

# Lecture 19

In this lecture we will learn about “Surface Tension”

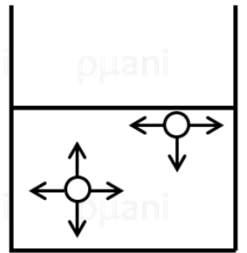
A molecule in the bulk water are in uniform force field. Whereas a molecule at the surface experiences a net inward force. Liquid surface in absence of other forces tend to adopt shapes to minimize their surface area. The surface layer seems to behave like a stretched membrane and tends to contract to reduce the surface area.

That is why liquid drops (be it mercury or liquid water) always takes the spherical shape. (Sphere has least surface area for a given volume).

The work ( $dw$ ) needed to change the area by an amount  $d\sigma$  is proportional to area  $d\sigma$

Thus,  $dw \propto d\sigma$

$$\Rightarrow dw = \gamma \times d\sigma$$



$\gamma$  is known as the surface tension. Higher the work necessary to change the same area means higher surface tension.

$\gamma$  has the unit of energy or work/area. Thus units are typically  $\text{J/m}^2$ . However it is expressed as force/length or Newton/metre. [ $1 \text{ J/m}^2 = 1 \text{ N/m}$ ]

Force per unit length acting at right angles to the line along the surface of the liquid.

Benzene  $\rightarrow 28.88 \text{ mN/m}$

Hg  $\rightarrow 472.0 \text{ mN/m}$

$\text{H}_2\text{O} \rightarrow 72.75 \text{ mN/m}$

Because (Helmholtz) energy decreases ( $dA < 0$ ) if the surface area decreases ( $d\sigma < 0$ ), surface have a natural tendency to contract.

A few definitions:

Bubble: A bubble is a region in which vapour is trapped by a thin film.

Cavity: A cavity is a vapour filled hole in a liquid.

True bubbles have two surface, each on each side of the film.

Cavities have only one surface.

Droplet: Droplet is a small volume of liquid at equilibrium surrounded by its vapour.

The cavities in a liquid are at equilibrium when the tendency for their surface area to decrease is balanced by the rise in internal pressure which would then result.

The pressure inside cavity is  $p_{in}$  and its radius is 'r', then outward force will be  $4\pi r^2 \times p_{in}$

The force inward arises from external pressure and surface tension.

Force due to external pressure =  $4\pi r^2 \times p_{out}$

Forces due to surface tension can be calculated as follows:

Changes in surface area when radius changes from r to (r + dr) is

$$\begin{aligned} d\sigma &= 4\pi(r + dr)^2 - 4\pi r^2 = 4\pi \times 2r \times dr \quad [dr \text{ is small so } (dr)^2 \text{ can be ignored}] \\ &= 8\pi r dr \end{aligned}$$

Since,  $dw = \gamma \times d\sigma$

So, work done when the surface is stretched is  $dw = 8\pi r \times dr \times \gamma$

Work = Force  $\times$  distance, the force opposing the stretching through a distance  $dr$  is equal to  $(8\pi r \times \gamma)$

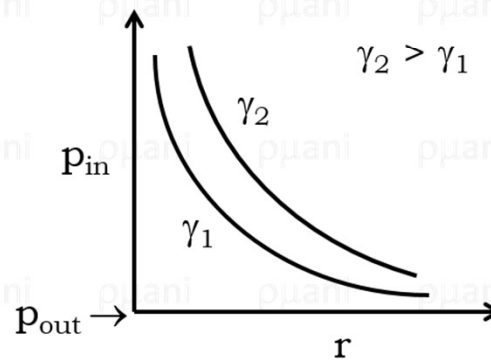
Thus, the total inward force is  $[4\pi r^2 \times p_{\text{out}} + 8\pi r \times \gamma]$

At equilibrium,  $4\pi r^2 \times p_{\text{in}} = 4\pi r^2 \times p_{\text{out}} + 8\pi r \times \gamma$

$$\Rightarrow p_{\text{in}} = p_{\text{out}} + \frac{2\gamma}{r}$$

Laplace equation

How will be the plot of  $p_{\text{in}}$  vs.  $r$ ?



Surface pressure: Collapse pressure

Since both  $\gamma$  and  $r$  are positive, so,  $p_{\text{in}} > p_{\text{out}}$

When  $r$  is very large,  $p_{\text{in}} \approx p_{\text{out}}$

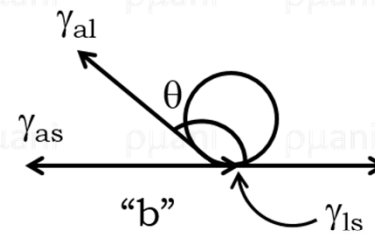
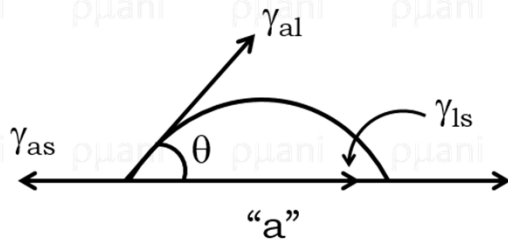
However, when ' $r$ ' is very small then  $p_{\text{in}} \gg p_{\text{out}}$

This explains why very small water bursts out and why seeding/nucleation is necessary for raining to happen.

### Angle of contact and Wetting of surface:

When a liquid is dropped on any solid surface or a liquid drop is placed on a solid surface then the surface of liquid near the solid surface is a curved one. The angle between tangent to the liquid surface at the point of contact and the solid surface inside the liquid is known as the 'angle of contact' and its magnitude depends on the 'liquid-solid surface' pair.

Two situation may appear:



where,  $\theta$  is the angle of solid-liquid-air interface and not solid-air-liquid interface.

From the above two diagram, at mechanical equilibrium,

$$\gamma_{as} = \gamma_{ls} + \gamma_{al} \times \cos \theta$$
$$\Rightarrow \boxed{\cos \theta = \frac{\gamma_{as} - \gamma_{ls}}{\gamma_{al}}} \quad \text{Young's equation}$$

Work = Force  $\times$  distance,  $dw = r \times d\sigma$   
 $\gamma = \text{Force/unit length}$

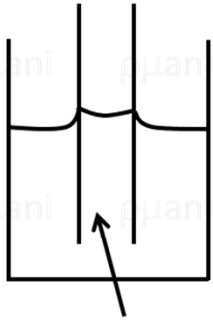
When  $\gamma_{as} > \gamma_{ls}$  then  $\cos \theta$  is (+)ve, i.e.  $\theta < 90^\circ$  and when  $\gamma_{as} < \gamma_{ls}$  then  $\cos \theta$  is (-)ve, i.e.  $\theta > 90^\circ$ .

The **first case** appears for **water on glass** and the **second case** appears for **mercury on glass**.

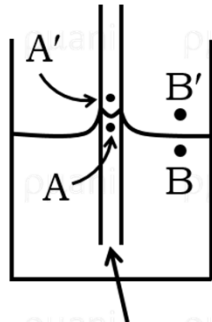
When  $\theta < 90^\circ$ , liquid is said to be **wetting** the surface and when  $\theta > 90^\circ$ , the liquid is said to be **non-wetting** for that surface.

### Rise of liquid in a capillary:

When a capillary is dipped into water then the water tends to adhere to the walls as shown below:



Thick capillary,  
rise is small



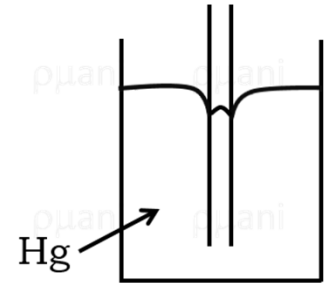
Thin capillary,  
rise is high

Pressure at B = pressure at B' = atmospheric pressure Pressure at A = less than atmospheric pressure, hence concave
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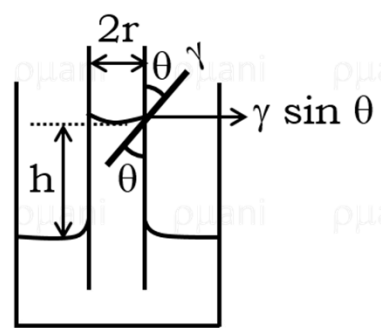
At point B, since the surface is flat so  $p_{in} = p_{out}$

However, at point 'A' since the surface is concave so pressure at point 'A' is less than that at point 'B' by  $\frac{2\gamma}{r}$  [where  $r$  = radius of capillary]. Thus in order to achieve mechanical equilibrium the liquid will rise inside the capillary. For thick capillary,  $r$  is large, hence small rise and for thin capillary  $r$  is small, hence high rise in thin capillary]

When a capillary is dipped into mercury then the surface will be convex. Thus, the pressure at point A will be higher than that at point B. Thus, instead of rise, there will be a depression of liquid level.



The pressure exerted by a column of liquid of density  $\rho$  and height 'h' is given by  $p = h \times \rho \times g$



Hydrostatic pressure difference =  $\frac{2\gamma}{r}$

[It should be  $\frac{2\gamma \cos \theta}{r}$  ?]

At equilibrium,  $p =$  hydrostatic pressure difference

i.e.  $h \times \rho \times g = \frac{2\gamma}{r}$

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

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

Contact line of the meniscus of the tube =  $2 \pi r$

$2 \pi r \times \gamma \cos \theta = (\pi r^2 h + v) \times \rho g$

If the radius of the concave meniscus is taken to be same as that of the radius of capillary then,

$v = \pi r^3 - \frac{2}{3} \pi r^3 = \frac{1}{3} \pi r^3$

$\Rightarrow 2 \pi r \times \gamma \cos \theta = (\pi r^2 h + \frac{1}{3} \pi r^3) \times \rho g$

$\Rightarrow \gamma = \frac{r \rho g (h + \frac{1}{3} r)}{2 \cos \theta}$

When  $\theta \rightarrow 0$  i.e.  $\cos \theta = 1$

$\Rightarrow \gamma = \frac{h \rho g r}{2}$  (neglecting volume 'v' to be very small)

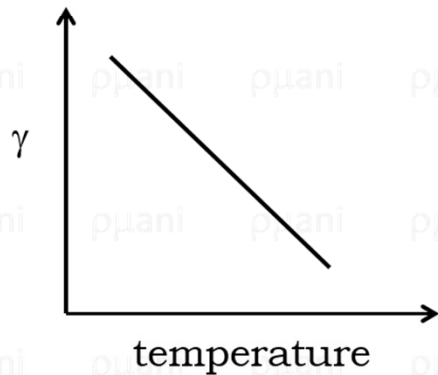


### Surface tension : Temperature dependence

Eötvös showed that,

$$\gamma = -K t + \text{constant} \text{ (empirical equation)}$$

Thus, a plot of  $\gamma$  vs.  $t$  will look like



We know that at critical temperature  $t_c$ , surface tension is zero, the above equation can be modified as

$$\gamma = -K (t - t_c) + \text{constant}$$

$$\Rightarrow \gamma = K (t_c - t) + \text{constant}$$

However, from experimental results, Ramsay and Shields showed that

$$\gamma = K (t_c - t - 6)$$

At critical temperature/point, liquid turns into vapour so surface tension is zero

At boiling point, liquid turns into vapour so surface tension is zero



Question: How does the height ( $h$ ) of water in the capillary depends on the radius ( $r$ ) of the capillary? Plot it.

Question: Show that for an inclined capillary the slanting height increases with increase in  $\theta$  (the angle the capillary makes with the vertical line).

Question: Many small drops do coalesce to form a large drop although it is entropically unfavourable or the reverse does not happen but that is entropically favourable – Why? Calculate the amount of work done/energy involved in both processes.