place where the rod touched the water is hence *away from* the rod, and thus the powder moves away from the centre towards the sides of the vessel.



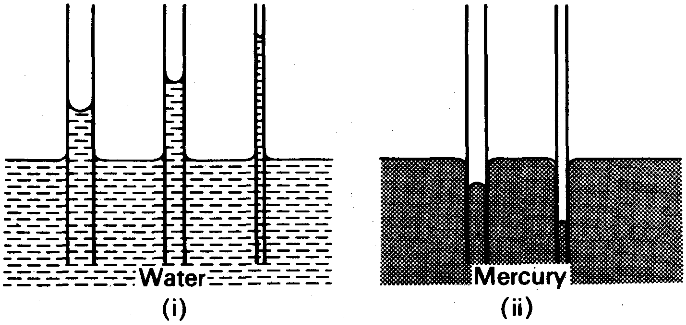
(i) (ii)

FIG. 5.6 Contraction of surface

A toy duck moves by itself across the surface of water when it has a small bag of camphor attached to its base. The camphor lowers the surface tension of the water in contact with it, and the duck is urged across the water by the resultant force on it.

Capillarity

When a capillary tube is immersed in water, and then placed vertically with one end in the liquid, observation shows that the water rises in the tube to a height above the surface. The narrower the tube, the greater is the height to which the water rises, Fig. 5.7 (i). See also p. 140). This phenomenon is known as *capillarity*, and it occurs when blotting-paper is used to dry ink. The liquid rises up the pores of the paper when it is pressed on the ink.



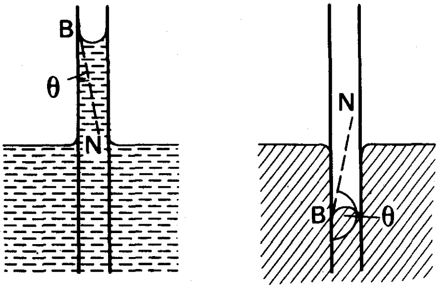
(i) (ii)

FIG. 5.7 Capillary rise and fall

When a capillary tube is placed inside mercury, however, the liquid is depressed *below* the outside level, Fig. 5.7 (ii). The depression increases as the diameter of the capillary tube decreases. See also p. 141.

Angle of Contact

In the case of water in a glass capillary tube, observation of the meniscus shows that it is hemispherical if the glass is clean, that is, the glass surface is tangential to the meniscus where the water touches it. In other cases where liquids rise in a capillary tube, the tangent BN to the liquid surface where it touches the glass may make an acute angle θ with the glass, Fig. 5.8 (i). The angle θ is known as the *angle of contact* between the liquid and the glass, and is always measured *through the liquid*. The angle of contact between two given surfaces varies largely with their freshness and cleanliness. The angle of contact between water and very clean glass is zero, but when the glass is not clean the angle of contact may be about 8° for example. The angle of contact between alcohol and very clean glass is zero.



(i) (ii)

FIG. 5.8 Angle of contact

When a capillary tube is placed inside mercury, observation shows that the surface of the liquid is depressed in the tube and is convex upwards. Fig. 5.8 (ii). The tangent BN to the mercury at the point B where the liquid touches the glass thus makes an obtuse angle, θ, with the glass when measured through the liquid. We shall see later (p. 160) that a liquid will rise in a capillary tube if the angle of contact is acute, and that a liquid will be depressed in the tube if the angle of contact is obtuse. For the same reason, clean water spreads over, or 'wets', a clean glass surface when spilt on it, Fig. 5.9 (i); the angle of contact is zero. On the other hand, mercury gathers itself into small pools or globules when spilt on glass, and does not 'wet' glass, Fig. 5.9 (ii). The angle of contact is obtuse.

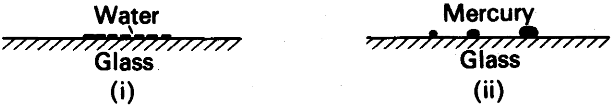


FIG. 5.9 Water and mercury on glass

The difference in behaviour of water and mercury on clean glass can be explained in terms of the attraction between the molecules of these substances. It appears that the force of *cohesion* between two molecules of water is less than the force of *adhesion* between a molecule of water and a molecule of glass; and thus water spreads over glass. On the other hand, the force of cohesion between two molecules of mercury is greater than the force of adhesion between a molecule of mercury and a molecule of glass; and thus mercury gathers in pools when spilt on glass.

Angle of Contact measurement

The angle of contact can be found by means of the method outlined in Fig. 5.10 (i), (ii).

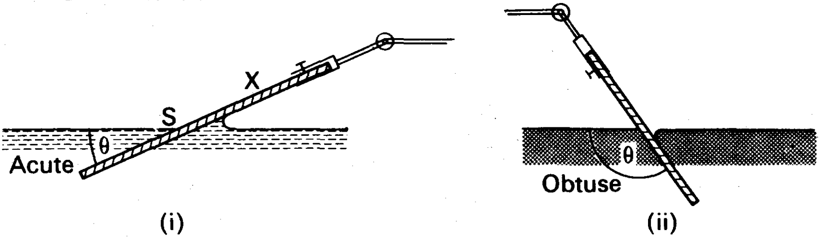


FIG. 5.10 Angle of contact measurement

A plate X of the solid is placed at varying angles to liquid until the surface S appears to be *plane* at X. The angle θ made with the liquid surface is then the angle of contact. For an obtuse angle of contact, a similar method can be adopted. In the case of mercury and glass, a thin plane mirror enables the liquid surface to be seen by reflection. For a freshly-formed mercury drop in contact with a clean glass plate, the angle of contact is 137°.

Measurement of Surface Tension by Capillary Tube Method

Theory. Suppose γ is the magnitude of the surface tension of a liquid such as water, which rises up a clean glass capillary tube and has an angle of contact zero. Fig. 5.11 shows a section of the meniscus M at B, which is a hemisphere. Since the glass AB is a tangent to the liquid, the surface tension forces, which act along the boundary of the liquid with the air, act vertically downwards on the glass. By the law of action and reaction, the glass exerts an equal force in an upward direction on the liquid. Now surface tension, γ, is the force per unit length acting in the surface of the liquid, and the length of liquid in contact with the glass is $2\pi r$, where r is the radius of the capillary tube.

$$\therefore\ 2\pi r \times \gamma = \text{upward force on liquid} \quad . \quad . \quad (1)$$

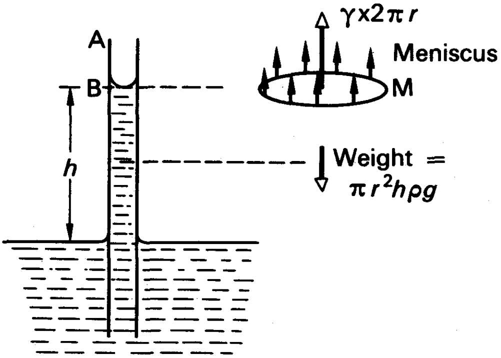


FIG. 5.11 Rise in capillary tube—theory

If γ is in newton metre $^{-1}$ and r is in metres, then the upward force is in *newtons.*

This force supports the weight of a column of height h above the outside level of liquid. The volume of the liquid $= \pi r^2 h$, and thus the mass, m, of the liquid column $=$ volume $\times$ density $= \pi r^2 h\rho$, where ρ is the density. The *weight* of the liquid $= mg = \pi r^2 h\rho g$.

If ρ is in kg m^{-3}, r and h in metres, and $g = 9{\cdot}8$ m s^{-2}, then $\pi r^2 h\rho g$ is in *newtons.*

From (1), it now follows that

$$\therefore\ 2\pi r\gamma = \pi r^2 h\rho g$$

$$\therefore\ \gamma = \frac{rh\rho g}{2} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If $r = 0{\cdot}2$ mm $= 0{\cdot}2\times10^{-3}$ m, $h = 6{\cdot}6$ cm for water $= 6{\cdot}6\times10^{-2}$ m, and $\rho = 1$ g cm^{-3} $= 1000$ kg m^{-3}, then

$$\gamma = \frac{0{\cdot}2\times10^{-3}\times6{\cdot}6\times10^{-2}\times1000\times9{\cdot}8}{2} = 6{\cdot}5\times10^{-2}\ \text{N m}^{-1}$$

In deriving this formula for γ it should be noted that we have (i) assumed the glass to be a tangent to the liquid surface meeting it, (ii) neglected the weight of the small amount of liquid above the bottom of the meniscus at B, Fig. 5.11.

Experiment. In the experiment, the capillary tube C is supported in a beaker Y, and a pin P, bent at right angles at two places, is attached to C by a rubber band, Fig. 5.12. P is adjusted until its point just touches the horizontal level of the liquid in the beaker. A travelling microscope is now focussed on to the meniscus M in C, and then it is focussed on to the point of P, the beaker being removed for this observation. In this way the height h of M above the level in the beaker is determined. The radius of the capillary at M can be found by cutting the tube at this place and measuring the diameter by the travelling microscope; or by measuring the length, l, and mass, m, of a mercury thread drawn into the tube, and calculating the radius, r, from the relation $r = \sqrt{m/\pi l\rho}$, where ρ is the density of mercury. The surface tension γ is then calculated from the formula $\gamma = rh\rho g/2$. Its magnitude for water at 15°C is $7{\cdot}33 \times 10^{-2}$ newton metre^{-1}.

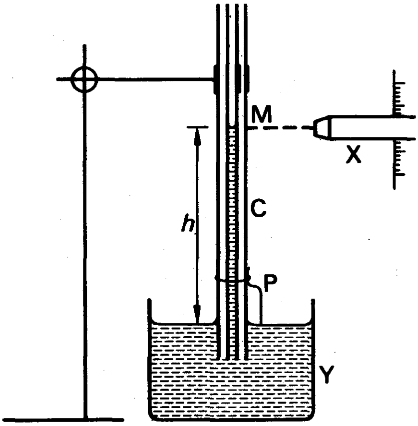


FIG. 5.12 Surface tension by capillary rise

Measurement of Surface Tension by Microscope Slide

Besides the capillary tube method, the surface tension of water can be measured by weighing a microscope slide in air, and then lowering it until it just meets the surface of water, Fig. 5.13. The surface tension force acts vertically downward round the boundary of the slide, and pulls the slide down. If a and b are the length and thickness of the slide,

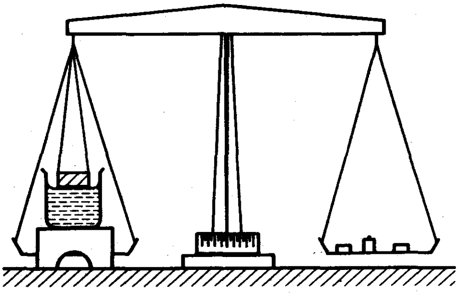


FIG. 5.13 Surface tension by microscope slide

then, since γ is the force per unit length in the liquid surface and $(2a+2b)$ is the length of the boundary of the slide, the downward force $= \gamma(2a+2b)$. If the mass required to counterbalance the force is m, then

$$\gamma(2a+2b) = mg,$$

$$\therefore \gamma = \frac{mg}{2a+2b}.$$

If $m = 0{\cdot}88$ gramme, $a = 6{\cdot}0$ cm, $b = 0{\cdot}2$ cm, then:

$$\gamma = \frac{0{\cdot}88\times10^{-3}\,(\text{kg})\times9{\cdot}8\,(\text{m s}^{-2})}{2\times(6+0{\cdot}2)\times10^{-2}\,(\text{m})} = 7{\cdot}0\times10^{-2}\ \text{N m}^{-1}.$$

Surface Tension of a Soap Solution

The surface tension of a soap solution can be found by a similar method. A soap-film is formed in a three-sided metal frame ABCD, and the apparent weight is found, Fig. 5.14. When the film is broken by piercing it, the decrease in the apparent weight, mg, is equal to the surface tension force acting downwards when the film existed. This is equal to $2\gamma b$, where b = BC, since the film has *two* sides.

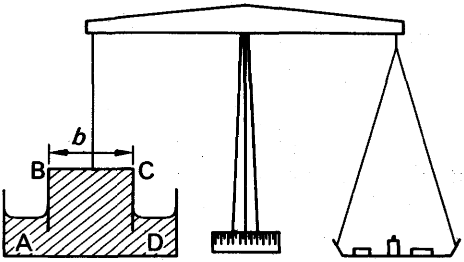


FIG. 5.14 Surface tension of soap film

$$\therefore 2\gamma b = mg,$$

$$\therefore \gamma = \frac{mg}{2b}.$$

It will be noted that the surface tension forces on the sides AB, CD of the frame act horizontally, and their resultant is zero.

A soap film can be supported in a vertical rectangular frame but a film of water can not. This is due to the fact that the soap drains downward in a vertical film, so that the top of the film has a lower concentration of soap than the bottom. The surface tension at the top is thus *greater* than at the bottom (soap diminishes the surface tension of pure water). The upward pull on the film by the top bar is hence greater than the downward pull on the film by the lower bar. The net upward pull supports the weight of the film. In the case of pure water, however, the surface tension would be the same at the top and bottom, and hence there is no net force in this case to support a water film in a rectangular frame.

Pressure Difference in a Bubble or Curved Liquid Surface

As we shall see presently, the magnitude of the curvature of a liquid, or of a bubble formed in a liquid, is related to the surface tension of the liquid.

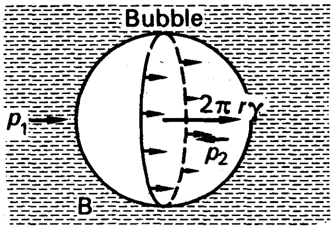


FIG. 5.15 Excess pressure in bubble

Consider a bubble formed inside a liquid, Fig. 5.15. If we consider the equilibrium of *one half*, B, of the bubble, we can see that the surface tension force on B plus the force on B due to the external pressure p_1 = the force on B due to the internal pressure p_2 inside the bubble. The force on B due to the pressure p_1 is given by $\pi r^2 \times p_1$, since πr^2 is the area of the circular face of B and pressure is 'force per unit area'; the force on B due to the pressure p_2 is given similarly by $\pi r^2 \times p_2$. The surface tension force acts round the *circumference* of the bubble, which has a length $2\pi r$; thus the force is $2\pi r\gamma$. It follows that

$$2\pi r\gamma + \pi r^2 p_1 = \pi r^2 p_2.$$

Simplifying,

$$\therefore 2\gamma = r(p_2 - p_1),$$

or

$$p_2 - p_1 = \frac{2\gamma}{r}.$$

Now $(p_2 - p_1)$ is the excess pressure, p, in the bubble over the outside pressure.

$$\therefore \textit{excess pressure, } p, = \frac{2\gamma}{r} \quad . \quad . \quad . \quad (1)$$

Although we considered a bubble, the same formula for the excess pressure holds for any curved liquid surface or meniscus, where r is its radius of curvature and γ is its surface tension, provided the angle of contact is zero. If the angle of contact is θ, the formula is modified by replacing γ by $\gamma \cos \theta$. Thus, in general,

$$\textit{excess pressure, } p, = \frac{2\gamma \cos \theta}{r} \quad . \quad . \quad . \quad (2)$$

Excess Pressure in Soap Bubble

A soap bubble has two liquid surfaces in contact with air, one inside the bubble and the other outside the bubble. The force on one half, B, of the bubble due to surface tension forces is thus $\gamma \times 2\pi r \times 2$, i.e., $\gamma \times 4\pi r$, Fig. 5.16. For the equilibrium of B, it follows that

$$4\pi r\gamma + \pi r^2 p_1 = \pi r^2 p_2,$$

where p_2, p_1 are the pressures inside and outside the bubble respectively. Simplifying,

$$\therefore p_2 - p_1 = \frac{4\gamma}{r},$$

$$\therefore \textit{excess pressure } p = \frac{4\gamma}{r} \quad . \quad . \quad . \quad . \quad (3)$$

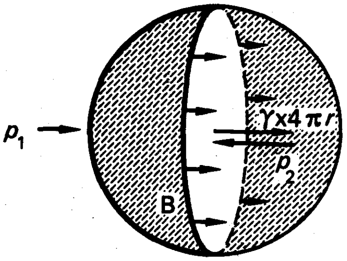


FIG. 5.16 Bubble in water

This result for excess pressure should be compared with the result obtained for a bubble formed inside a liquid, equation (1).

If γ for a soap solution is 25×10^{-3} N m^{-1}, the excess pressure inside a bubble of radius 0·5 cm or $0{\cdot}5 \times 10^{-2}$ m is hence given by:

$$p = \frac{4 \times 25 \times 10^{-3}}{0{\cdot}5 \times 10^{-2}} = 20 \text{ N m}^{-2}.$$

Two soap-bubbles of unequal size can be blown on the ends of a tube, communication between them being prevented by a closed tap in the middle. If the tap is opened, the *smaller* bubble is observed to collapse gradually and the size of the larger bubble increases. This can be explained from our formula $p = 4\gamma/r$, which shows that the pressure of air inside the smaller bubble is greater than that inside the larger bubble. Consequently air flows from the smaller to the larger bubble when communication is made between the bubbles, and the smaller bubble thus gradually collapses.

Since the excess pressure in a bubble is inversely-proportional to the radius, the pressure needed to form a very small bubble is high. This explains why one needs to blow hard to start a balloon growing. Once the balloon has grown, less air pressure is needed to make it expand more.

Surface Tension of Soap-Bubble

The surface tension of a soap solution can be measured by blowing a small soap-bubble at the end B of a tube connected to a manometer M, Fig. 5.17. The tap T is then closed, the diameter *d* of the bubble is measured by a travelling microscope, and the difference in levels *h* of the liquid in the manometer is observed with the same instrument. The excess pressure, *p*, in the bubble $= h\rho g$, where ρ is the density of the liquid in M.

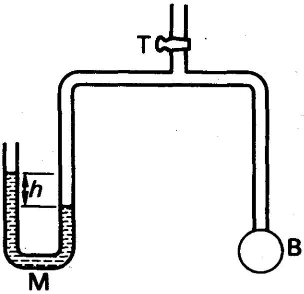


FIG. 5.17
Surface tension of soap-bubble

$$\therefore h\rho g = \frac{4\gamma}{r} = \frac{4\gamma}{d/2}.$$

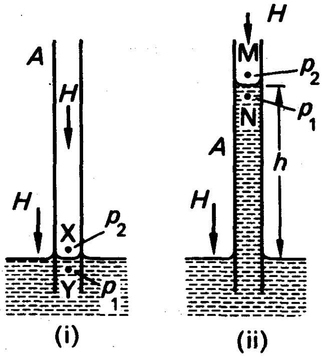
$$\therefore \gamma = \frac{h\rho g d}{8}.$$

Rise or Fall of Liquids in Capillary Tubes

From our knowledge of the angle of contact and the excess pressure on one side of a curved liquid surface, we can deduce that some liquids will rise in a capillary tube, whereas others will be depressed.

Suppose the tube A is placed in water, for example, Fig. 5.18 (i). At first the liquid surface becomes concave upwards in the tube, because the angle of contact with the glass is zero. Consequently the pressure on the air side, X, of the curved surface is greater than the pressure on the liquid side Y by $2\gamma/r$, where γ is the surface tension and r is the radius of curvature of the tube. But the pressure at X is atmospheric, H. Hence the pressure at Y must be less than atmospheric by $2\gamma/r$. Fig. 5.18 (i) is therefore impossible because it shows the pressure at Y equal to the atmospheric pressure. Thus, as shown in Fig. 5.18 (ii), the liquid ascends the tube to a height h such that the pressure at N is less than at M by $2\gamma/r$, Fig. 5.18 (ii). A similar argument shows that a liquid rises in a capillary tube when the angle of contact is acute.

The angle of contact between mercury and glass is obtuse (p. 133). Thus when a capillary tube is placed in mercury the liquid first curves downwards. The pressure inside the liquid just below the curved surface is now greater than the pressure on the other side, which is atmospheric, and the mercury therefore moves down the tube until the excess pressure $= 2\gamma \cos\theta/r$, with the usual notation. A liquid thus falls in a capillary tube if the angle of contact is obtuse.



(i) (ii)

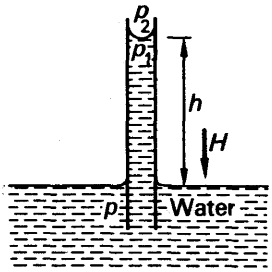
FIG. 5.18
Capillary rise by excess pressure

Capillary Rise and Fall by Pressure Method

We shall now calculate the capillary rise of water by the excess pressure formula $p = 2\gamma/r$, or $p = 2\gamma\cos\theta/r$.

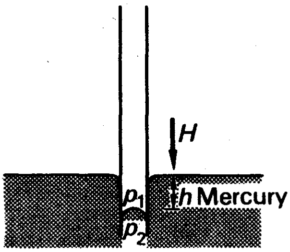
In the case of a capillary tube dipping into water, the angle of contact is practically zero, Fig. 5.19 (i). Thus if p_2 is the pressure of the atmosphere, and p_1 is the pressure in the liquid, we have

$$p_2 - p_1 = \frac{2\gamma}{r}.$$



(i)

FIG. 5.19
Excess
pressure
application



(ii)

Now if H is the atmospheric pressure, h is the height of the liquid in the tube and ρ its density,

$$p_2 = H \text{ and } p_1 = H-h\rho g,$$

$$\therefore\ H-(H-h\rho g) = \frac{2\gamma}{r},$$

$$\therefore\ h\rho g = \frac{2\gamma}{r},$$

$$\therefore\ h = \frac{2\gamma}{r\rho g} \quad . \quad . \quad . \quad \text{(i)}$$

The formula shows that h increases as r decreases, i.e., the narrower the tube, the greater is the height to which the water rises (see Fig. 5.7 (i), p. 132).

If the height l of the tube above the water is *less* than the calculated value of h in the above formula, the water surface at the top of the tube now meets it at an *acute angle of contact* θ. The radius of the meniscus is therefore $r/\cos\theta$, and $l\rho g = 2\gamma/(r/\cos\theta)$, or

$$l = \frac{2\gamma\cos\theta}{r\rho g} \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

Dividing (ii) by (i), it follows that

$$\cos\theta = \frac{l}{h}.$$

Thus suppose water rises to a height of 10 cm in a capillary tube when it is placed in a beaker of water. If the tube is pushed down until the top is only 5 cm above the outside water surface, then $\cos\theta = \frac{5}{10} = 0{\cdot}5$. Thus $\theta = 60°$. The meniscus now makes an angle of contact of 60° with the glass. As the tube is pushed down further, the angle of contact increases beyond 60°. When the top of the tube is level with the water in the beaker, the meniscus in the tube becames plane. (See Example 2, p. 141.)

With Mercury in Glass

Suppose that the depression of the mercury inside a tube of radius r is h, Fig. 5.19 (ii). The pressure p_2 below the curved surface of the mercury is then greater than the (atmospheric) pressure p_1 outside the curved surface; and, from our general result,

$$p_2 - p_1 = \frac{2\gamma\cos\theta}{r},$$

where θ is the supplement of the obtuse angle of contact of mercury with glass, that is, θ is an acute angle and its cosine is positive. But $p_1 = H$ and $p_2 = H+h\rho g$, where H is the atmospheric pressure.

$$\therefore\ (H+h\rho g)-H = \frac{2\gamma\cos\theta}{r}.$$

$$\therefore\ h\rho g = \frac{2\gamma\cos\theta}{r}.$$

$$\therefore\ h = \frac{2\gamma\cos\theta}{r\rho g} \quad . \quad . \quad . \quad (1)$$

The height of depression, *h*, thus increases as the radius *r* of the tube decreases. See Fig. 5.7 (ii), p. 132.

EXAMPLES

1. Define surface tension of a liquid and describe a method of finding this quantity for alcohol.

It water rises in a capillary tube 5·8 cm above the free surface of the outer liquid, what will happen to the mercury level in the same tube when it is placed in a dish of mercury? Illustrate this by the aid of a diagram. Calculate the difference in level between the mercury surfaces inside the tube and outside. (S.T. of water = 75×10^{-3} N m^{-1}. S.T. of mercury = 547×10^{-3} N m^{-1}. Angle of contact of mercury with clean glass = 130°. Density of mercury = 13600 kg m^{-3}.) (*L.*)

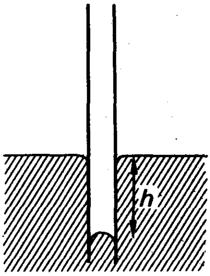


FIG. 5.20 Example

Second part. The mercury is depressed a distance *h* below the outside level, and is convex upward, Fig. 5.20. Suppose *r* is the capillary tube radius.

For water, $h = 5\cdot8$ cm $= 5\cdot8\times10^{-2}$ m, $\gamma = 75\times10^{-3}$ newton m^{-1}, $\rho = 1000$ kg m^{-3}, $g = 9\cdot8$ m s^{-2}.

From $\gamma = rh\rho g/2$,

$$\therefore\ 75\times10^{-3} = r\times5\cdot8\times10^{-2}\times1000\times9\cdot8/2 \text{ (r in metre).}$$

For mercury, $\rho = 13\cdot6\times10^3$ kg m^{-3}, $\gamma = 547\times10^{-3}$ newton m^{-1}.

$$\therefore\ h = \frac{2\gamma\cos 50^\circ}{r\rho g}$$

$$= \frac{2\times547\times10^{-3}\cos 50^\circ\times5\cdot8\times10^{-2}\times1000\times9\cdot8}{13\cdot6\times10^3\times9\cdot8\times75\times10^{-3}\times2}$$

$$= 0\cdot02 \text{ m} = 2 \text{ cm.}$$

2. On what grounds would you anticipate some connection between the surface tension of a liquid and its latent heat of vaporization?

A vertical capillary tube 10 cm long tapers uniformly from an internal diameter of 1 mm at the lower end to 0·5 mm at the upper end. The lower end is just touching the surface of a pool of liquid of surface tension 6×10^{-2} N m^{-1}, density 1200 kg m^{-3} and zero angle of contact with the tube. Calculate the capillary rise, justifying your method. Explain what will happen to the meniscus if the tube is slowly lowered vertically until the upper end is level with the surface of the pool. (*O. & C.*)

Suppose S is the meniscus at a height *h* cm above the liquid surface. The tube tapers uniformly and the change in radius for a height of 10 cm is (0·05 − 0·025) or 0·025 cm, so that the change in radius per cm height is 0·0025 cm. Thus at a height *h* cm, radius of meniscus S is given by

$$r = (0\cdot05 - 0\cdot0025\,h)\times10^{-2} \text{ m}$$

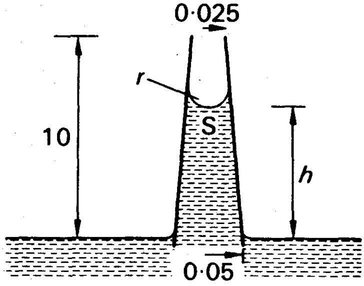


FIG. 5.21 Example

The pressure above S is atmospheric, A. The pressure below S is $(A-h\rho g)$.

$$\therefore \text{ pressure difference } = (h\times 10^{-2})\rho g = \frac{2\gamma}{r} = \frac{200\gamma}{0{\cdot}05-0{\cdot}0025h}.$$

$$\therefore\ 0{\cdot}05h-0{\cdot}0025h^2 = \frac{200\gamma}{\rho g} = \frac{200\times 6\times 10^{-2}}{10^{-2}\times 1200\times 9{\cdot}8} = 0{\cdot}102.$$

$$\therefore\ h^2-20h = -40 \text{ (approx.)}.$$

$$\therefore\ (h-10)^2 = 100-40 = 60.$$

$$\therefore\ h = 10-\sqrt{60} = 2{\cdot}2 \text{ cm}.$$

If the tube is slowly lowered the meniscus reaches the top at some stage. On further lowering the tube the angle of contact changes from zero to an acute angle. When the upper end is level with liquid surface the meniscus becomes plane.

3. 'The surface tension of water is $7{\cdot}5\times 10^{-2}$ newton m^{-1} and the angle of contact of water with glass is zero.' Explain what these statements mean. Describe an experiment to determine *either* (*a*) the surface tension of water, *or* (*b*) the angle of contact between paraffin wax and water.

A glass U-tube is inverted with the open ends of the straight limbs, of diameters respectively 0·500 mm and 1·00 mm, below the surface of water in a beaker. The air pressure in the upper part is increased until the meniscus in one limb is level with the water outside. Find the height of water in the other limb. (The density of water may be taken as 1000 kg m^{-3}.) (*L.*)

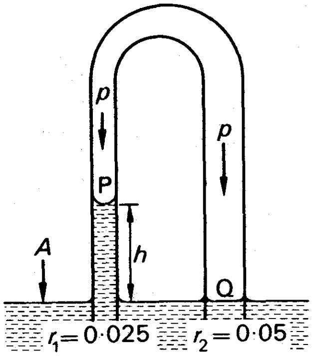


FIG. 5.22 Example (radii in cm)

Suppose p is the air pressure inside the U-table when the meniscus Q is level with the water outside and P is the other meniscus at a height h. Let A be the atmospheric pressure. Then, if r_1 is the radius at P,

$$p-(A-h\rho g)=\frac{2\gamma}{r_1} \qquad \text{(i)}$$

since the pressure in the liquid below P is $(A-h\rho g)$.

The pressure in the liquid below Q = A. Hence, for Q,

$$p-A=\frac{2\gamma}{r_2} \qquad \text{(ii)}$$

where r_2 is the radius.

From (i) and (ii), it follows that

$$h\rho g=\frac{2\gamma}{r_1}-\frac{2\gamma}{r_2}$$

$$\therefore h=\frac{1}{\rho g}\left[\frac{2\gamma}{r_1}-\frac{2\gamma}{r_2}\right]$$

$$=\frac{1}{9800}\left[\frac{2\times 0{\cdot}075}{0{\cdot}25\times 10^{-3}}-\frac{2\times 0{\cdot}075}{0{\cdot}5\times 10^{-3}}\right]$$

$$=3{\cdot}1\times 10^{-2}\text{ m (approx).}$$

Effects of surface tension in measurements

When a hydrometer is used to measure relative density or density, the surface tension produces a downward force F on the hydrometer. If r is the radius of the stem and the angle of contact is zero, then $F=2\pi r\gamma$. For a narrow stem, the error produced in reading the relative density from the graduations is small.

Another case of an undesirable surface tension effect occurs in measurements of the height of liquid columns in glass tubes. The height of mercury in a barometer, for example, is depressed by surface tension (p. 114). If the tubes are wide, surface tension forces can be neglected. If they are narrow, the forces must be taken into account. As an illustration, consider an inverted U-tube dipping into two liquids B and C. Fig. 5.23. These can be drawn up into the tubes to heights

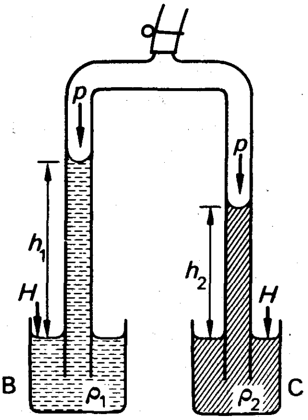


FIG. 5.23 Comparison of densities

h_1, h_2 respectively above the outside level. In the absence of surface tension forces, $p+h_1\rho_1 g$ = atmospheric pressure H, where p is the air pressure at the top of the tubes $= p+h_2\rho_2 g$. Thus $h_1\rho_1 = h_2\rho_2$, or $h_1/h_2 = \rho_2/\rho_1$. Thus the liquid densities may be compared from the ratio of the heights of the liquid columns.

To take account of surface tension, we proceed as follows. Using the notation on p. 137.

$$p-p_1 = \frac{2\gamma_1}{r_1},$$

where p is the air pressure at the top of the tubes, p_1 is the pressure in the liquid near the meniscus of the tube in B, γ_1 is the surface tension of the liquid, and r_1 is the radius. But, from hydrostatics, $p_1 = H-h_1\rho_1 g$.

$$\therefore p-(H-h_1\rho_1 g) = \frac{2\gamma_1}{r_1}$$

$$\therefore H-p = h_1\rho_1 g-\frac{2\gamma_1}{r_1} \quad . \quad . \quad . \quad \text{(i)}$$

If γ_2 is the surface tension of the liquid in C, and r_2 is the radius of the tube in the liquid, then, by similar reasoning,

$$H-p = h_2\rho_2 g-\frac{2\gamma_2}{r_2} \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

From (i) and (ii),

$$\therefore h_2\rho_2 g-\frac{2\gamma_2}{r_2} = h_1\rho_1 g-\frac{2\gamma_1}{r_1}.$$

Re-arranging,

$$\therefore h_2 = \frac{\rho_1}{\rho_2}h_1-\frac{2}{\rho_2 g}\left(\frac{\gamma_1}{r_1}-\frac{\gamma_2}{r_2}\right),$$

which is an equation of the form $y = mx+c$, where c is a constant, $h_2 = y$, $h_1 = x$, and $\rho_1/\rho_2 = m$. Thus by taking different values of h_2 and h_1, and plotting h_2 against h_1, a straight-line graph is obtained whose *slope* is equal to ρ_1/ρ_2, the ratio of the densities. In this way the effect of the surface tension can be eliminated.

Variation of Surface Tension with Temperature. Jaeger's Method

By forming a bubble inside a liquid, and measuring the excess pressure, JAEGER was able to determine the variation of the surface tension of a liquid with temperature. One form of the apparatus is shown in Fig. 5.24 (i). A capillary or drawn-out tubing A is connected to a vessel W containing a funnel C, so that air is driven slowly through A when water enters W through C, so that air is driven slowly through A when water enters W through C. The capillary A is placed inside a beaker containing the liquid L, and a bubble forms slowly at the end of A when air is passed through it at a slow rate.

Fig. 5.24. (ii) shows the bubble at three possible stages of growth. The radius grows from that at *a* to a hemispherical shape at *b*. Here its pressure is larger since the radius is smaller. If we consider the bubble growing to *c*, the radius of *c* would be *greater* than that of *b* and hence it cannot contain the increasing pressure. The downward force on the bubble due to the pressure, in fact, would be greater than

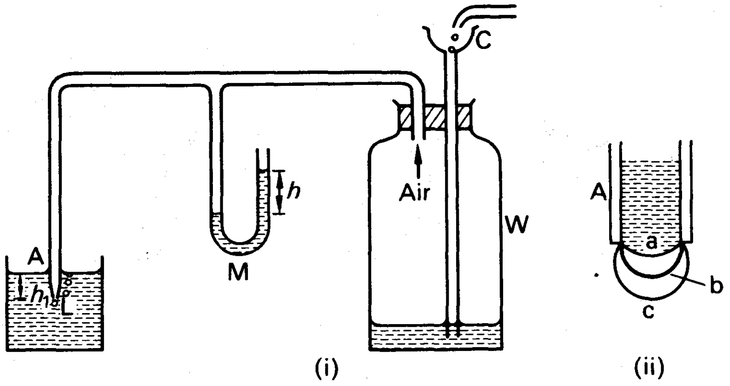


FIG. 5.24 Jaeger's method

the upward force due to surface tension. Hence *the bubble becomes unstable and breaks away from A when its radius is the same as that of A.* Thus as the bubble grows the pressure in it increases to a maximum, and then decreases as the bubble breaks away. The maximum pressure is observed from a manometer M containing a light oil of density ρ, and a series of observations are taken as several bubbles grow.

The maximum pressure inside the bubble = $H+h\rho g$ where h is the maximum difference in levels in the manometer M, and H is the atmospheric pressure. The pressure outside the bubble = $H+h_1\rho_1 g$, where h_1 is the depth of the orifice of A below the level of the liquid L, and ρ_1 is the latter's density.

$$\therefore \text{ excess pressure} = (H+h\rho g)-(H+h_1\rho_1 g) = h\rho g - h_1\rho_1 g.$$

But $$\text{excess pressure} = \frac{2\gamma}{r},$$

where r is the radius of the orifice of A (p. 158).

$$\therefore \frac{2\gamma}{r} = h\rho g - h_1\rho_1 g,$$

$$\therefore \gamma = \frac{rg}{2}(h\rho - h_1\rho_1).$$

By adding warm liquid to the vessel containing L, the variation of the surface tension with temperature can be determined. Experiment shows that the surface tension of liquids, and water in particular, *decreases* with increasing temperature along a fairly smooth curve. Various formulae relating the surface tension to temperature have been proposed, but none has been found to be completely satisfactory. The decrease of surface tension with temperature may be attributed to the greater average separation of the molecules at higher temperature. The force of attraction between molecules is then reduced, and hence the surface energy is reduced, as can be seen from the potential energy curve on p. 126.

Surface Tension and Surface Energy

We now consider the surface energy of a liquid and its relation to its surface tension γ. Consider a film of liquid stretched across a horizontal frame ABCD, Fig. 5.25. Since γ is the force per unit length, the force on the rod BC of length $l = \gamma \times 2l$, because there are two surfaces to the film.

Suppose the rod is now moved a distance b from BC to B′C′ against the surface tension forces, so that the surface area of the film increases. The temperature of the film then usually decreases, in which case the surface tension alters (p. 145). If the surface area increases under *isothermal* (constant temperature) conditions, however, the surface tension is constant; and we can then say that, if γ is the surface tension at that temperature,

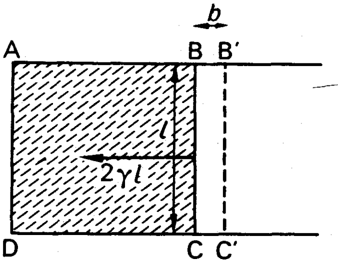


FIG. 5.25
Surface energy and work

$$\text{work done in enlarging surface area} = \text{force} \times \text{distance},$$
$$= 2\gamma l \times b = \gamma \times 2lb.$$

But $2lb$ is the total increase in surface area of the film.

$$\therefore \text{ work done per unit area in enlarging area} = \gamma.$$

Thus the surface tension, γ, can be defined as *the work done per unit area in increasing the surface area of a liquid under isothermal conditions.* This is also called the *free surface energy.*

Surface energy and Latent heat

Inside a liquid molecules move about in all directions, continually breaking and reforming bonds with neighbours. If a molecule in the surface passes into the vapour outside, a definite amount of energy is needed to permanently break the bonds with molecules in the liquid. This amount of energy is the work done in overcoming the inward force on a molecule in the surface, discussed on p. 129. Thus the energy needed to evaporate a liquid is related to its surface energy or surface tension. The latent heat of vaporisation, which is the energy needed to change liquid to vapour at the boiling point, is therefore related to surface energy.

Surface energy

As we have seen, when the surface area of a liquid is increased, the surface energy is increased. The molecules which then reach the surface are slowed up by the inward force, so the average translational kinetic energy of all the liquid molecules is reduced. On this account the liquid cools while the surface is increased, and heat flows in from the surroundings to restore the temperature.

The increase in the *total surface energy per unit area E* is thus given by

$$E = \gamma + H \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where H is the heat per unit area from the surroundings. Advanced theory shows that $H = -\theta\left(\frac{d\gamma}{d\theta}\right)$, where θ is the absolute temperature and $d\gamma/d\theta$ is the corresponding gradient of the γ v. θ graph, the variation of surface tension with temperature. Thus

$$E = \gamma - \theta\frac{d\gamma}{d\theta} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

In practice, since γ decreases with rising temperature, $d\gamma/d\theta$ is negative, and E is thus greater than γ. At 15°C, for example, $\gamma = 74\times10^{-3}$ N m^{-1}, $d\gamma/d\theta = -0{\cdot}15 \times 10^{-3}$ N m^{-1} K^{-1}, $\theta = 288$ K. Thus, from (2),

$$E = (74+288\times0{\cdot}15)\times10^{-3} = 0{\cdot}117 \text{ N m}^{-1} = 0{\cdot}117 \text{ J m}^{-2}.$$

The variation of E with temperature is shown in Fig. 5.26, together with the similar variation of L, the latent heat of vaporisation (see p. 146). Both vanish at the critical temperature, since no liquid exists above the critical temperature whatever the pressure.

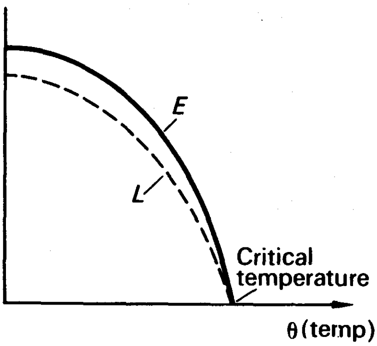


FIG. 5.26 Variation of E and L with temperature

EXAMPLES

1. A soap bubble in a vacuum has a radius of 3 cm and another soap bubble in the vacuum has a radius of 6 cm. If the two bubbles coalesce under isothermal conditions, calculate the radius of the bubble formed.

Since the bubbles coalesce under isothermal conditions, the surface tension γ is constant. Suppose R is the radius in cm, $R\times10^{-2}$ m, of the bubble formed.

Then $\quad$ work done $= \gamma\times$ surface area $= \gamma\times8\pi R^2\times10^{-4}$

But $\quad$ original work done $= (\gamma\times8\pi\,.\,3^2\times\gamma\times8\pi\,.\,6^2)\times10^{-4}$

$$\therefore\ \gamma\times8\pi R^2 = \gamma\times8\pi.3^2+\gamma.8\pi.6^2.$$

$$\therefore\ R^2 = 3^2+6^2.$$

$$\therefore\ R = \sqrt{3^2+6^2} = 6{\cdot}7 \text{ cm}.$$

2. (i) Calculate the work done against surface tension forces in blowing a soap bubble of 1 cm diameter if the surface tension of soap solution is $2{\cdot}5\times10^{-2}$ N m^{-1}. (ii) Find the work required to break up a drop of water of radius 0·5 cm into drops of water each of radii 1 mm. (Surface tension of water $= 7\times10^{-2}$ N m^{-1}.)

(i) The original surface area of the bubble is zero, and the final surface area $= 2\times 4\pi r^2$ (two surfaces of bubble) $= (2\times 4\pi \times 0{\cdot}5^2)\times 10^{-4} = 2\pi\times 10^{-4}$ m^2.

$$\therefore \text{ work done} = \gamma \times \text{increase in surface area.}$$

$$= 2{\cdot}5\times 10^{-2}\times 2\pi\times 10^{-4} = 1{\cdot}57\times 10^{-5} \text{ J.}$$

(ii) Since volume of a drop $= \frac{4}{3}\pi r^3$,

$$\text{number of drops formed} = \frac{\frac{4}{3}\pi\times 0{\cdot}5^3}{\frac{4}{3}\pi\times 0{\cdot}1^3} = 125.$$

$\therefore$ final total surface area of drops

$$= 125\times 4\pi r^2 = 125\times 4\pi\times 0{\cdot}1^2\times 10^{-4},$$

$$= 5\pi\times 10^{-4} \text{ m}^2.$$

But original surface area of drop $= 4\pi\times 0{\cdot}5^2\times 10^{-4} = \pi\times 10^{-4}$ m^2.

$$\therefore \text{ work done} = \gamma \times \text{change in surface area,}$$

$$= 7\times 10^{-2}\times (5\pi-\pi)\times 10^{-4} = 8{\cdot}8\times 10^{-5} \text{ J.}$$

EXERCISES 5

What are the missing words in the statements 1–8?

1. The units of surface tension are . . .

2. The dimensions of surface tension are . . .

3. Small drops of mercury are spherical because the surface area is a . . .

4. The excess pressure in a soap-bubble is given by . . .

5. The excess pressure at the meniscus of water in a capillary tube is . . .

6. A liquid will not 'wet' the surface of a solid if the angle of contact is . . .

7. Surface tension may be defined as the 'force . . .'

8. Surface tension may also be defined as the '. . . per unit area'.

Which of the following answers, A, B, C, D or E, do you consider is the correct one in the statements 9–12?

9. A molecule of a liquid which reaches the surface from the interior gains energy because *A* it reaches the surface with higher speed than when inside the liquid, *B* it overcomes a force of repulsion on molecules at the surface, *C* it overcomes a force of attraction on molecules at the surface, *D* its temperature increases, *E* the gravitational potential energy due to the earth is then higher.

10. If a section of a soap bubble through its centre is considered, the force on one half due to surface tension is *A* $2\pi r\gamma$, *B* $4\pi r\gamma$, *C* $\pi r^2\gamma$, *D* $2\gamma/r$, *E* $2\pi r^2\gamma$.

11. If water has a surface tension of 7×10^{-2} N m^{-1} and an angle of contact with water of zero, it rises in a capillary of diameter 0·5 mm to a height of *A* 70 cm, *B* 7·0 cm, *C* 6·2 cm, *D* 5·7 cm, *E* 0·5 cm.

12. In an experiment to measure the surface tension of a liquid by rise in a capillary tube which tapers, the necessary radius r would be best obtained *A* by cutting the tube at the position of the meniscus and measuring the diameter here directly, *B* by drawing up a thread of mercury of length l and using 'mass =

$\pi r^2 l\rho'$, *C* by measuring the diameter of the lower end of the tube with a travelling microscope, *D* by measuring the upper end of the tube with a travelling microscope, *E* by finding the average of the two measurements in C and D.

13. Define *surface tension.* A rectangular plate of dimensions 6 cm by 4 cm and thickness 2 mm is placed with its largest face flat on the surface of water. Calculate the force due to surface tension on the plate. What is the downward force due to surface tension if the plate is placed vertical and its longest side just touches the water? (Surface tension of water = $7{\cdot}0 \times 10^{-2}$ N m^{-1}.)

14. What are the *dimensions* of surface tension? A capillary tube of 0·4 mm diameter is placed vertically inside (i) water of surface tension $6{\cdot}5 \times 10^{-2}$ N m^{-1} and zero angle of contact, (ii) a liquid of density 800 kg m^{-3}, surface tension $5{\cdot}0 \times 10^{-2}$ N m^{-1} and angle of contact 30°. Calculate the height to which the liquid rises in the capillary in each case.

15. Define the *angle of contact.* What do you know about the angle of contact of a liquid which (i) wets glass, (ii) does not wet glass?

A capillary tube is immersed in water of surface tension $7{\cdot}0 \times 10^{-2}$ N m^{-1} and rises 6·2 cm. By what depth will mercury be depressed if the same capillary is immersed in it? (Surface tension of mercury = 0·54 N m^{-1}; angle of contact between mercury and glass = 140°; density of mercury = 13600 kg m^{-3}.)

16. (i) A soap-bubble has a diameter of 4 mm. Calculate the pressure inside it if the atmospheric pressure is 10^5 N m^{-2}. (Surface tension of soap solution = $2{\cdot}8 \times 10^{-2}$ N m^{-1}.) (ii) Calculate the radius of a bubble formed in water if the pressure outside it is $1{\cdot}000 \times 10^5$ N m^{-2} and the pressure inside it is $1{\cdot}001 \times 10^5$ N m^{-2}. (Surface tension of water = $7{\cdot}0 \times 10^{-2}$ N m^{-1}.)

17. Define *surface tension* of a liquid. State the units in which it is usually expressed and give its dimensions in mass, length, and time.

Derive an expression for the difference between the pressure inside and outside a spherical soap bubble. Describe a method of determining surface tension, based on the difference of pressure on the two sides of a curved liquid surface or film. (*L.*)

18. Explain briefly (*a*) the approximately spherical shape of a rain drop, (*b*) the movement of tiny particles of camphor on water, (*c*) the possibility of floating a needle on water, (*d*) why a column of water will remain in an open vertical capillary tube after the lower end has been dipped in water and withdrawn. (*N.*)

19. Define the terms surface tension, angle of contact. Describe a method for measuring the surface tension of a liquid which wets glass. List the principal sources of error and state what steps you would take to minimize them.

A glass tube whose inside diameter is 1 mm is dipped vertically into a vessel containing mercury with its lower end 1 cm below the surface. To what height will the mercury rise in the tube if the air pressure inside it is 3×10^3 N m^{-2} below atmospheric pressure? Describe the effect of allowing the pressure in the tube to increase gradually to atmospheric pressure. (Surface tension of mercury = 0·5 N m^{-1}, angle of contact with glass = 180°, density of mercury = 13600 kg m^{-3}, $g = 9{\cdot}81$ m s^{-2}.) (*O. & C.*)

20. Explain how to measure the surface tension of a soap film.

The diameters of the arms of a U-tube are respectively 1 cm and 1 mm. A liquid of surface tension $7{\cdot}0 \times 10^{-2}$ N m^{-1} is poured into the tube which is placed vertically. Find the difference in levels in the two arms. The density may be taken as 1000 kg m^{-3} and the contact angle zero. (*L.*)

21. Explain what is meant by surface tension, and show how its existence is accounted for by molecular theory.

Find an expression for the excess pressure inside a soap-bubble of radius R and surface tension T. Hence find the work done by the pressure in increasing the radius of the bubble from a to b. Find also the increase in surface area of the bubble, and in the light of this discuss the significance of your result. (*C.*)

22. A clean glass capillary tube, of internal diameter 0·04 cm, is held vertically with its lower end below the surface of clean water in a beaker, and with 10 cm of the tube above the surface. To what height will the water rise in the tube? What will happen if the tube is now depressed until only 5 cm of its length is above the surface? The surface tension of water is $7{\cdot}2 \times 10^{-2}$ N m^{-1}.

Describe, and give the theory of some method, other than that of the rise in a capillary tube, of measuring surface tension. (*O. & C.*)

23. Explain (*a*) in terms of molecular forces why the water is drawn up above the horizontal liquid level round a steel needle which is held vertically and partly immersed in water, (*b*) why, in certain circumstances, a steel needle will rest on a water surface. In each case show the relevant forces on a diagram. (*N.*)

24. The force between two molecules may be regarded as an attractive force which increases as their separation decreases and a repulsive force which is only important at small separations and which there varies very rapidly. Draw sketch graphs (*a*) for force-separation, (*b*) for potential-energy separation. On each graph mark the equilibrium distance and on (*b*) indicate the energy which would be needed to separate two molecules initially at the equilibrium distance.

With the help of your graphs discuss briefly the resulting motion if the molecules are displaced from the equilibrium position. (*N.*)

25. Explain briefly the meaning of *surface tension* and *angle of contact.*

Account for the following: (*a*) A small needle may be placed on the surface of water in a beaker so that it 'floats', and (*b*) if a small quantity of detergent is added to the water the needle sinks.

A solid glass cylinder of length l, radius r and density σ is suspended with its axis vertical from one arm of a balance so that it is partly immersed in a liquid of density ρ. The surface tension of the liquid is γ and its angle of contact with the glass is α. If W_1 is the weight required to achieve a balance when the cylinder is in air and W_2 is the weight required to balance the cylinder when it is partly immersed with a length $h(< l)$ below the free surface of the liquid, derive an expression for the value of $W_1 - W_2$. If this method were used to measure the surface tension of a liquid, why would the result probably be less accurate than that obtained from a similar experiment using a thin glass plate? (*O. & C.*)

26. Explain in terms of molecular forces why some liquids spread over a solid surface whilst others do not.

A glass capillary tube of uniform bore of diameter 0·050 cm is held vertically with its lower end in water. Calculate the capillary rise. Describe and explain what happens if the tube is lowered so that 4·0 cm protrudes above the water surface. Assume that the surface tension of water is $7{\cdot}0 \times 10^{-2}$ N m^{-1}. (*N.*)

27. Define *surface tension.* Describe how the surface tension of water at room temperature may be determined by using a capillary tube. Derive the formula used to calculate the result.

A hydrometer has a cylindrical glass stem of diameter 0·50 cm. It floats in water of density 1000 kg m^{-3} and surface tension $7{\cdot}2 \times 10^{-2}$ N m^{-1}. A drop of liquid detergent added to the water reduces the surface tension to $5{\cdot}0 \times 10^{-2}$ N m^{-1}. What will be the change in length of the exposed portion of the glass stem? Assume that the relevant angle of contact is always zero. (*N.*)

28. The lower end of a vertical clean glass capillary tube is just immersed in water. Why does water rise up the tube?

A vertical capillary tube of internal radius r m has its lower end dipping in water of surface tension T newton m^{-1}. Assuming the angle of contact between water and glass to be zero, obtain from first principles an expression for the pressure excess which must be applied to the upper end of the tube in order just to keep the water levels inside and outside the tube the same.

A capillary of internal diameter 0·7 mm is set upright in a beaker of water with one end below the surface; air is forced slowly through the tube from the upper end, which is also connected to a U-tube manometer containing a liquid of density 800 kg m^{-3}. The difference in levels on the manometer is found to build up to 9·1 cm, drop to 4·0 cm, build up to 9·1 cm again, and so on. Estimate (*a*) the depth of the open end of the capillary below the free surface of the water in the beaker, (*b*) the surface tension of water. [State clearly any assumptions you have made in arriving at these estimates.] (*O.*)

29. It is sometimes stated that, in virtue of its surface tension, the surface of a liquid behaves as if it were a stretched rubber membrane. To what extent do you think this analogy is justified?

Explain why the pressure inside a spherical soap bubble is greater than that outside. How would you investigate experimentally the relation between the excess pressure and the radius of the bubble? Show on a sketch graph the form of the variation you would expect to obtain.

If olive oil is sprayed on to the surface of a beaker of hot water, it remains as separated droplets on the water surface; as the water cools, the oil forms a continuous thin film on the surface. Suggest a reason for this phenomenon. (*C.*)

30. Describe the capillary tube method of measuring the surface tension of a liquid.

An inverted U-tube (Hare's apparatus) for measuring the specific gravity of a liquid was constructed of glass tubing of internal diameter about 2 mm. The following observations of the heights of balanced columns of water and another liquid were obtained:

Height of water (cm)	2·8	4·2	5·4	6·9	8·5	9·8	11·6
Height of liquid (cm)	2·0	3·8	5·3	7·0	9·1	10·7	13·0

Plot the above results, explain why the graph does not pass through the origin, and deduce from the graph an accurate value for the specific gravity of the liquid. (*N.*)

31. How does simple molecular theory account for surface tension? Illustrate your account by explaining the rise of water up a glass capillary.

A light wire frame in the form of a square of side 5 cm hangs vertically in water with one side in the water-surface. What additional force is necessary to pull the frame clear of the water? Explain why, if the experiment is performed with soap-solution, as the force is increased a vertical film is formed, whereas with pure water no such effect occurs. (Surface tension of water is $7{\cdot}4 \times 10^{-2}$ N m^{-1}.) (*O. & C.*)

32. Define *surface tension* and state the effect on the surface tension of water of raising its temperature.

Describe an experiment to measure the surface tension of water over the range of temperatures from 20°C to 70°C. Why is the usual capillary rise method unsuitable for this purpose?

Two unequal soap bubbles are formed one on each end of a tube closed in the middle by a tap. State and explain what happens when the tap is opened to put the two bubbles into connection. Give a diagram showing the bubbles when equilibrium has been reached. (*L.*)