

Surface Tension

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Content

Molecular forces of cohesion & adhesion, Molecular range: sphere of influence, Surface tension, Free energy, Excess pressure across a curved film or membrane, Capillarity, Contact angle, Capillary rise method.

References

Elements of Properties of Matter – D. S. Mathur
Fundamentals of Physics – David Halliday, Jearl Walker, and
Robert Resnick

CHAPTER XIV

SURFACE TENSION—CAPILLARITY

232. Molecular Forces. Since surface tension is essentially a molecular phenomenon, we had better have first a clear idea as to what forces operate between molecules.

There are two types of molecular forces : (i) **forces of adhesion, or adhesive forces**, and (iii) **forces of cohesion or cohesive forces**.

(i) *Adhesion is the force of attraction between molecules of different substances*, and is different for different pairs of substances, e.g., gum has a greater adhesive force than water or alcohol.

(ii) *Cohesion, on the other hand, is the force of attraction between molecules of the same substance*. This force is different from the ordinary gravitational force and does not obey the ordinary inverse square law, the force varying inversely probably as the eighth power of the distance between two molecules and thus decreases rapidly with distance, — in fact it is '*appreciable when the distance between two molecules is inappreciable and becomes inappreciable when the distance is appreciable*.'* It is the greatest, in the case of solids, less in the case of liquids and the least in the case of gases, almost negligible at ordinary temperature and pressure, when the molecules lie very much further apart for it to be appreciable. This explains at once why a solid has a definite shape, a liquid has a definite free surface and a gas has neither.

✱ **233. Molecular Range—Sphere of Influence.** The maximum distance up to which the force of cohesion between two molecules can act is called their *molecular range*, and is generally of the order of 10^{-7} cms. in the case of solids and liquids, being different for different substances. *A sphere drawn around a molecule as centre, with a radius equal to its molecular range is called the sphere of influence† of the molecule*. Obviously, the molecule is affected only by the molecules inside this sphere, i.e., it attracts and is, in turn, attracted by them, remaining unaffected by the molecules outside it, as they lie beyond its range of attraction. **Laplace** (1804) and **Gauss** (1830) were the first to have evolved this theory of cohesive force between molecules in order to satisfactorily explain the various effects of surface tension, like capillarity etc.

✓ **234. Surface Tension.** It is a general experience that a liquid in small quantity, free from any external force, like that due to

*As N K. Adam remarked in his '*Physics and Chemistry of Surfaces*,' if the force were gravitational in character and obeyed the inverse square law, 'the surface tensions of the ocean would be far greater than that of a cup full of water, because the distant parts would act with sensible effect'

†It is also sometimes referred to as the *sphere of molecular attraction*, or, *molecular activity*.

gravity, will always assume the form of a spherical drop — e.g., rain drops, small quantities of mercury placed on a clean glass plate etc.

Now, for a given volume, a sphere has the least surface area. Thus, a liquid always tends to have the least surface area. The following experiments beautifully illustrate this tendency of a liquid to decrease its surface area.

1. If we take a wire-ring and dip it in a soap solution, we find that, on taking it out, a thin film is formed across the ring. If we place a moistened

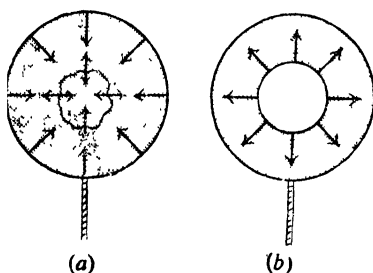


Fig 277.

cotton loop lightly on the film, it will remain in any form or position in which it is placed, as shown in Fig. 277 (a); for, the soap-film lies both inside and outside the loop and at every point on the loop, therefore, there are equal and opposite forces, tending to pull it outward (due to the outside film) and inwards (due to the inside film), thus cancelling each other out. But if the film inside the loop be pricked, so that the film there disappears, we find that the loop at once gets stretched into the form of a circular ring, as shown in Fig. 277 (b), because the inward forces having all vanished, only the outward forces are left acting

perpendicularly to it at every point. Now, for a given perimeter, a circle encloses the greatest area, so that the loop now encloses the maximum area. In other words, the area of the film left between the loop and the wire ring is now reduced to a minimum, clearly showing that the film has a tendency to contract or shrink, or that there is tension in it.

2. If we place a greased needle on a piece of blotting paper and put the paper lightly on the surface of water, the blotting paper will soon sink to the bottom but the needle will remain floating on the surface. Careful observation will show that there is a small depression formed below and around the needle, and that the free surface of water is slightly extended. The weight of the needle is here supported by the tension in the depression. If one end of the needle be made to pierce the surface of water, it rapidly goes slantingly down to the bottom.

3. If we immerse an ordinary camel hair paint brush in water, its hair all spread out, presenting a sort of a bushy appearance, but the moment it is withdrawn, they all come closer together in a more or less compact mass, as though bound down by some sort of a contracting membrane.

4. Yet another beautiful experiment, often performed for fun by junior students, is the rapid movement of a camphor scorpion on water. What they do is simply to arrange pieces of camphor together, in the shape of a scorpion, and put it on water, when, due to the reduction in the surface tension of water, on account of the camphor gradually dissolving into it, the camphor is drawn or pulled aside by the surrounding uncontaminated water of a higher surface tension. And, since we have camphor dissolving more rapidly at some points than at others, this force due to surface tension is not uniform all round, with the result that the 'scorpion' scampers about haphazardly in different directions.

If, however, the water be already contaminated with some grease etc., its surface tension may be reduced to an extent that the camphor has no further possibility of reducing it. In such a case, therefore, the movement of the camphor may altogether stop.

The above experiments clearly show that the surface of a liquid behaves as though it were covered with an elastic skin or membrane, having a natural tendency to contract, with the important difference, however, that whereas in the case of the membrane or skin, the tension increases as the skin is stretched, or its surface area is increased, in accordance with Hooke's Law, it is quite independent of the area of the surface in the case of a liquid, unless the liquid film is reduced in thick-

ness to less than 10^{-7} cms., when the tension in it decreases rapidly. This tension or pull in the surface of a liquid is called its **surface tension**, and may be defined as *the force per unit length of a line drawn in the liquid surface, acting perpendicularly to it at every point, and tending to pull the surface apart along the line.*

235. **Explanation of Surface Tension.** An extension of the kinetic theory of gases to the case of liquids easily explains the phenomenon of surface tension and the credit for it must go to **Laplace**, who first attempted it.

Consider four molecules, *A, B, C* and *D* of a liquid, with their spheres of influence drawn around them, as shown in Fig. 278,—sphere *A* being well inside the liquid, *B*, near to the free surface of the liquid, *C*, just on the free surface and *D*, above the free surface.

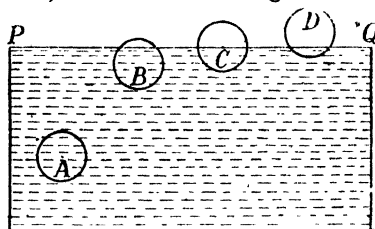


Fig. 278.

Since the sphere of influence of *A* lies wholly inside the liquid, it is attracted equally in all directions by the other molecules lying within its sphere of influence, so that there is no resultant cohesive force on it one way or the other, and it, therefore, merely possesses its *thermal velocity*.

The sphere of influence of molecule *B*, on the other hand, lies partly outside the liquid, and this part contains only a comparatively few molecules of the gas or vapour above the liquid, so that the upper half of the sphere contains fewer molecules attracting it upwards, than the lower half, attracting it downwards, and so there is a *resultant downward force* acting on *B*.

The molecule *C* lies on the surface of the liquid, so that full one-half of its sphere of influence lies above the surface of the liquid, containing only a few molecules of the gas or vapour, whereas there are liquid molecules in its entire lower half, and thus, the resultant downward force in this case is the *maximum*. This downward or inward force exerted per unit area of a liquid surface is called its *internal, intrinsic or cohesion pressure*, and is the cause of cohesion. It is this pressure which is represented by the term a/v^2 in **van de Waal's** modified gas-equation. ✓

In the case of the molecule *D*, which has passed out of the liquid surface, only a part of the sphere of influence lies inside the liquid, so that the downward force on it decreases, and when the sphere of influence passes entirely outside the liquid surface, there is no downward force on the molecule at all, and it is free to wander about as a molecule of the vapour or gas. We thus see that *all over the surface of the liquid there is a downward pull due to the attraction between the molecules.*

✓ 236. **Surface Film and Surface Energy.** If a plane be drawn parallel to the free surface layer and at a distance equal to the molecular range from it, the layer of the liquid, lying in-between the free

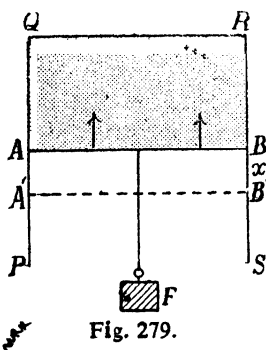
surface and this plane is called the *surface-film*. Clearly, all the molecules in the film are being acted upon by a resultant cohesive force in the downward direction, the magnitude of which increases as the free surface of the liquid is approached.

When a molecule is brought from the interior of the liquid to the surface-film, work has to be done against the downward cohesive force acting on it, and its potential energy is thus increased. *It follows, therefore, that the potential energy of the molecules in the surface-film is greater than that of those inside the liquid.*

Since, however, *the potential energy of a system tends towards a minimum, (i.e., a system tends to have the lowest possible potential energy), the film tends to have the least surface area, (its thickness being fixed) in order that the number of molecules in it may be a minimum.* The potential energy per unit area of the surface-film is called its *surface energy*.

Now, before a molecule can be brought to the surface of the liquid, room has to be made for it, and this is done by separating the adjacent molecules on the surface. *Work is, therefore, done against the cohesive forces between the molecules in the surface, and not against the internal or downward cohesive force, for the molecules are moved in a direction perpendicular to this latter force.* It thus appears that *in increasing the surface area of a liquid, work is done as though the surface under a state of tension were being extended, very much like a rubber sheet being extended.* The analogy, however, does not go far; for, as already indicated, whereas in the case of a rubber sheet, the tension increases with extension or increases in its surface area, it is quite independent of the surface area in the case of a surface-film, and is the same at all points in it.

✓ 237. **Free Energy of a Surface and Surface Tension.** Take a rectangular framework of wire PQRS, (Fig. 279), with a horizontal wire AB placed across it, free to move up and down, and form a soap-film across AQRB, by dipping it in a soap solution. The wire AB is pulled upwards by the surface tension of the film, acting perpendicularly to the wire and in the plane of the film. To keep the wire in position, therefore, a force has to be applied downwards, equal and opposite to the upward force due to surface tension. Let this downward force be equal to F including the weight of the wire AB, which is also acting downwards. Then, if T be the surface tension of the film, i.e., if T be the *force per unit length of the film* and l , the length of the



wire AB, we have upward force acting on the wire $AB = 2l.T$, because the film has *two surfaces* and each has a surface tension T . Since the film is in equilibrium, it is clear that

$$2l.T = F.$$

Now, if the wire AB be pulled downwards through a small

distance x into the position $A'B'$, i.e., if the film be extended by an area $l.x$ on each side, we have

$$\text{work done} = x = F \times 2.l.x$$

The film gets cooled on being stretched, because the drawing out of the molecules from the interior against the attractive force results in a retardation of their thermal agitation, with a consequent lowering of temperature*. It, therefore, takes up heat from the atmosphere to come to its original temperature. *This heat absorbed together with the mechanical work done, forms the energy of the new surface area $2lx$ of the film formed.*

If, therefore, E be the surface energy of the film and Q ergs of heat be absorbed per unit area of the new surface formed†, we have,

$$E \times 2l.x = 2.l.T.x + Q.2.l.x.$$

Or, $E = T + Q.$ [Dividing throughout by $2lx$.

Or, $T = (E - Q) = (\text{surface energy} - \text{heat energy per unit area})$
i.e., $= \text{potential energy per unit area.}$

$T = \text{work done in creating unit area of the film.}$

Thus, the surface tension of a liquid may be defined as the amount of work done in increasing the surface area of the liquid-film by unity, or as the mechanical part of the surface energy of the liquid film. This mechanical part of the surface energy of a liquid-film is free energy, so that, the surface tension of a liquid is equal to the free energy of the liquid film or surface.‡

238. **Pressure Difference Across a Liquid Surface—Drops and Bubbles.** (i) Suppose the free surface of a liquid is *plane*, as shown in Fig. 280 (i), then, the resultant force due to surface tension on a molecule on its surface is *zero*, and the cohesion-pressure is, therefore, just *nominal*. ✓

(ii) If the free surface of the liquid be *concave*, [Fig. 280 (ii)], the resultant force on a molecule on the surface would be upwards, and the cohesion pressure is, therefore, *decreased*. ✓

(iii) And, finally, if the liquid surface be *convex*, as shown in Fig. 280 (iii), the resultant force due to surface tension on a molecule

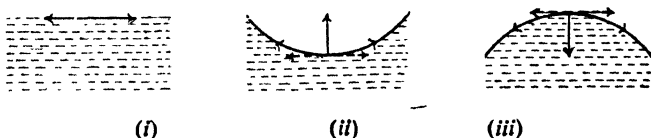


Fig. 280.

*This is clearly an example of *Le Chatelier's principle*, viz., that 'if one of the factors of any system in equilibrium is changed, thus disturbing the equilibrium, the effect produced tends to restore that factor to its original value.' Thus, a lowering of the temperature of the surface results in a rise in its tension, which increases the force opposing enlargement of its surface.

†It can be shown that the value of Q is equal to $\theta.dT/d\theta$, where θ is the absolute temperature and $dT/d\theta$, the rate of change of surface tension with temperature.

‡Surface tension of a liquid is generally, but *erroneously*, defined as the surface energy of the liquid surface. But, obviously, the surface energy can be equal to the surface tension *only* if the heat absorbed by the film be ignored.

on the surface will be directed downwards, so that the cohesion-pressure is, in this case, *increased*.

✓ **239. Excess Pressure inside a Liquid Drop.** It must be clear from the above that the molecules near the surface of a drop, (which is a *convex* surface), experience a resultant pull *inwards*. The pressure inside it must, therefore, be greater than the pressure outside it. Let this excess pressure inside over the pressure outside the drop be p . Then, if r be the radius of the drop, and T , its surface tension, we have, considering the equilibrium of one-half of the drop—say, the upper half, or the upper hemisphere,—the upward thrust on the plane face $ABCD$, (Fig. 281), due to the excess pressure p is equal to $p \cdot \pi r^2$.

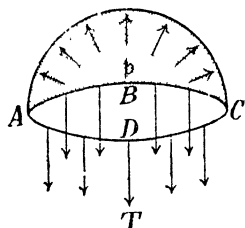


Fig. 281.

And, force due to surface tension, acting downwards on it and round its edge, is equal to $T \cdot 2\pi r$. Since the hemisphere is in equilibrium, we have

$$p \cdot \pi r^2 = T \cdot 2\pi r,$$

whence,

$$p = \frac{T \cdot 2\pi r}{\pi r^2} = \frac{2T}{r}.$$

✓ **240. Excess Pressure inside a Soap Bubble.** If, instead of a drop of liquid, we consider a bubble, there are *two* surfaces to be considered, and *not one*, because it is like a spherical shell or a hollow cylinder, having an inner and an outer surface; so that, the force due to surface tension in this case is $2 \times 2\pi r \cdot T$, (i.e., $4\pi r \cdot T$ due to each surface). Therefore, for equilibrium of the hemisphere, we have, in this case,

$$p \cdot \pi r^2 = 2 \times 2\pi r \cdot T = 4\pi r T,$$

whence,

$$p = \frac{4\pi r \cdot T}{\pi r^2} = \frac{4T}{r}.$$

It will thus be seen that the excess pressure inside a drop or a bubble is inversely proportional to its radius (i.e., $p \propto 1/r$); so that, the smaller the bubble, the greater the excess pressure inside it.

This can be beautifully shown by blowing two soap bubbles, of *unequal* sizes, at the two ends of a tube of the form of the letter *T*, as shown in Fig. 282, and then putting them into communication with each other. The air passes from the smaller one into the bigger one, (because the pressure inside the smaller one is greater than that inside the bigger one), so that the smaller bubble goes on shrinking, and the bigger one goes on swelling, until the smaller one is reduced to a *hemisphere*; for, then, any further shrinkage would mean an increase in its radius and, therefore, a decrease in the pressure inside it. Equilibrium between the two bubbles is attained when the curvatures of the two become the *same*.

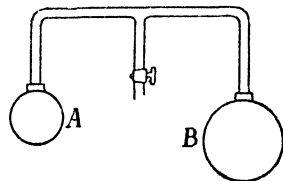


Fig. 282.

241. Determination of the Surface Tension of a Bubble. The expression for the excess pressure inside a bubble, deduced in §240, affords us a simple method of determining the surface tension of the bubble. For, if we have a vertical glass tube AB , (Fig. 283), with a fine orifice or aperture at its lower end B , connected to a manometer M , and a stop-cock S , then, on dipping AB into the experimental liquid, a liquid film is formed at the orifice. This film is then blown into a bubble at B , by opening the stop-cock for a while and allowing some air to come into AB . The difference h in the heights of the liquid columns in M is noted. Then, if ρ be the density of the manometer-liquid, the excess pressure inside the bubble is clearly equal to $h\rho g$. But, as we know, the excess pressure inside the bubble is also equal to $4T/r$, where T is its surface tension. Hence, equating the two, we have

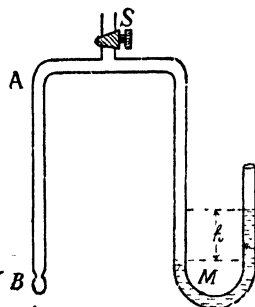


Fig. 283.

$$4T/r = h\rho g, \quad \text{whence,} \quad T = r.h\rho g/4,$$

where r is the radius of curvature of the bubble which is obtained from its diameter, measured accurately by means of a travelling microscope.

It will easily be seen that for accuracy of the result, the value of h should be large, i.e., the excess pressure inside the bubble should be large. This would be so, if the bubble be small or the size of the aperture at B be small.

242. Work done in Blowing a Bubble. If, for the sake of simplicity, we neglect the cooling produced when a film is stretched, the work done in blowing a bubble is easily calculated out as follows :

We know, from § 237 above, that

work done in creating a film = *surface tension* \times *area of the film formed*.

If, therefore, the radius of the bubble blown be r , the area of the film forming the bubble = $2 \times 4\pi r^2$, for it has two surfaces, an inner and an outer one, each of surface area $4\pi r^2$.

Therefore, *work done in blowing the bubble* = $T \times 8\pi r^2 = 8\pi r^2 T$.

243. Curvature, Pressure and Surface Tension. If we have a curved liquid surface at rest, the inward pressure on it due to surface tension must be balanced by an equal pressure acting outwards.

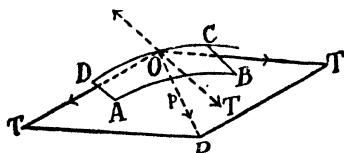


Fig. 284.

Consider a portion $ABCD$ of a liquid surface, (Fig 284), *cylindrical in form*, i.e., curved only in one direction. Then, the force of surface tension T acts at right angles to every unit length of its boundary. The forces

over AB and CD are equal and opposite and hence cancel out, but those over AD and BC , though equal in magnitude are inclined to each other, and have thus a resultant p , normal to the surface, as shown.

To determine the value of p , consider unit length of the surface at O , (Fig. 285), taken along the direction of DA . Forces T and T act at the point O , as shown, their resultant being $OP = T.d\theta$.

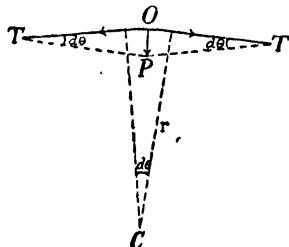


Fig. 285.

Thus, a force $T.d\theta$ acts inwards on an area equal to $1 \times r.d\theta$, where r is the radius of curvature of the surface, (because we are considering unit length of the surface of breadth $r.d\theta$). If a resultant pressure p acts outward on this area, the total force directed outward on the area is equal to $p.r.d\theta$.

For this element of the liquid surface to be at rest, therefore, we have
whence,

$$p.r.d\theta = T.d\theta, \\ p = T/r \text{ dynes/cm}^2.$$

This resultant pressure is, therefore, the difference of pressure on the two sides of the surface, which is required to balance the effect due to surface tension. *It follows, therefore, that the pressure must be greater on the concave side than on the convex side, to balance the effect of surface tension on the surfaces.*

If the surface be curved in two directions, as shown in Fig. 286, and the radii of the two curvatures be r_1 and r_2 respectively, the pressure due to the curvature of AB and CD will be T/r_1 and that due to the curvature of AD and BC will be T/r_2 ; and, therefore, the total difference of pressure on the two sides of the surface will be given by

$$p = \left(\frac{T}{r_1} + \frac{T}{r_2} \right) = T \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$$

And, if one of the surfaces be convex and the other, concave, the radii r_1 and r_2 of the two surfaces will have opposite signs. So that, in such a case, we shall have

$$p = T(1/r_1 - 1/r_2).$$

Combining the cases, therefore, we may put the general relation as

$$p = T(1/r_1 \pm 1/r_2).$$

Now, let us consider a few special cases :

(i) *Case of a spherical surface.* In the case of a spherical surface, like that of a liquid drop, or an air bubble inside a liquid, we have $r_1 = r_2 = r$, say ; so that, excess pressure inside it is given by

$$p = T \left(\frac{1}{r} + \frac{1}{r} \right) = \frac{2T}{r}. \quad [\text{See } \S 239]$$

In the case of an air or a soap bubble, because there are two surfaces, an inner and an outer one, we have

$$p = 2 \times \frac{2T}{r} = \frac{4T}{r}. \quad [\text{See } \S 240]$$

(ii) *Case of a cylindrical surface.* In this case, one of the radii is infinite, whereas the other is the same as the radius (r) of the cylinder.

So that, for one single surface, $p = T/r$,
and for two surfaces, $p = 2T/r$.

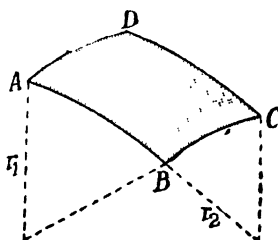


Fig. 286.

(iii) Case of a catenoid. Here, the surface being one of revolution, with no difference of pressure, we have $p = 0$. And, therefore,

$$\left(\frac{1}{r_1} \pm \frac{1}{r_2}\right) = 0.$$

An example of such a surface is that of a soap-film, supported in-between two parallel rings with its two ends burst, to make the pressure difference zero.

244. Layer of liquid between two plates. It is common experience that if two plates of glass be placed one over the other, there is no difficulty in separating them, but if a drop of liquid, say, water, be placed in between them and squeezed into a thin layer, it may, require considerable force to pull them apart. The reason will be clear from the following :

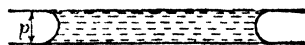


Fig. 287.

The thin layer or film of water wets the plates over an almost circular area, which is concave outwards, as shown in Fig. 287.

If d be the thickness of the water layer in-between the plates, the radius of curvature of the two concave edges of the liquid layer is nearly $d/2$. Thus, if r be the radius of the circular area or film of water, the excess pressure p inside the liquid-film over the outside atmospheric pressure is given by

$$p = T \left(\frac{1}{r} - \frac{2}{d} \right),$$

where T is the surface tension of the water-film.

Since r is very large compared with d , $1/r$ is almost negligible in comparison with $2/d$; so that, we have

$$p = T \left(0 - \frac{2}{d} \right). \text{ Or, } p = - \frac{2T}{d}.$$

Thus, the pressure inside the film is less than the outside atmospheric pressure, (as is clear from the $-ve$ sign of p), by $2T/d$ and, therefore, the excess pressure of the atmosphere on the two plates pushes them closer together, making d still smaller and r larger, thus further increasing p .

Now, if A be the circular area over which the water wets the plates, the total force which squeezes them together is equal to

$$\frac{2T}{d} \times A = \frac{2AT}{d} = \frac{2\pi r^2.T}{d}.$$

This much force, perpendicular to their surface, will, therefore, be needed to pull them apart. Obviously, the smaller the value of d , i.e., the thinner the layer of water, the greater the force required to separate them.

245. Shape of Liquid Meniscus in a Capillary Tube. We know that a liquid meniscus in a capillary tube is concave for a liquid, like water and convex for a liquid, like mercury. Let us see what determines its shape.

Let a capillary tube of glass be dipped vertically in a liquid, meeting its surface at P , (Fig. 288). Then, a liquid molecule at P , in contact with the tube there, will be attracted outward by the solid molecules of the tube near to it, due to the force of adhesion.

and attracted inwards by the near molecules of the liquid, due to the *force of cohesion*; the resultant force on it will, therefore, be the resultant of these two forces of adhesion and cohesion.

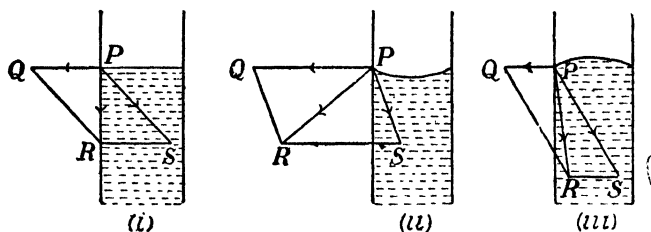


Fig. 288.

Now, the resultant force of adhesion acts at right angles to the tube at the point P . Let it be represented by the straight line PQ . And, the resultant force of cohesion acts at an angle of 45° to the vertical, and is represented by the straight line PS , so that, the two forces acting on the molecule are inclined to each other at an angle of 135° . Their resultant, obtained by the ordinary law of parallelogram of forces, is represented by the diagonal PR of the parallelogram $PQRS$, with PQ and PS as adjacent sides. Its direction will naturally depend upon the relative magnitudes of the two forces PQ and PS , and the following different cases arise :

- (i) If PQ/PS be equal to $1/\sqrt{2}$, i.e., if $PS = \sqrt{2}.PQ$, the resultant, (PR) will lie along the vertical, as shown in Fig. 288 (i).
- (ii) If PS be smaller than $\sqrt{2}.PQ$, the resultant (PR) will lie outside the liquid, as shown in Fig. 288 (ii).
- (iii) If PS be greater than $\sqrt{2}.PQ$, then, PQ will lie inside the liquid, as shown in Fig. 288 (iii).

What happens to molecule P , happens to all other molecules in contact with the glass of the tube. And since a liquid cannot permanently withstand a shearing stress, its surface at every point will be at right angles to the resultant force there, when the liquid attains the position of equilibrium.

Thus, in the *first case*, when the resultant force PR acts along the vertical, i.e., when $PS = \sqrt{2}.PQ$, or, the cohesive force is $\sqrt{2}$ times the adhesive force, the molecules of the liquid are neither raised nor lowered and the liquid surface remains flat or plane.

In the *second case*, when PR lies outside the liquid, i.e., when $PS < \sqrt{2}.PQ$, or the cohesive force is less than $\sqrt{2}$ times the adhesive force, the molecules of the liquid near the walls of the tube are raised up against the tube, those in the middle remaining practically unaffected, thus making the liquid surface *concave upwards*, as in the case of water and other liquids which wet the walls of the tube.

And, when PR lies inside the liquid, i.e., when $PS > \sqrt{2}.PQ$, or, the cohesive force is greater than $\sqrt{2}$ times the adhesive force, the liquid molecules near the walls of the tube are depressed there, making the surface *convex upwards*, as in the case of mercury and other liquids, which do not wet the walls of the tube.

246. Angle of Contact.

(i) **Case of a liquid in contact with a solid.** When a liquid meets a solid, its surface near its plane of contact with the solid is, in general, curved. The angle between the tangent to the liquid surface at the point of contact and the solid surface, inside the liquid, is called the angle of contact for that pair of solid and liquid.

The angle may have any value between 0° and 180° . For most liquids and glass, it is less than 90° ; for mercury and glass it is about 140° . It really depends upon the nature of the liquid and the solid, and is not altered by a change in the inclination of the solid.

In the figures shown, [Fig. 289 (i) and (ii)]; $\angle PQR$ is the *angle of contact*. It is *acute* in (i) and *obtuse* in (ii); for, in the former case, the liquid rises up a little alongside the glass plate, dipped in the liquid, and the angle between QR , the tangent to the liquid surface and the part QP of the plate, *inside the liquid*, is acute, whereas, in the latter case, the liquid is depressed a little where it comes into contact with the glass plate, and the angle between the tangent PR to the liquid surface on the part QP of the plate, *inside the liquid*, is obtuse.

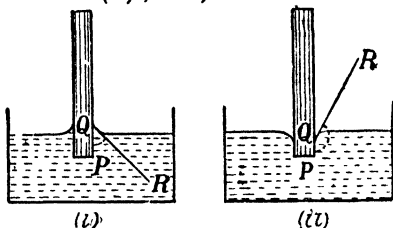


Fig. 289.

For pure water and clean glass, the angle of contact is 0° . For ordinary water and glass it is about 18° ; and if the surface of the glass be contaminated with grease, its value may be as much as 35° .

(ii) **Case of two liquids in contact with each other and with air.** If two liquids, not miscible with each other, be brought into contact as at O , (Fig. 290); both being in contact with air, three surface tensions are to be taken into consideration, (a) that of the surface between air and liquid I, viz., T_1 ; (b) that of the surface between air and liquid II viz., T_2 ; and (c) that between liquid I and liquid II, viz., T_3 .

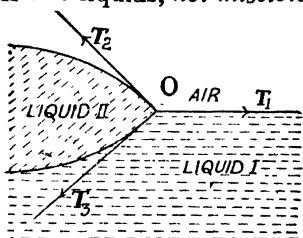


Fig. 290.

For equilibrium T_1 , T_2 and T_3 should be represented by the three sides of a triangle, taken in order. This triangle of forces is known as **Neumann's triangle**. In actual practice, we come across no two pure liquids for which the *Neumann's triangle* may be constructed,—one of the surface tensions being always greater than the other two; so that, the equilibrium condition shown in the figure is never attained. Thus, for example, in the case of water, mercury and air, the water drop, when placed over mercury, spreads all over its surface, provided both water and mercury are pure. This is so, because the surface tension of mercury is about 550 dynes/cm., and that of water, only 75 dynes/cm. But, if the mercury surface be contaminated with grease, its surface tension

decreases and some water drops may stay on it, so that, in that case, the construction of *Neumann's triangle* can be possible.

(iii) Case of a solid, liquid and air in contact. This is a more important case than the previous one, for we have to consider three surface tensions, viz., T_1 for air-liquid, T_2 for air-solid and T_3 for liquid-solid surfaces respectively, (Fig. 291).

Let θ be the angle of contact of the liquid with the solid, —*acute*, in case (a) and *obtuse* in case (b). For equilibrium, therefore, T_3 plus the component $T_1 \cos \theta$ of T_1 , in the direction of T_3 , must be balanced by T_2 , i.e.,

$$T_3 + T_1 \cos \theta = T_2.$$

Or, $T_1 \cos \theta = T_2 - T_3$, whence, $\cos \theta = (T_2 - T_3)/T_1$.

Clearly, therefore, if T_2 is greater than T_3 , $\cos \theta$ will be positive, i.e., θ will be less than 90° ; and if T_2 is less than T_3 , $\cos \theta$ will be

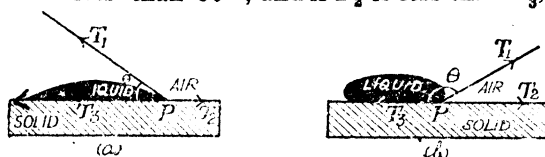


Fig. 291.

negative, and θ will lie between 90° and 180° . If, however, $T_2 > T_1 + T_3$, there will be no equilibrium, and the liquid will spread over the solid, as happens when a water drop is placed over a perfectly clean plate of glass, or a grease-free mercury surface.

247. Measurement of the Angle of Contact. For mercury and glass, the angle of contact may be determined by the following simple method due to *Gay Lussac*.

A small round-bottomed glass flask is nearly filled with mercury (more than $\frac{3}{4}$ ths of it), and its mouth closed tightly by a rubber bung, through which passes a glass rod R to adjust the level of mercury in it. The flask is then clamped in the inverted position, as shown in Fig. 292 (a), and the rod (R) is moved in or out, until the

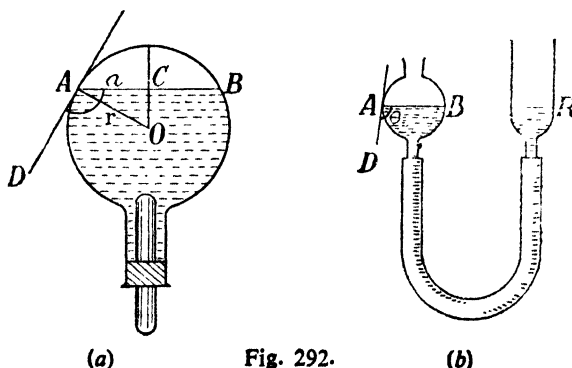


Fig. 292.

surface of mercury is plane where it meets the glass, i.e., no meniscus or curved portion (or capillary curve, as it is sometimes called), appears there. This can be tested by observing the image of a printed sheet of paper held against the flask, by the light reflected

at grazing incidence from the mercury surface. An undistorted image indicates that the surface of mercury is *plane* where it meets the glass.

The mercury surface in the flask forms a circular sheet of diameter AB , which is measured by means of a pair of calipers, whence the radius AC of the sheet is known. Let it be denoted by a . Then, if r be the radius of the bulb of the flask, and $\angle BAO = \phi$, we have

$$\cos \phi = \frac{a}{r}. \text{ Or, } \phi = \cos^{-1} \frac{a}{r}. \quad \dots (i)$$

Now, if a tangent AD be drawn to the spherical bulb at A , the angle of contact θ , for mercury and glass, is clearly equal to the angle BAD .

$$\text{Or, } \theta = \angle BAD = \angle BAO + \angle OAD. \\ \text{Or, } \theta = (\phi + 90^\circ). \quad \dots (ii)$$

So that, knowing ϕ , from relation (i) above, the value of θ can be easily determined.

A better arrangement for making the surface of mercury plane is the one shown in Fig. 292 (b). Here, the level of mercury in the spherical bulb, which is open at both ends, is adjusted by raising or lowering the reservoir of mercury (R), connected to it by an India-rubber tubing. The procedure otherwise is the same as in the first experiment.

Another simple method to determine the angle of contact for mercury and glass is to insert a small slanting glass plate AB into mercury, as shown in Fig. 293, and to adjust its inclination until the mercury meets the glass at P without curvature, i.e., the surface of mercury is horizontal there. Then, the angle of contact for mercury and glass is equal to $(180 - \phi)$ where $\angle APC = \phi$.

To measure the angle ϕ , a plumb line is dropped from A .

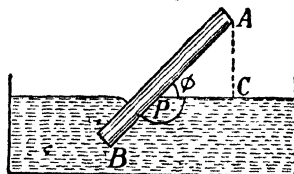


Fig. 293.

$$\text{Then, clearly, } \tan \phi = \frac{AC}{PC}. \text{ Or, } \phi = \tan^{-1} \frac{AC}{PC}.$$

For measuring the angle of contact between water and glass, coated with wax, a similar method was used by Adam.

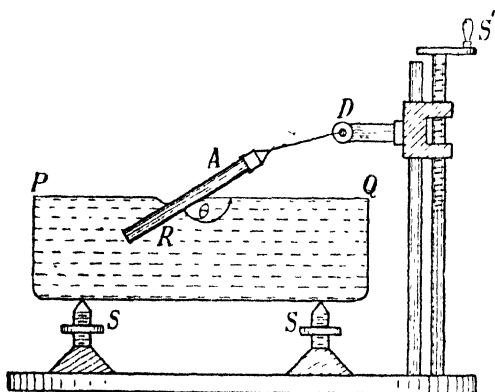


Fig. 294.

A glass trough is coated on the inside with wax, so that it may be filled with water above the level of the sides, and is supported by two screws, S and S' , (Fig. 294), such that, by working them up or down, the top of the trough is made *perfectly horizontal*. It is then filled with water and any impurities on its surface skimmed off by moving lightly across it a wax-coated glass plate.

A glass plate *A*, also coated with wax, is clamped, as shown, so that it can be moved up or down in the vertical plane, about a horizontal axis at *D*, by means of a screw *S'*. It is then dipped into the water, and its angle of inclination adjusted until the water surface touching it is perfectly horizontal. Then, the angle θ between the lower part of the plate and the horizontal water surface is the angle of contact for water and the wax-coated glass plate, and is measured as in the above case for mercury and glass.

The angle θ , in this case, is found to depend on whether the plate is lowered into the water or raised up and hence two readings are taken—one, when the plate is lowered and the other, when it is raised, and their mean is taken as the correct value of θ , or the required *angle of contact*.

✓248. **Rise of Liquid in a Capillary Tube.** One of the most striking effects of surface tension is to raise a liquid in a capillary tube dipped into it,—a capillary tube being just a tube of a very fine bore (from the Latin word, *capillus*—a hair). It is for this reason that surface tension is also sometimes called *capillarity*.

When a capillary tube is dipped in a liquid like water, which wets it and for which the angle of contact may be taken to be zero, the liquid immediately rises up into it, and if the tube be a *fine* one, the shape of the liquid meniscus is spherical and concave upwards, as shown at *B*, (Fig. 295).*

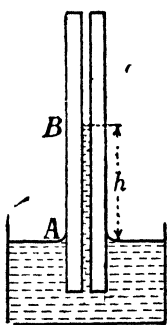


Fig. 295.

Let r be the radius of the tube at *B*, the point up to which the liquid rises into it. Then, it will be practically the same as the radius of the concave meniscus, so that the excess pressure above the meniscus over that immediately below it is $2T/r$, i.e., the pressure in the liquid, just below the meniscus, is less than the atmospheric pressure above it by $2T/r$. And, since the pressure on the liquid surface, outside the tube, is atmospheric, the liquid will be forced up into the tube, until the hydrostatic pressure of the liquid column in the tube equals this excess pressure $2T/r$. If the liquid rises to a height h , the hydrostatic pressure due to the liquid column in the tube on the surface of the liquid will clearly be $h.\rho.g$, where ρ is the density of the liquid.†

$$\therefore 2T/r = h.\rho.g. \quad \text{Or,} \quad 2T = r.h.\rho.g,$$

whence,

$$T = \frac{r.h.\rho.g}{2} \quad \dots (i)$$

*The rise of a liquid in a capillary tube was first explained by *Hawksbee* in a book of his, published in the year 1709, as being due to the attraction of the glass for the liquid. Observing that a liquid does not rise higher in a thick-walled tube than in a thin-walled one, he naturally concluded that only the molecules close to the surface of the glass must be concerned in this attraction. As mentioned already, we now know that the forces between molecules causing surface tension are precisely the same as those operating in the cases of cohesion, solution or chemical reaction.

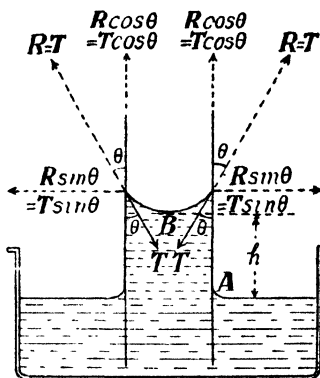
†It will thus be seen that the capillary tube acts like a *manometer*, giving the difference of pressure above and immediately below the liquid meniscus.

Thus, knowing r , h , ρ and g , the surface tension T of the liquid can be easily determined.

In case, however, the angle of contact for the liquid be not zero and the tube be not narrow, the surface tension T of the liquid acts *inwards* along the tangent to the liquid meniscus at every point of its contact with the inner surface of the tube, making an angle θ with the wall of the tube, (Fig. 296). where θ is the *angle of contact* for the liquid and the glass of the tube.

There is thus exerted an *inward* pull on the glass in *this* direction at all these points.

Since, in accordance with Newton's third law of motion, action and reaction are equal and opposite, there is an *equal* and opposite reaction R exerted by the glass on the liquid. This reaction R (equal to T) may be resolved into two rectangular components—(i) $R \cos \theta / \text{cm.} = T \sin \theta / \text{cm.}$, along the vertical, in the upward direction and (ii) $R \sin \theta / \text{cm.} = T \sin \theta / \text{cm.}$, at right angles to it, in the outward direction, as shown. Taking the whole meniscus into consideration, the horizontal or outward components all cancel each other out, and only the vertical components are effective, which are thus added up.



• Fig 296.

Now, if r be the *radius of curvature* of the tube at the height of the meniscus, then, obviously, the meniscus touches it along a length $2\pi r$, the *circumference* of the circle of radius r ; so that, the *total upward force* on the liquid in the tube is $2\pi r.T \cos \theta$. It is *this force* which supports the weight of the column h of the liquid in the tube, (where h is the length of the column from the horizontal surface A of the liquid, outside the tube, to the bottom of the meniscus at B) *plus* the weight of a volume v of the liquid, *in the meniscus itself*, —i.e., the weight of a total volume of the liquid, $\pi r^2.h + v$, (where $\pi r^2.h$ is the volume of the liquid column h).

$$\therefore 2\pi r.T \cos \theta = (\pi r^2.h + v). \rho.g,$$

where ρ is the density of the liquid.

$$\text{Or,} \quad T = \left(\frac{\pi r^2.h + v}{2\pi r.\cos \theta} \right) \cdot \rho.g.$$

If the volume of the liquid in the meniscus be negligible, in comparison with that in the column h , i.e., if the tube of a very fine bore, we have

$$T = \frac{\pi r^2.h \cdot \rho.g}{2\pi r \cos \theta} = \frac{r.h.\rho.g}{2 \cos \theta}, \quad \dots (ii)$$

the relation being known as *Jurin's Equation*.

N.B. In case the capillary tube is not vertical, but inclined at an angle α to it, we take into consideration only the *vertical height* (h) of the liquid

*For experimental details of the method, see page 504.

column in it, which will obviously be equal to $l \cos \alpha$, where l is the length of the tube occupied by the liquid. So that, here,

$$T = r \cdot \rho \cdot g \cdot l \cos \alpha / 2 \cos \theta.$$

If, however, v be not negligible, its value may be determined by taking the meniscus to be *hemispherical* in shape, (since the tube is narrow), of radius nearly equal to r , i.e., the same as that of the tube at that place, so that the volume of the liquid in the meniscus is equal to the difference between the volumes of a cylinder of radius r and length r and a hemisphere of radius r .

$$\text{Or, } v = \pi r^2 \cdot r - \frac{2}{3} \cdot \pi r^3 = \pi r^3 - \frac{2}{3} \cdot \pi r^3. \quad \left\{ \begin{array}{l} \text{volume of a cylinder} = \pi r^3, \\ \text{of a sphere, } 4\pi r^3/3; \text{ and of a} \\ \text{hemisphere} = 2\pi r^3/3. \end{array} \right.$$

$$\text{Or, } v = \frac{1}{3} \pi r^3.$$

In this case, therefore,

$$2\pi r \cdot T \cos \theta = (\pi r^2 \cdot h + \frac{1}{3} \pi r^3) \rho \cdot g = \pi r^2 \cdot (h + \frac{1}{3} r) \cdot \rho \cdot g.$$

$$\text{Or, } T = \frac{\pi r^2 \cdot (h + \frac{1}{3} r) \cdot \rho \cdot g}{2\pi r \cdot \cos \theta} \quad \left\{ \begin{array}{l} \text{i.e., the effective height of the liquid} \\ \text{column is now } h + \frac{1}{3} r, \text{ and not } h. \end{array} \right.$$

And, in case $\theta = 0$, $\cos \theta = 1$; so that, we then have

$$T = \frac{r(h + \frac{1}{3} r) \cdot \rho \cdot g}{2} \text{ dynes/cm.}$$

But if θ be greater than 90° , $\cos \theta$ is *negative* and the liquid column in the tube is depressed below the liquid level outside it, i.e., h is *negative*. Hence it is that we find it so difficult to introduce mercury, (for which $\theta = 140^\circ$ nearly), into a fine capillary tube.

Again, if we introduce into water, a capillary tube, with its *inside coated with paraffin wax* to make $\theta > 90^\circ$, the surface of the water column also, inside the tube, lies below that in the outer vessel.

And, further, we may come across two liquids for which the values of T are the same but whose angles of contact (θ) are different. They will naturally rise to different heights when the same capillary tube is introduced into them.

249. Rise of Liquid in a Tube of Insufficient Length. We have seen above, how a liquid rises up into the capillary tube, dipped

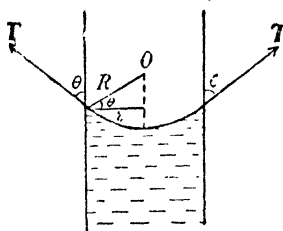


Fig. 297.

into it, until the weight of the liquid in the tube is just balanced by the force due to its surface tension. If θ be the angle of contact between the liquid and the tube, and R , the radius of the liquid meniscus in the tube, we have $r = R \cos \theta$, (Fig. 297), where r is the radius of the tube; so that, relation (ii), above, now becomes

$$T = \frac{R \cos \theta \cdot h \cdot \rho \cdot g}{2 \cos \theta} = \frac{R h \cdot \rho \cdot g}{2},$$

where h is the height of the liquid column in the tube.

Hence, clearly,

$$R \cdot h = 2T / \rho \cdot g, \text{ a constant.}$$

Now, with the tube sufficiently longer than h , it is the value of h alone that changes to satisfy the above relation for T . But, if the tube be smaller than the calculated value of h , the only variable in the above relation is R , because now $h = l$, the length of the tube (a

constant) and so is θ a constant for the given liquid and the tube. The liquid thus just spreads over the walls of the tube at the top and its meniscus acquires a new radius of curvature R' , such that $R'.l = 2T/\rho.g$, or, that $R'.l = R.h = \text{a constant}$.

250. Rise of Liquid in a Conical Capillary Tube. Suppose we take a conical capillary tube, (*i.e.*, a capillary tube with a fine conical bore) ABC , with a hole at its upper end, (Fig. 298), and dip it in a liquid, like water, which wets its walls. We shall find that the liquid rises up into it to a height h , above the liquid surface, in accordance with the relation,

$$h = 2T \cos \alpha / R.\rho.g, \quad \dots \dots (i)$$

where α is the semi-vertical angle of the tube, and R , the radius of the tube at the liquid meniscus FG .

Let the vertical height AD of the apex of the cone from the liquid surface be denoted by l , and the radius of the tube, where it meets the liquid surface, (*i.e.*, of the portion BC of it), by r . Then, from the similar right-angled triangles AEF and ADB , we have

$$\frac{FE}{BD} = \frac{AE}{AD}$$

$$\text{Or,} \quad \frac{R}{r} = \frac{l-h}{l}, \quad \text{whence,} \quad R = \left(\frac{l-h}{l} \right).r.$$

Putting this value of R in relation (i), above, we have $h = \frac{2.l.T.\cos \alpha}{(l-h).r.\rho.g}$

$$\text{So that,} \quad h(l-h) = \frac{2.l.T.\cos \alpha}{r.\rho.g}.$$

$$\text{Or,} \quad h^2 - hl + \frac{2.l.T.\cos \alpha}{r\rho g} = 0,$$

which is a quadratic equation in h .

$$\text{So that,} \quad h = \frac{l \pm \sqrt{l^2 - 4 \times \frac{2.l.T.\cos \alpha}{r.\rho.g}}}{2}$$

$$\text{Or,} \quad h = \frac{l}{2} \pm \sqrt{\frac{l^2}{4} - \frac{2l.T.\cos \alpha}{r.\rho.g}}, \quad \dots \dots (ii)$$

whence the height h , up to which the liquid rises into the tube, can be easily determined.

And, if the tube be only slightly conical, we have $\cos \alpha = 1$, very nearly. In that case, therefore,

$$h = \frac{l}{2} + \sqrt{\frac{l^2}{4} - \frac{2lT}{r.\rho.g}}.$$

N.B. The $-ve$ sign is not usually indicated.

Further, in such a tube, R is practically equal to r , *i.e.*, it is practically a uniform capillary tube, as shown in Fig. 295, and, therefore, for the liquid to rise up to the top into the tube, the minimum value of T should be greater than $r.l.\rho.g/2$.

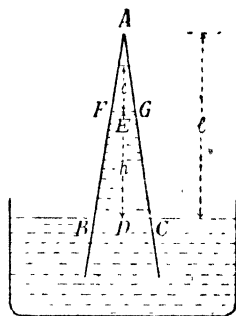


Fig. 298

251. Energy required to raise a liquid in a capillary tube. We have seen above how when a capillary tube is dipped vertically into a liquid which wets the walls of the tube, there is a rise of the liquid inside the tube. *The rise, obviously, takes place against the action of gravity and the liquid, therefore, must gain in potential energy.* The question, therefore, arises as to where does it get this increase in its potential energy from. For, according to the law of conservation of energy, energy can only be converted from one form into another, but cannot be created. The explanation is, however, simple.

We have three surfaces of separation to consider when a capillary tube is immersed in a liquid, viz., (i) *an air-liquid surface* (ii) *an air-glass surface* and (iii) *a glass-liquid surface*, each having its own surface tension, different from the others, and *equal to its free surface energy per unit area.*

Now, as the *plane* liquid surface in the tube acquires a curvature, (i.e., becomes concave), the air-liquid surface increases and, as the liquid rises in the tube, the glass-liquid surface increases, the air-glass surface decreasing by an equal amount. Thus, the surface energy of the air-liquid and the glass-liquid surfaces increases while that of the air-glass surface decreases by the same amount. *In other words, the energy required to raise the liquid in the capillary tube is obtained from the surface energy of the air-glass surface.*

On the other hand, a liquid, which does not wet the walls of the tube, gets depressed inside it, below its level outside the tube. In this case, obviously, the glass-liquid surface decreases, whereas the air-glass surface increases by an equal amount, resulting in a *net increase* in the surface energy of the whole system. This energy is derived from the depression of the liquid inside the tube, whose gravitational potential energy is thus decreased by an equal amount.

252. Rise of a Liquid Between Two Parallel Plates. An almost similar case to the above is that of two vertical plates kept parallel and close to each other in a liquid, when the liquid rises in between them, (if it wets the plates). Let us calculate the height to which it rises.

If d be the distance between the two plates and, r , the radius of the meniscus, (which is *cylindrical*, in this case), we have $\frac{d}{2r} = \cos \theta$, whence, $2r \cos \theta = d$, or $r = d/2 \cos \theta$, where θ is the angle of contact for the liquid and the plates.

Now, we know that the pressure just below the meniscus is less than the pressure just above it by an amount equal to $T\left(\frac{1}{r} + \frac{1}{r'}\right)$, where r and r' are the radii of the two curvatures, at right angles to each other. Since the meniscus is cylindrical, one of the curvatures has a radius equal to that of the cylinder and the other, a radius equal to ∞ , (the surface being plane), so that $r' = \infty$, and, therefore, $1/r' = 0$, and hence the excess pressure just above the meniscus over that just below it is equal to T/r . Or, substituting the value of r , we have *excess pressure above the meniscus* $= \frac{T}{d/2 \cos \theta} = \frac{2T \cos \theta}{d}$.