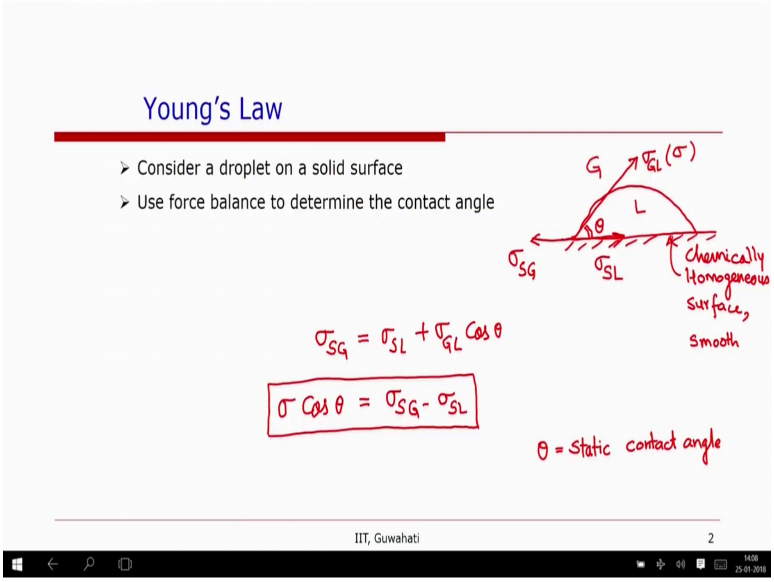
Multiphase Microfluidics
Dr. Raghvendra Gupta
Department of Chemical Engineering
Indian Institute of Technology, Guwahati

Lecture - 09
Interfaces, Surface Tension and Wetting (Contd...)

Hello. So, in today’s lecture we will be continuing our discussion of Interfaces Surface Tension and Wetting. In the previous lecture or in the previous discussion on the same topic, we focused on what interfaces what is the surface tension. And in this lecture and in the previous lecture, we briefly described about the wetting or the contact angle and contact line. In this lecture, we will focus more about the wetting the contact line between the 3 phases and the related phenomena.

(Refer Slide Time: 01:18)



Young’s Law

- Consider a droplet on a solid surface
- Use force balance to determine the contact angle

$$\sigma_{SG} = \sigma_{SL} + \sigma_{GL} \cos\theta$$

$$\boxed{\sigma \cos\theta = \sigma_{SG} - \sigma_{SL}}$$

θ = Static contact angle

IIT, Guwahati

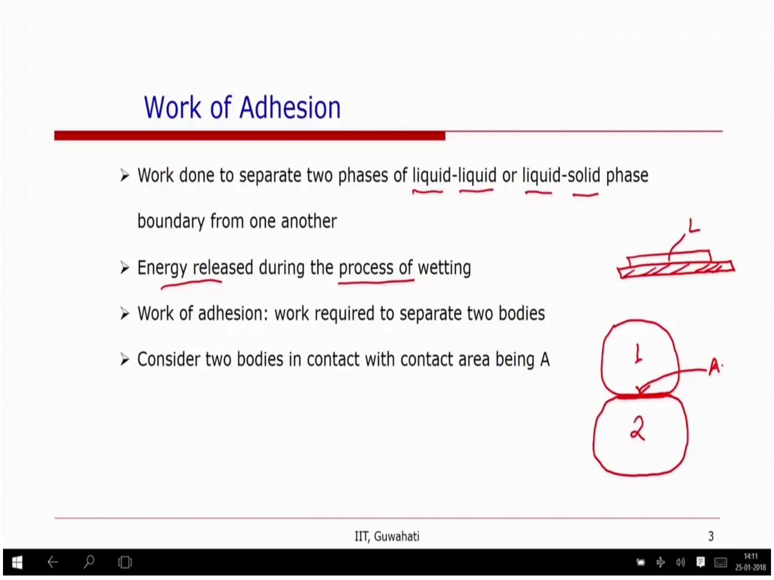
2

So, to review we will look back at the Young’s law. So, Young’s law is that when we have a solid surface, and there is a 3 phase contact on the surface. So, if we have a liquid droplet and this outside the moment is gas, then the three different surface tension; we have here is sigma GL, which is also called simply sigma; this is sigma solid liquid, and this is sigma solid gas.

So, by using a force balance, we can simply write that sigma as g is equal to if this angle is theta, the theta is called static contact angle. in this case the solid surface is assumed to be homogeneous. Now let us see, chemically homogeneous surface this surface is also smooth.

So, theta is the contact angle; by having the force balance we have sigma SG is equal to sigma SL plus sigma GL cos theta or we can simply write that sigma cos theta, we can just get rid of the subscript GL; that is equal to sigma SG minus sigma SL. So, that is Young's law, that we have already seen and it combines or it gives the contact angle in terms of the surface tension for the 3 phases.

(Refer Slide Time: 04:16)



Work of Adhesion

- Work done to separate two phases of liquid-liquid or liquid-solid phase boundary from one another
- Energy released during the process of wetting
- Work of adhesion: work required to separate two bodies
- Consider two bodies in contact with contact area being A

IIT, Guwahati

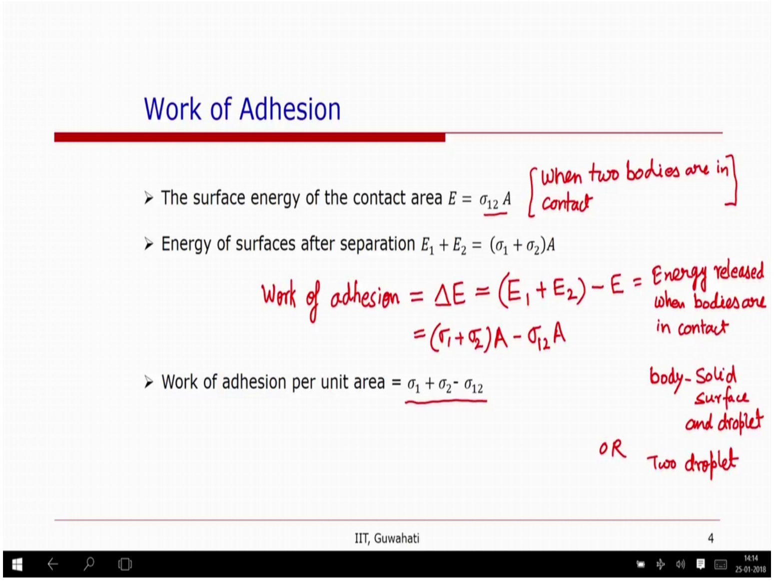
Now, our next we will look at the concept of work of adhesion. So, as you will know; that the adhesive force or the adhesion refers to the attraction between 2 different phases, or 2 different set of molecules or that to 2 different materials. So, here what we are looking at that work of adhesion is the work required to separate 2 phases of 2 different phases. These 2 different phases might be 2 different liquids or it may be a liquid and the solid phase, and then we have to separate them or the work required to subject them from one another each what is called work of adhesion.

So, this is the energy that is released during the process of writing. So, when you have a solid surface, and when this solid surface is being wetted by a liquid film. Thus, energy of the system changes; so the energy that is released during the process each work of adhesion. And you can also think it as the work that is required to separate 2 bodies. So, you might have seen say for example, in our bathrooms, we generally have a a soap sometimes we keep it on a smooth surface. And the soap when it is wet it gets step to the solid surface.

And if the surface wet there is a small liquid film that forms between the 2 solid surfaces, and then it requires significant amount of force to separate the soap from the solid surface. So, that is a simple example from our day to day life for this adhesive phenomena. Another example is if you have to glass lights, and a small amount of liquid each tab between them we generally need to do a lot of work to separate these 2 lights from each other, and that is because of capital. So, consider that 2 bodies that are in contact with each other.

So, let us say this is body one, and another advantage body 2 and the area that they are in contact edge a as we have seen here.

(Refer Slide Time: 07:18)



Work of Adhesion

- The surface energy of the contact area $E = \underline{\sigma_{12}} A$ [When two bodies are in contact]
- Energy of surfaces after separation $E_1 + E_2 = (\sigma_1 + \sigma_2)A$

$$\text{Work of adhesion} = \Delta E = (E_1 + E_2) - E = \text{Energy released when bodies are in contact}$$
$$= (\sigma_1 + \sigma_2)A - \sigma_{12} A$$

- Work of adhesion per unit area = $\underline{\sigma_1 + \sigma_2 - \sigma_{12}}$

body - Solid surface and droplet

OR Two droplet

IIT, Guwahati

4

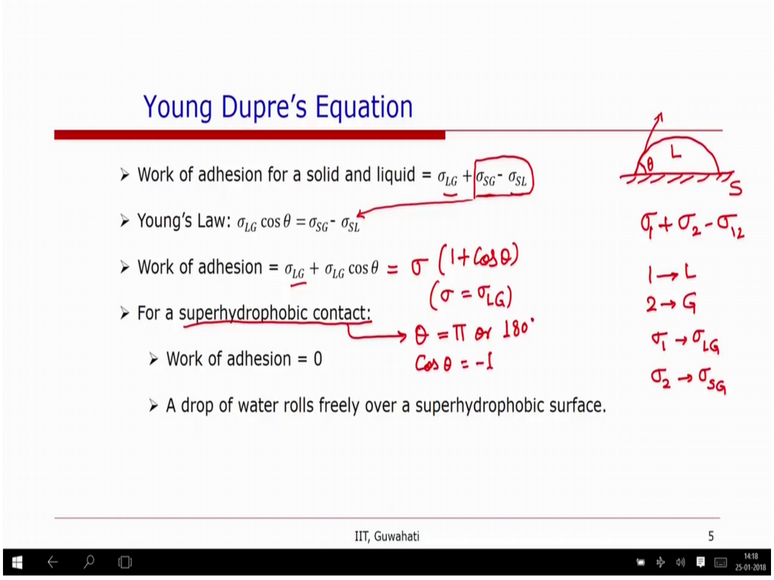
So, the surface energy of the contact area, after the contact the surface energy for the contact area is sigma 1 2 into a; that is the energy when 2 bodies are in contact. before contact or after this contact has been removed and the bodies are separate, the energy will be E 1 plus E 2. So, that is sigma 1 plus sigma 2 into A. So, sigma 1 and sigma 2 are the surface tensions of body 1 and body 2.

And sigma 1 2 is the surface tension between body one or the fluid 1 and fluid 2, or the solid 1 and fluid 2. As the case may be; so the work of adhesion is the distance between

2, the delta e. So, that means, it will be equal to delta e is equal to the energy, when bodies are separated which is E 1 plus E 2, minus the energy when the bodies are in contact.

So, this edge the energy released and bodies are in contact. And these body may be a solid surface one droplet or 2 droplets. So, this is equal to sigma 1 plus sigma 2 into a which is your a is the contact area minus sigma 1 to A. Remember that the energy for the other surface area to be same. So, when we get this energy per unit area of work of adhesion per unit what we get is; sigma 1 plus sigma 2 minus sigma 1 2. So, that is one we had as work of adhesion.

(Refer Slide Time: 10:31)


Young Dupre's Equation

- Work of adhesion for a solid and liquid = $\underline{\sigma_{LG}} + \boxed{\sigma_{SG} - \sigma_{SL}}$
- Young's Law: $\sigma_{LG} \cos\theta = \sigma_{SG} - \sigma_{SL}$
- Work of adhesion = $\underline{\sigma_{LG}} + \sigma_{LG} \cos\theta = \sigma\,(1+\cos\theta)$ $(\sigma = \sigma_{LG})$
- For a superhydrophobic contact: $\rightarrow \theta = \pi$ or 180° $\cos\theta = -1$
  - Work of adhesion = 0
  - A drop of water rolls freely over a superhydrophobic surface.

$\sigma_1 + \sigma_2 - \sigma_{12}$

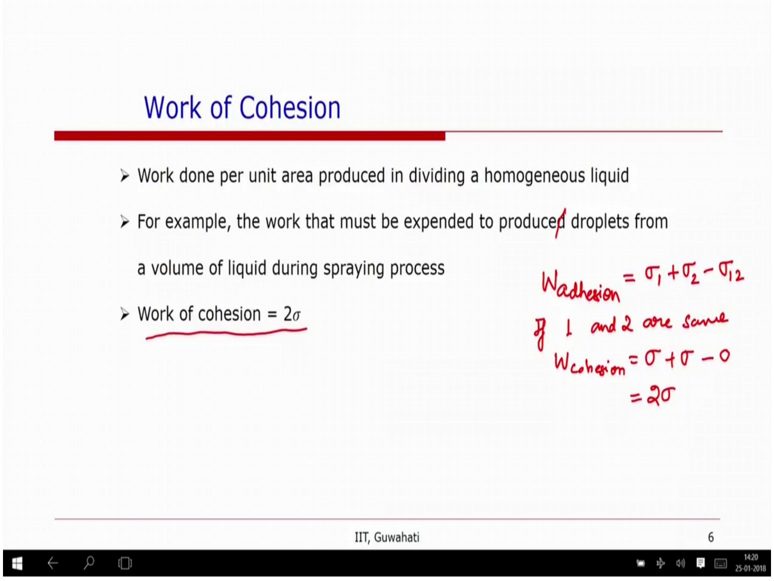
$1 \rightarrow L$
$2 \rightarrow G$
$\sigma_1 \rightarrow \sigma_{LG}$
$\sigma_2 \rightarrow \sigma_{SG}$

Or or is specifically for the contact between solid and liquid, younger Dupre he gave an equation. So, if we apply the same analysis considering that this is valid for a considering the case of a solid wall and a liquid. And we can write that this is work of adhesion for this case is equal to sigma 1 plus sigma 2. So, we have sigma 1 plus sigma 2 minus sigma 1 2; where let us see this one refers to liquid phase, and 2 refers to gas phase. So, sigma 1 is the surface tension, with the gas of liquid phase, and sigma 2 is surface concern of solid winter gas phase. So, we have sigma 1 plus sigma 2 minus sigma 1 2. So now, we have solid and liquid phases in context a minus sigma l.

Now from the Young's law we had just seen the sigma liquid gas cos theta is equal to sigma SG minus SL. So, we can substitute this to sigma SG minus SL from here, and we get work of addition as sigma LG or sigma liquid gas plus sigma liquid gas cos theta. So, that is simply sigma 1 plus cos theta we have sigma h denoted for sigma liquid gas if we remove or if we drop the subscripts. And work of adhesion is the surface tension into 1 plus cos theta. We have let us remind ourselves. theta is the contact angle between the 2 phases; so for a super hydrophobic surface.

For a super hydrophobic surface, the contact angle will be theta is equal to pi or 180 degree for a super hydrophobic surfaces. So, that means, cos theta is equal to minus 1. So, the work of adhesion for a super hydrophobic surface is 0 and you can see from here. so, that means, that no one is required for a drop of water to move it over the hydrophobic surface. So, the drop of water roles freely over a super hydrophobic surface.

(Refer Slide Time: 13:56)



Work of Cohesion

- Work done per unit area produced in dividing a homogeneous liquid
- For example, the work that must be expended to produce~~d~~ droplets from a volume of liquid during spraying process
- Work of cohesion = 2σ

$W_{adhesion} = \sigma_1 + \sigma_2 - \sigma_{12}$

If 1 and 2 are same

$W_{cohesion} = \sigma + \sigma - 0$

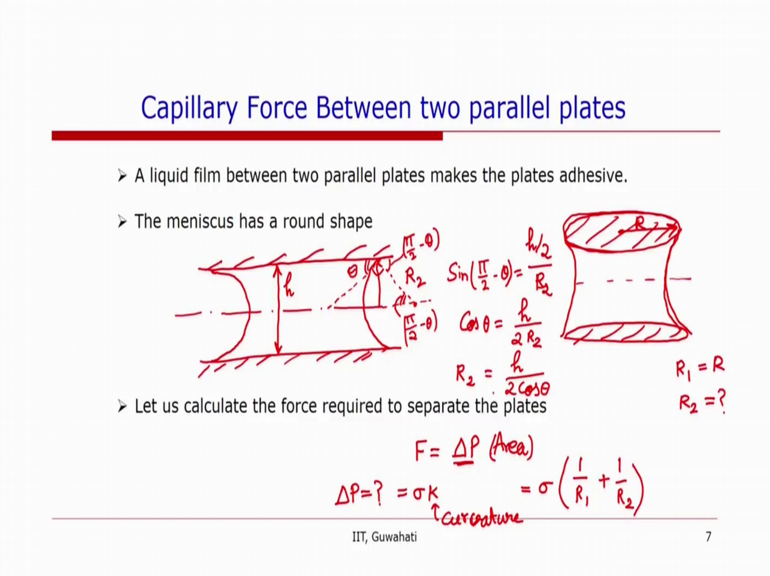
$= 2\sigma$

Now, what of cohesion? So, as we discussed earlier that the adhesion refers to the attractive forces between 2 heterogeneous 2 different materials. Now if we are talking about the does a breakup of a liquid volume into droplets, then the word that will be relevant here will be what we will call the work of cohesion.

So, in that case what we will have that sigma 1 and sigma 2 will be equal and sigma 1 2. So, if you look at from the work of adhesion, the work of adhesion then we have is equal to sigma 1 plus sigma 2 minus sigma 1 2. If 1 and 2 are same, then what we have is this becomes work of cohesion.

And in this case because one and 2 are the same; so, we can say that sigma 1 equal to sigma 2 that is sigma minus sigma 1 2. So, there is no surface tension in the same phase. So, that is 0; so that becomes 2 sigma; so, that is why we have work of cohesion is 2 sigma. And that then example for this will be say and we want to produce droplets from a volume of liquid during the spring process and number of other examples. So, that is work of cohesion.

(Refer Slide Time: 15:54)



Capillary Force Between two parallel plates

- A liquid film between two parallel plates makes the plates adhesive.
- The meniscus has a round shape

$\sin\left(\frac{\pi}{2}-\theta\right)=\frac{h/2}{R_2}$

$\cos\theta=\frac{h}{2R_2}$

$R_2=\frac{h}{2\cos\theta}$

$R_1=R$

$R_2=?$

- Let us calculate the force required to separate the plates

$F=\underline{\Delta P}\,(\text{Area})$

$\Delta P=?\;=\sigma \underset{\uparrow \text{curvature}}{K}\;=\sigma\left(\frac{1}{R_1}+\frac{1}{R_2}\right)$

IIT, Guwahati

7

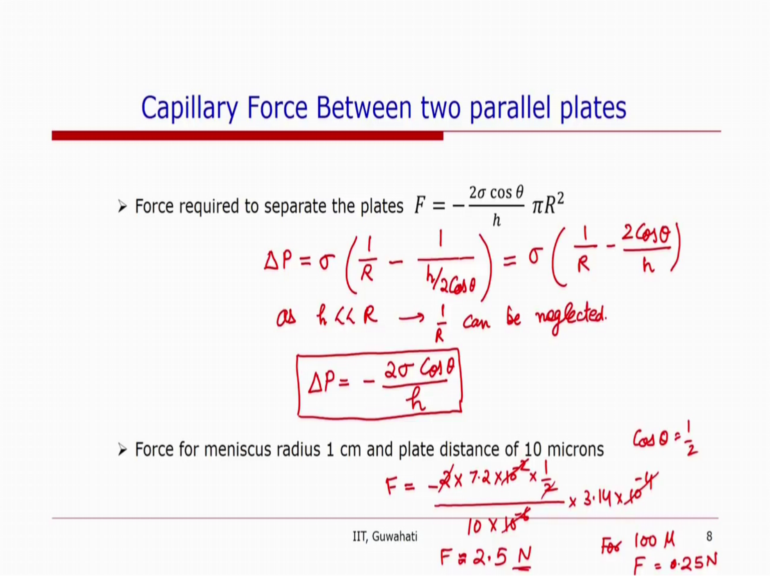
Now, we will look at some of the examples of capillary sources. Especially, which are relevant for microfluidic applications. So, first example in this case is the capillary forces between 2 parallel plates. So, as we just described that the capillary forces between 2 parallel plates and there are number of real life examples. So, if we draw a picture of this, let us say you have 2 solid plates which are separated by a distance and the distance between the plates is as, because of capillarity you might have noticed sometimes that the shape of this edge current.

So, if you look at this the liquid between the 2 phased you will have a interface something like this, and a solid decision contact with the solid wall and same. So, we can say that the radius of this and a, and the contact angle here is theta. it is just the distance between 2 as we have already said that is edge. So, what we need to know is the force required to separate the 2 phases. Now this is the force will be, there will be a pressure difference and to go overcome that pressure difference the phase the force that is required is to overcome the Laplace tracer. So, this F is equal to delta P into the area.

So, our task is now to find out what is delta P and delta P is sigma kappa. A kappa is curvature, we can further write this as sigma 1 over R 1 plus R 2 which edge as curvature is 1 over radius of curvature and the radius of curvature of the surface edge. the sum of the 2 principal curvature. So, for this surface the 2 principal curvatures, one principle curvature is this one. And the other one is this. So, the one radius is about so, we will take this as R, now R 1 is equal to R what remains to be known as what is R 2. So now, R 2 is we want to find. R 2 is this radius the distance.

From this point to the center of which this coverage apart; so, we know that this is h and this is h pi 2, and this angle is theta then this angle is 90 degree and this is pi by 2 minus theta. So, this angle will also be phi by 2 minus theta. So, we can write sin pi by 2 minus theta is equal to h by 2 divided by R 2 or cos theta is equal to h by 2 R 2 or 2 is equal to h over 2 cos theta. So, we have the curvature as h over 2 cos theta.

(Refer Slide Time: 21:52)



Capillary Force Between two parallel plates

- Force required to separate the plates $F = -\frac{2\sigma\cos\theta}{h}\pi R^2$

$$\Delta P = \sigma\left(\frac{1}{R} - \frac{1}{h/2\cos\theta}\right) = \sigma\left(\frac{1}{R} - \frac{2\cos\theta}{h}\right)$$

as $h << R \rightarrow \frac{1}{R}$ can be neglected.

$$\boxed{\Delta P = -\frac{2\sigma\cos\theta}{h}}$$

- Force for meniscus radius 1 cm and plate distance of 10 microns $\cos\theta = \frac{1}{2}$

$$F = -\frac{\cancel{2} \times 7.2 \times 10^{-2} \times \frac{1}{\cancel{2}}}{10 \times 10^{-6}} \times 3.14 \times 10^{-4}$$

$F \approx 2.5\ \underline{N}$

For $100\ \mu$ $F = 0.25N$

IIT, Guwahati

8

So, we have delta P is equal to sigma kappa 1 over R, minus 1 over h over 2 cos theta. So, you might be wondering why we have this as minus.

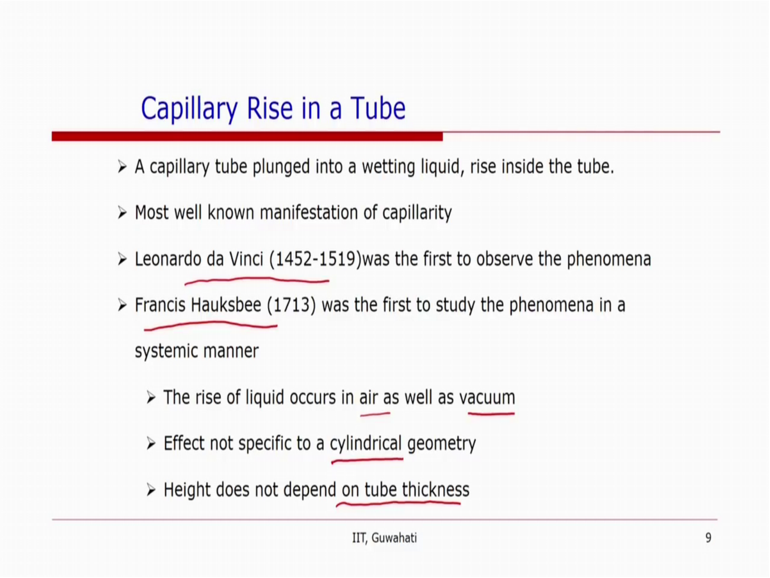
This is minus because they interfaced edge the it is is concave in shape. So, to take into account that into account this is minus. So, we have sigma 1 over R minus 2 cos theta over edge and as h edge very small compared to R. So, 1 over R can be neglected. So, we have delta p is equal to minus 2 sigma cos theta over h ok. And when we multiply this by the cross-sectional area we grant the force required to separates the plates. So, let us just to have a feel of the numbers that what was the force that will be required to separate the place. we can calculate F is equal to say for water and air water.

The surface tension is 0.072 R we can write 7.2 into 10 to the power minus 2. In as a units cos theta let us say take cos theta an average value of about half. So, half and h consider the plate distance of about 10 microns. So, 10 into 10 to the power minus 6 meters into 3 0.14 into 10 to the power 10 raised to the power minus 4. So, what we have is F is about 10 to the power minus 6. This all cancel out; what we have is 2 and 2 also, cancelling out and the. So, the force in this case is about; that means, the previous edge by R square (Refer Time: 24:52) distance of 10 microns we have this.

When they coming among 7.2 into 3.14. So, as I said is 7 into 3 about; so, 0. 25 N. So, let us say this will be about 2.5 you can quite a bit forced to separate the what now suppose to separate the 2 plates. So, this is just to get the feeling of the order of magnitude of the forces that is required to separate the plates. We can see that if the distance between the plates is more than this force will be. So, if it is 100 micron, then for 100 micron. The force will be 0.25 Newton; so this is the force that is important or that becomes dominant on given.

The distance between the plates which is more.

(Refer Slide Time: 26:01)



Capillary Rise in a Tube

- A capillary tube plunged into a wetting liquid, rise inside the tube.
- Most well known manifestation of capillarity
- Leonardo da Vinci (1452-1519)was the first to observe the phenomena
- Francis Hauksbee (1713) was the first to study the phenomena in a systemic manner
  - The rise of liquid occurs in air as well as vacuum
  - Effect not specific to a cylindrical geometry
  - Height does not depend on tube thickness

IIT, Guwahati

Another very popular and very common example of capillary edge the capillaries arranged in a tube. So, when we have this capillary where is in a tube, some common examples we always see that the big of a candle we see we burn the candle, and the liquid wets rises in the candle by this capillarity phenomena and then the flame is maintained at the top. Similarly one of a very complex a phenomena that happens is when you lighted a [FL] which is a lightening arkin lamp, which in India different languages we would called it [FL] or [FL] it has a ghee in it.

And that ghee is in the winter let us say it is wet chilly winter, and then it is in the solids 3. Then the flame can only be maintained when the heat provided by the by the flame by radiation or convection and conduction combined, it is sufficient to melt this ghee so that it rises in the by the capillarity phenomena.

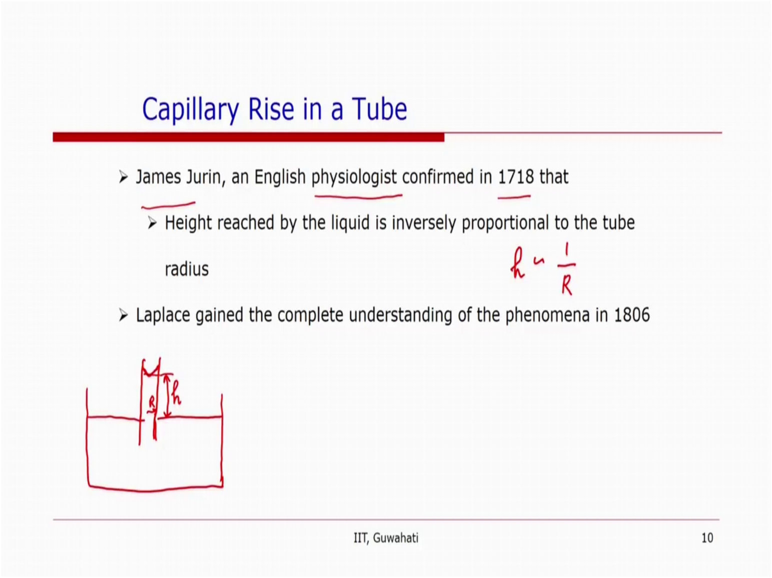
So, this burning of lamp or burning of a candle or burning of a [FL] they are a very classical example of where the capillary has edge a common phenomena. So, incidentally this capillary rise is the first phenomena of fist well known phenomena of capillarity, in it was first observed by leonardo da vinci in 14th or 15th century. Now he hypothesized, that the fountains that come out from the mountains, they are also deactivated and this happens because of the capillary rise phenomena. But of course, as we know now that this is of 2.

So, after that several scientists have looked at the phenomena and had tried and tried to understood. A Francis Hauksbee was the first one who studied this phenomena in a systemic manner. And he concluded the following. And the rise of liquid occurs in air as well as vacuum. So, this might look like the trivial region, but before him one of the scientists gave a notion that the rise of liquid of the it because in the capillary the air cannot cross flow easily.

So, there is a a small vacuum to fill that vacuum the liquid rises. So, he showed from the experiments that the liquid rise occurs in air as well as in vacuum. He also showed that this typical phenomena, because this phenomena is easily observed in glass capillaries, one because glass is transparent another is glass capillaries are very common in our day to day life on in laboratories.

So, he showed that this phenomena is not only limited to glass capillaries or not only hinted to celebrate with capillaries. It can also be observed it is also observed the. The liquid rises we have 2 plates in parallel 2 parallel plates or 2 plates in between plates also then if you tries. he also showed that the height of the liquid rise, it does not depend on the thickness of the channel. So, as your thickness of the tube is one mm or if the thickness of the tube is 10 mm it does not depend on it. So, these are some observations that he made in 18th century.

(Refer Slide Time: 31:19)


Capillary Rise in a Tube

- James Jurin, an English physiologist confirmed in 1718 that
  - Height reached by the liquid is inversely proportional to the tube radius

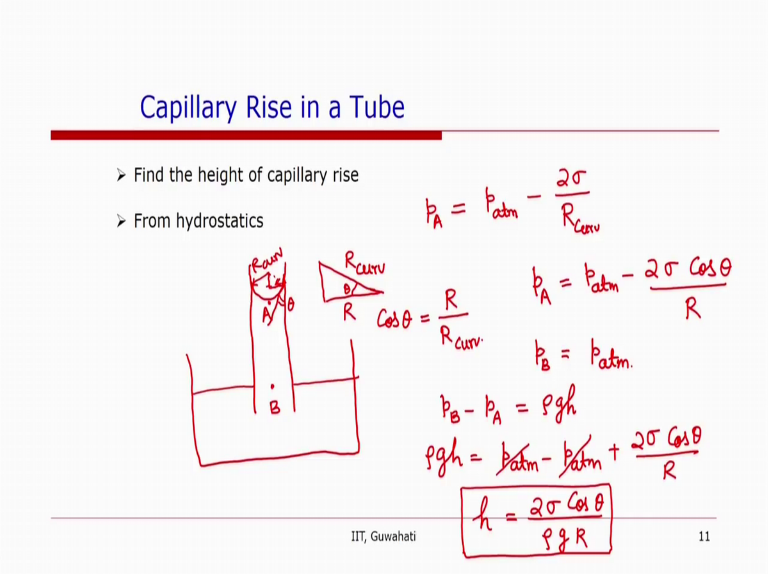
$h \propto \frac{1}{R}$

- Laplace gained the complete understanding of the phenomena in 1806

Now, the law that determines the height of capillarity rise was given by a physiologist an English physiologist whose name was James Jurin in 1718. And he found that height that is reached by the liquid. So, the height of the liquid in a capillary, if you have a vessel or a tube filled with liquid and then it will capillary kept in that.

So the height of the liquid that rises which proportional to the 1 inverse with proportional to the radius of the chain; so that is the first probably the first observation of capillarity and then about a century later not last gain the complete understanding on the phenomena and capillarity surface tension and so on.

(Refer Slide Time: 32:42)



Capillary Rise in a Tube

- Find the height of capillary rise
- From hydrostatics

$$p_A = p_{atm} - \frac{2\sigma}{R_{curv}}$$

$$\cos\theta = \frac{R}{R_{curv}}$$

$$p_A = p_{atm} - \frac{2\sigma\cos\theta}{R}$$

$$p_B = p_{atm}.$$

$$p_B - p_A = \rho g h$$

$$\rho g h = \cancel{p_{atm}} - \cancel{p_{atm}} + \frac{2\sigma\cos\theta}{R}$$

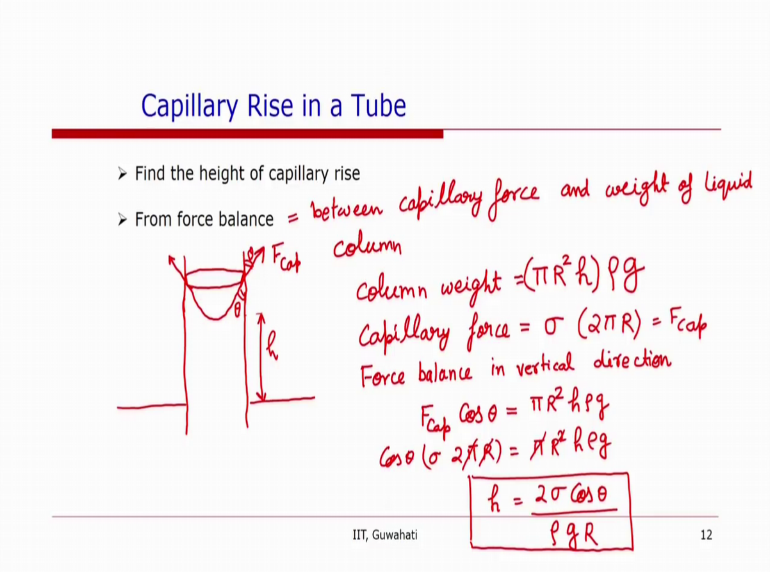
$$\boxed{h = \frac{2\sigma\cos\theta}{\rho g R}}$$

So,. So, we will look at the rise of capillarity from different angles and try to find the relationship. So, capillary rise in a liquid if we consider the capillary and consider a point b here and consider point just below it as point a. And the contact angle is theta. So, the pressure at point a is atmospheric pressure minus 2 sigma over radius of curvature of this interface. So, it is a cylindrical tube and this interface it has a a spherical shape, and it will be a part of a sphere.

So, if we look at this the radius of curvature, then we can basically find the radius of curvature from here. So, this angle between this and tangent to it this theta then the angle between the 2 normals the normal to the tube, and the normal to the interface, then also be theta. So, we will have this drawn here image, this angle is theta this is tube radius R, this is the radius of curvature.

So, we have cos theta is equal to R or curvature. So, we can substitute here PA is equal to p atmosphere minus 2 sigma cos theta over R. now the pressure at the level of the liquid in the this vessel or in this stub edge equal to the atmospheric pressure. So, the difference between the 2 is hydrostatic pressure. So, we can say that PB minus PA is equal to rho gh. So, we substitute that here, then we have rho gh is equal to pgh atmospheric pressure minus p atmospheric plus 2 sigma cos theta in. So, these 2 cancel out and we have h is equal to 2 sigma cos theta over rho gr. So, this derivation of this expression we have obtained based the arguments for pressure. Now the same expression can be obtained by assuming the or by you can seek in the force balance.

(Refer Slide Time: 37:10)



Capillary Rise in a Tube

- Find the height of capillary rise
- From force balance = between capillary force and weight of liquid column

column weight $=(\pi R^2 h)\rho g$

Capillary force $= \sigma\,(2\pi R) = F_{cap}$

Force balance in vertical direction

$$F_{cap}\cos\theta = \pi R^2 h\rho g$$

$$\cos\theta(\sigma\, 2\cancel{\pi}\cancel{R}) = \cancel{\pi} R^2 h\rho g$$

$$\boxed{h = \frac{2\sigma\cos\theta}{\rho g R}}$$

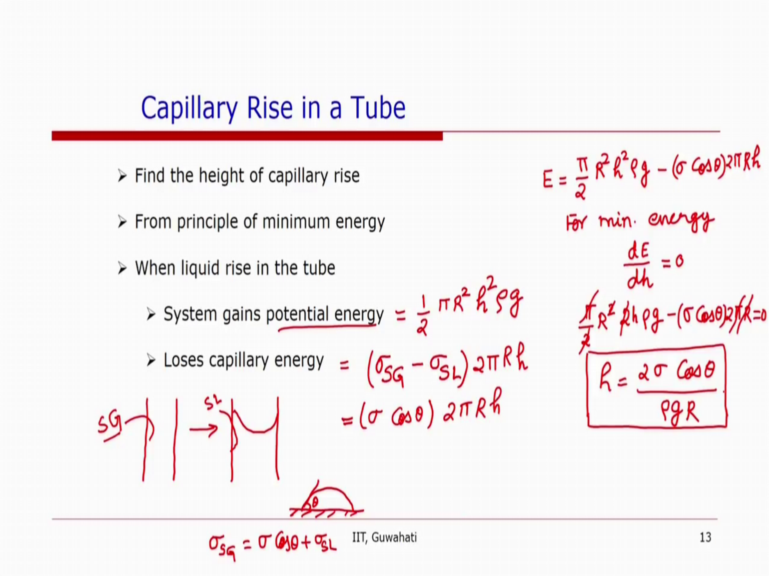
IIT, Guwahati

So, if now we look at the capillary, the force acting this will be in this direction on the contact line. So, there are 2 forces acting on it. The balance between capillary force, and weight of liquid column; so if the height of this liquid column is h the electrical attempt this here to make things clearer, it might not be that contact, so if this height of the liquid column is h then we have weight pi R square h is the volume this liquid into density. So, that is mass into g. So, that is weight of this liquid column. Now capillary force is equal to sigma into 2 pi R we can treat it as a tension in the line, but the direction of this force edge not in the vertical direction.

So, force balance in vertical direction. And the so, this is F capillary. So, that is equal to F capillary this angle is theta. So, this angle is also theta. So, we have capillary cos theta is equal to column width pi R square h rho g. now please do not confuse that there will be 2 components of this because the force is acting everywhere on this. So, that combined is F capillary in the vertical component is F capillary cos theta. So, we substitute this F capillary. Here then we have sigma 2 pi R is equal to pi R square h rho g. pi and pi cancel out R cancel out, um we have h is equal to this is cos theta as so, this is cos theta.

So, h is equal to 2 sigma 2 sigma cos theta divided by rho gR. So, we can also in the height of the liquid column from the force balance and what we have learnt and then the force in these cases we want to apply the surface tension force. Sigma into the radius not on the radius for the circumference of the interface.

(Refer Slide Time: 42:06)



Capillary Rise in a Tube

- Find the height of capillary rise
- From principle of minimum energy
- When liquid rise in the tube
  - System gains potential energy $= \frac{1}{2}\pi R^2 h^2 \rho g$
  - Loses capillary energy $= (\sigma_{SG} - \sigma_{SL}) 2\pi R h$

$= (\sigma \cos\theta) 2\pi R h$

$E = \frac{\pi}{2} R^2 h^2 \rho g - (\sigma \cos\theta) 2\pi R h$

For min. energy

$\frac{dE}{dh} = 0$

$\frac{\cancel{\pi}}{\cancel{2}} R^2 \cancel{2} h \rho g - (\sigma \cos\theta) 2\cancel{\pi} R = 0$

$\boxed{h = \frac{2\sigma \cos\theta}{\rho g R}}$

$\sigma_{SG} = \sigma \cos\theta + \sigma_{SL}$

Now, you can also use the principle of energy minimization to obtain the height of capillary rise. So, when we have a liquid rising in a tube then there are 2 changes in the energy. The system gains some potential energy, which is equal to half pi R square h square rho g. And the system loses capillary energy which h equal to sigma SG.

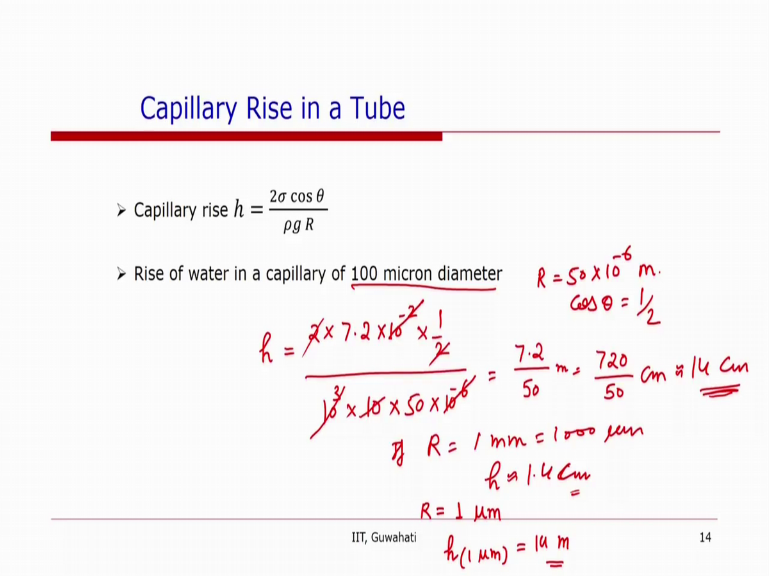
So, to remember this when we have their watch when there is no liquid, than this is surface and gas or solid and gas. And then it changes then we have a liquid here. So, the energy changes from solid gas to solid liquid in this case. So, sigma SL sigma SG minus sigma SL; so, the change in the energy will be originally energy one sigma SG, the surface energy sigma SG into area of the cross section, and then it has reduced to sigma

SL. So, the change in the energy is sigma SG minus sigma SL, and this multiplied by 2 pi rh which is the surface area on the norm.

So, the total change in the system energy e is equal to half um pi by 2 R square h square rho g. now you might remember that sigma g minus sigma SL from the Young's law. sigma SG is equal to sigma cos theta plus sigma SL. So, sigma SG minus sigma SL is cos theta. So, this is equal to sigma cos theta. So, this is the gain in the energy, and this is the sigma cos theta into 2 pi Rh. So, this is minus sigma cos theta 2 pi Rh capital here. And the radius of the channel the 2 pi Rh. Now for minimum energy we have de by dh is equal to 0; that means, phi by 2 R square 2 h rho g minus sigma cos theta 2 pi R is equal to 0.

So, we will have 2; 2 is cancel out. then we can divide rho by R. So, w will have h is equal to 2 sigma cos theta divided by rho g R ok. So, that is the expression of capillary rise in a cube using the energy minimization.

(Refer Slide Time: 47:37)



Capillary Rise in a Tube

- Capillary rise $h = \frac{2\sigma\cos\theta}{\rho g R}$
- Rise of water in a capillary of 100 micron diameter

$R = 50 \times 10^{-6}$ m.

$\cos\theta = 1/2$

$$h = \frac{\cancel{2} \times 7.2 \times \cancel{10^{-2}} \times \frac{1}{\cancel{2}}}{\cancel{10^{3}} \times \cancel{10} \times 50 \times \cancel{10^{-6}}} = \frac{7.2}{50} \text{ m} = \frac{720}{50} \text{ cm} \approx 14 \text{ cm}$$

If $R = 1$ mm $= 1000$ μm

$h \approx 1.4$ cm

$R = 1$ μm

$h_{(1\,\mu m)} = 14$ m

IIT, Guwahati

Now, let us just put the numbers here to have an idea about the capillary rise. So, a typical let us say we take a capillary of 10-micron diameter. So, the radius is 50 micron. oh sorry um 50 micron or 50 to 10 to minus 6 meters. So, h is equal to for water 2 into we again take cos theta is equal to half 2 into 7.2 into 10 to the power minus 2 is the surface transfer for air water cos theta.

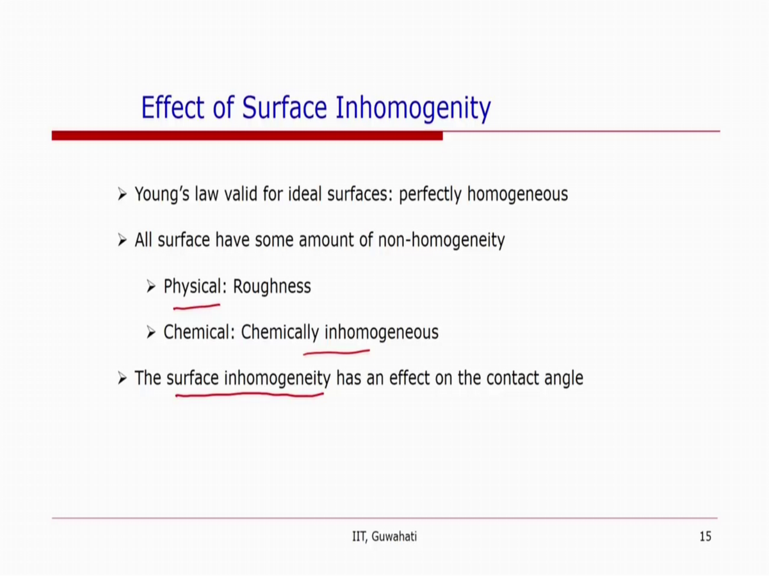
We have taken to be half, and rho for air is about 10 to the power 3 at stake g approximately 10 in meter per second square, and cos theta and R edge 50 into 10 to the power minus 6. So, this to and 2 will cancel out, and what we even end of with 10 to the power minus 6, this becomes minus 2. So, of this all cancel out, and we have this about 7.2 divided by 50 meters or 720 divided by 50 centimetre. So, that is about 14 centimetre. So, that is considering the length of the capillary or considering.

The size of the capillary that is quite a large height, if R is equal to say 1 mm. Then this number will reduce h is about one tenth of it because this is the thousand microns. So, edges 1.4 centimetre ok. So, that is to give you an idea about the numbers, if this height h let us say s radius is allowed 1 micron.

An h for 1 micron capillary h 100 times of this; so, 14 meter of the rise of sap in the trees; the rise of liquid water in the trees h are determined by the capillarity phenomena. And so, depending on the size of the capillaries that appear in the plants that determine the maximum height that the tree can achieve.

So, we have looked at 2 examples of capillarity, one is the force that is required to separate the 2 plates, and other is in the capillarity rise. Now we will look at some effect of surface in homogeneities.

(Refer Slide Time: 51:17)



Effect of Surface Inhomogenity

- Young's law valid for ideal surfaces: perfectly homogeneous
- All surface have some amount of non-homogeneity
  - Physical: Roughness
  - Chemical: Chemically inhomogeneous
- The surface inhomogeneity has an effect on the contact angle

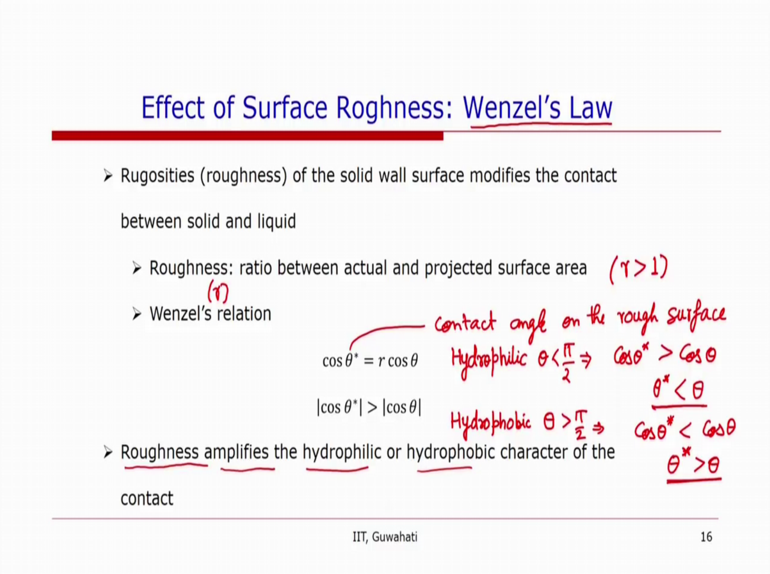
IIT, Guwahati

15

So, at the start of this lecture, when describing the Young's law, we say or we assume that the surface is chemically homogeneous; that means, it has it is made up of only one chemical material or one chemical substance. There is no (Refer Time: 51:40) there is no inhomoge inhomogeneities on the surface. And the it is smooth. So, there is no other fluids on it. ideally no matter what do we do, we will always have some amount of roughness. And some amount of chemical in homogeneities or chemical inhomogeneities caused by the dirt on the surface of the solid.

So, we need to take into account on of these and see if the contact angle there is. Actually, it has been seen it has been observed that the contact angle varies on such surfaces. So the surface in homogeneities both physical surface inhomogenity in terms of the roughness and the chemical inhomogenity in terms of the structure of the material or the different chemicals that are there on the surface, or the different materials that are there on the surface both of them to contact angle.

(Refer Slide Time: 52:43)



Effect of Surface Roghness: Wenzel's Law

- Rugosities (roughness) of the solid wall surface modifies the contact between solid and liquid
  - Roughness: ratio between actual and projected surface area $(r > 1)$ (r)
  - Wenzel's relation

$$\cos\theta^* = r\cos\theta$$

$$|\cos\theta^*| > |\cos\theta|$$

Contact angle on the rough surface

Hydrophilic $\theta < \frac{\pi}{2} \Rightarrow \cos\theta^* > \cos\theta$

$\theta^* < \theta$

Hydrophobic $\theta > \frac{\pi}{2} \Rightarrow \cos\theta^* < \cos\theta$

$\theta^* > \theta$

- Roughness amplifies the hydrophilic or hydrophobic character of the contact

IIT, Guwahati 16

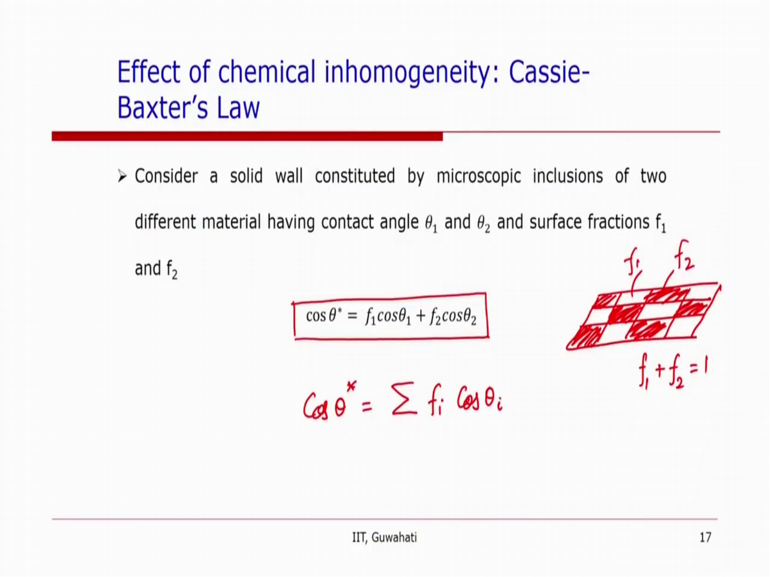
So, 2 different laws describe the 2 effects for the first for the physical effect or the roughness effect, that is given by Wenzel's law we are not going to derive it here. So, the roughness roughness is given me.

Let us say here by R and it is the ratio of actual and the projected surface area. So, if the material is rough and the actual area will of course, the more than the projected surface area. So, rh always going to be greater than one, and Wentzel derived a relationship that cos theta star. So, theta star edge the contact angle on a rough surface. So, he said he derived that cos theta star is equal to R cos theta now if R is equal to one. So, let us consider the case when material is hydrophilic. So, theta is less than pi by 2 and; that means, cos theta star is less than cos theta. And as theta increase, cos theta will decrease so that means, theta star. So, that a what does that mean the cos theta star is greater than cos theta.

So, theta star is based on theta. Similarly one can show that the hydrophobic material the theta star is greater than theta. So, for an hydrophobic material, theta is greater than pi by 2. And cos theta will be negative; so cos theta is the will be negative and if it is multiplied by will be greater than one and it will be less than cos theta; so, that means, theta will be theta star will be greater that theta.

So, this says that if the material is hydrophilic, it becomes small hydro for my more hydrophilic. And if the material is hydrophobic it becomes more hydrophobic. So, that is what we have concluded here that the roughness. it implies it amplifies or enhances the hydrophilic or hydrophobic character of the contact.

(Refer Slide Time: 56:30)



Effect of chemical inhomogeneity: Cassie-Baxter's Law

- Consider a solid wall constituted by microscopic inclusions of two different material having contact angle θ_1 and θ_2 and surface fractions f_1 and f_2

$$\boxed{\cos\theta^* = f_1 cos\theta_1 + f_2 cos\theta_2}$$

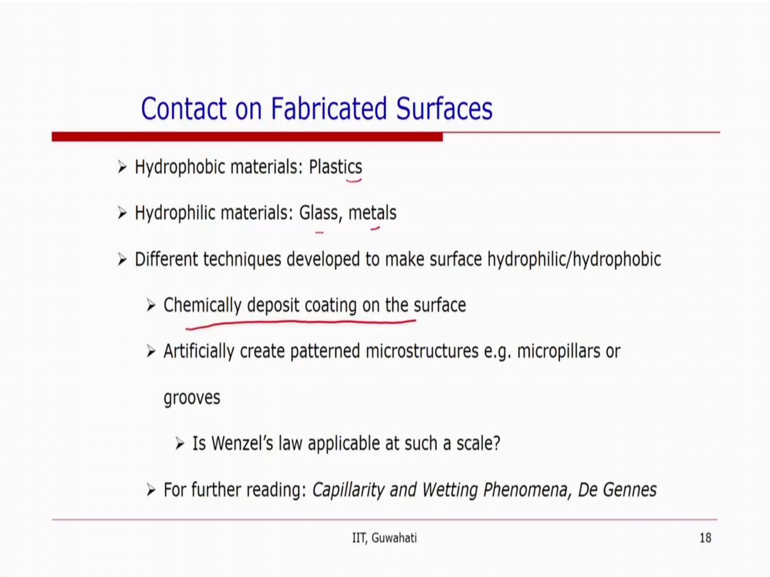
$$Cos\,\theta^* = \sum f_i\, Cos\,\theta_i$$

IIT, Guwahati

Now, coming to the chemical in inhomogenities; so, the material may be made up of a number of inhomogeneities, but for simplicity let us consider a ball that is constituted of 2 different chemicals. So, the fraction of this the first material is f 1 and second material is f 2 and of course, if there are only 2 matters and we have F 1 plus f 2 is equal to 1. So, it can be shown Cassie Baxter law of they have shown some and that cos theta star is equal to s one cos theta 1 plus f 2 cos theta 2. So, that is the apparent contact angle when the material is microscopically in homogeneous if we have a number of materials and we can write this in general cos theta star is equal to sigma as I cos theta I.

Now, in this case, we have 2 assume that the roughness or the size of roughness is small ok. So this property of the material that by changing the roughness or changing the material physically or chemically the surface property.

(Refer Slide Time: 58:25)



Contact on Fabricated Surfaces

- Hydrophobic materials: Plastics
- Hydrophilic materials: Glass, metals
- Different techniques developed to make surface hydrophilic/hydrophobic
    - Chemically deposit coating on the surface
    - Artificially create patterned microstructures e.g. micropillars or grooves
        - Is Wenzel's law applicable at such a scale?
    - For further reading: *Capillarity and Wetting Phenomena, De Gennes*

IIT, Guwahati 18

Or the contact angle contact properties of the material can be changed. So, different materials are used in microfluidic applications depending on what applications where using. So, for example, um say plastic different kind of plastics which are hydrophobic materials and the glass and marbles are hydrophilic materials. And now different techniques. So with the recent developments in material science and microphovbic micropollars.

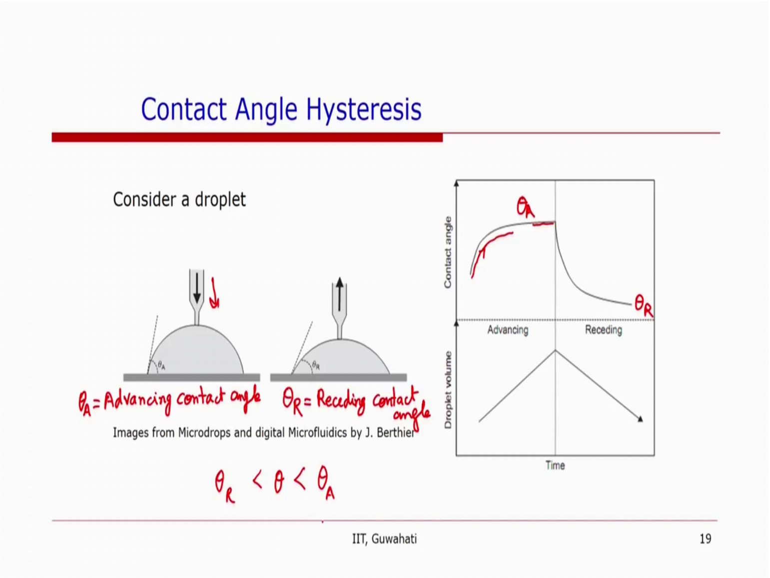
Different normal materials are being made, and now they are used to change the properties of the material on typical and typical is teflon coating on the frying pans that we have in our kitchens. So, that can be done by chemically depositing a coating of the hydrophobic material say if we want to make a hydrophilic surface to be hydro hydrophilic surface to be hydrophobic and one can deposit a a chemical coating on the surface of the hydrophilic material, with the chemical coating which is hydrophobic in nature.

Or other way one can have a microstructure patterns or micro fillers or groups on the surface. For example, all of us have seen of the lotus leaves and seen that the water does not stick to the lotus. Leave it just rolls to over it. So, lotus leave is almost super hydrophobic surface.

So, by inspired by this phenomena in nature, people have a tried to develop in a surface edge which are on which can achieve super hydrophobic nature. So, in such cases one need to take into account they help in lot of research behind that what is the wetting and deviating nature on such surfaces.

So, we are not going to cover this. So, one of the questions for example, there will be that can we directly use Wenzel's law even than we have micro filler of; so, safe in size. So, I suggest that you can read the book by designs capillarity and wetting phenomena; where this has been described in detail or digital micro fluidics and micro drops by. But here in both the books which has been describes in here it.

(Refer Slide Time: 61:02)



Contact Angle Hysteresis

Consider a droplet

θ_A = Advancing contact angle θ_R = Receding contact angle

Images from Microdrops and digital Microfluidics by J. Berthier

$\theta_R < \theta < \theta_A$

IIT, Guwahati

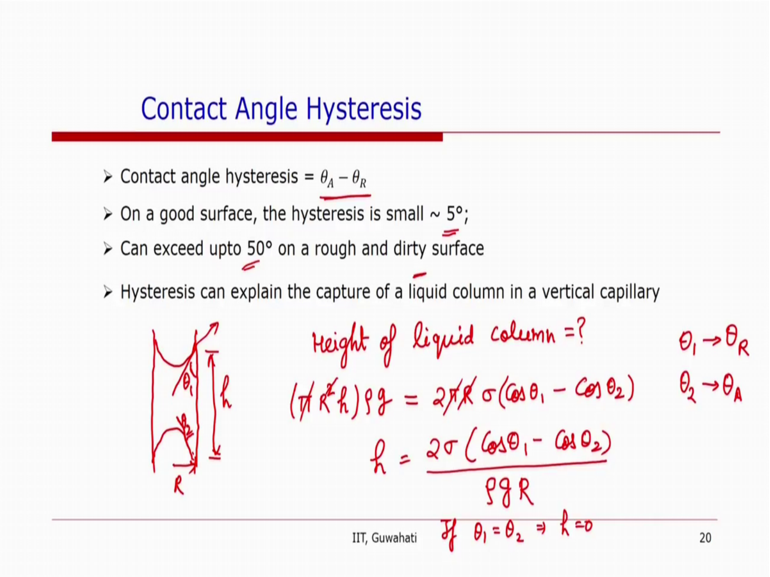
19

So, the next topic that we come here is contact angle hysteresis. So, if you might remember say probably in your high school you might have studied about magnetic hysteresis is that the the phenomena that occurs in one direction does not or cut in the same way or it it is not contained in the same way in the other direction.

So, that is what hysteresis generally defer to; so, contact angle hysteresis the typical example think about a droplet being dropped on a solid surface using a prepaid. And initially what happens as the droplet volume increases as the volume of this droplet is increasing the contact angle start increasing, and then that the droplet does not move rather or the contact angles start increasing. And the volume of the propagating integers as we can see here and then it has you say.

Constant value which is what we call theta a or theta a is called advancing contact and if then this droplet is sucked back by the prepaid as you can see from here, then first the angle is reduced, and this angle is called receding contact angle. So, the angle keeps reducing and then it achieves a value. So, and then that is theta R and this is theta F.

(Refer Slide Time: 63:48)



Contact Angle Hysteresis

- Contact angle hysteresis = $\theta_A - \theta_R$
- On a good surface, the hysteresis is small ~ 5°;
- Can exceed upto 50° on a rough and dirty surface
- Hysteresis can explain the capture of a liquid column in a vertical capillary

Height of liquid column =?

$\theta_1 \rightarrow \theta_R$

$\theta_2 \rightarrow \theta_A$

$$(\cancel{\pi} R^{\cancel{2}} h)\rho g = 2\cancel{\pi}\cancel{R}\,\sigma(\cos\theta_1 - \cos\theta_2)$$

$$h = \frac{2\sigma(\cos\theta_1 - \cos\theta_2)}{\rho g R}$$

If $\theta_1 = \theta_2 \Rightarrow h = 0$

IIT, Guwahati

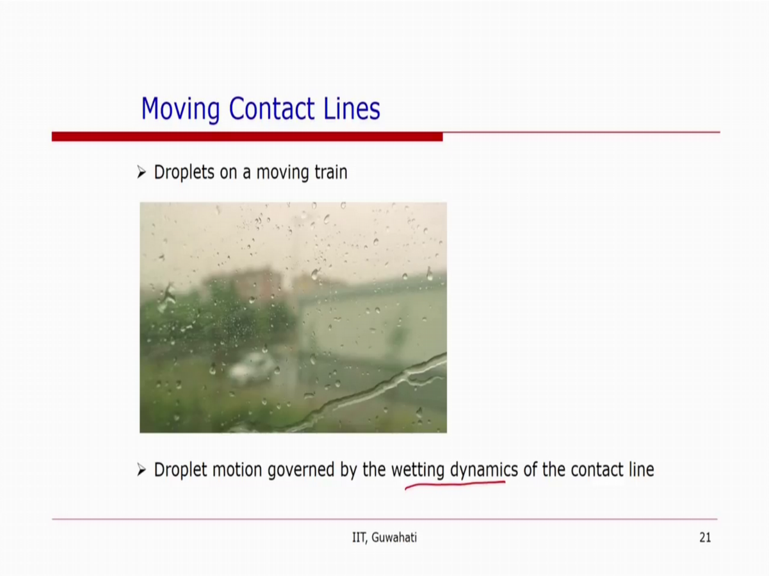
So, the aesthetic contact angle is between theta A between theta R and theta A ok. And the contact angle hysteresis is theta a minus theta R.

The difference between the advancing and receding contact angle is called contact angle hysteresis. On in good surface which is say are typically smooth and not quite clear, the hysteresis can be very small say about 5 degree. But it can exceed up to 50 degree on a rough and dirty surface. So, the surface properties can change the hysteresis. So, hysteresis can also explain say for example, power many times we see that there is a in the capillary, there is some amount of liquid that is that is remained they are (Refer Time: 64:36) So, if the contact angle at this is theta 1 and the contact angle the another direction is theta 2.

Then we can write the balance between the 2 here the um the height of this height of liquid column can be obtained by the force balance. So, we can write the force on the wake of this is equal to 2 2 it is pi R square h which is volume into rho into g a h is the height of this problem, rho is the density g is the gravity and R is the radius of the capillary. And that will be equal to the force in this direction will be 2 pi R sigma cos theta 1 minus 2 pi R sigma cos theta 2. So, we can have h is equal to pi and R are cancelled. So, here we have h is equal to 2 sigma cos theta 1 minus cos theta 2 divided by rho gr.

And we can see if theta 1 is equal to theta 2 then here the maximum that because theta 1 is limited by theta R, the receding contact angle, and theta 2 um by at advance in contact angle. So, the h maximum that can be is t sigma cos theta R minus cos theta 2 cos theta A over rho g R ok. So, that is about the contact angle hysteresis.

(Refer Slide Time: 67:47)



Moving Contact Lines

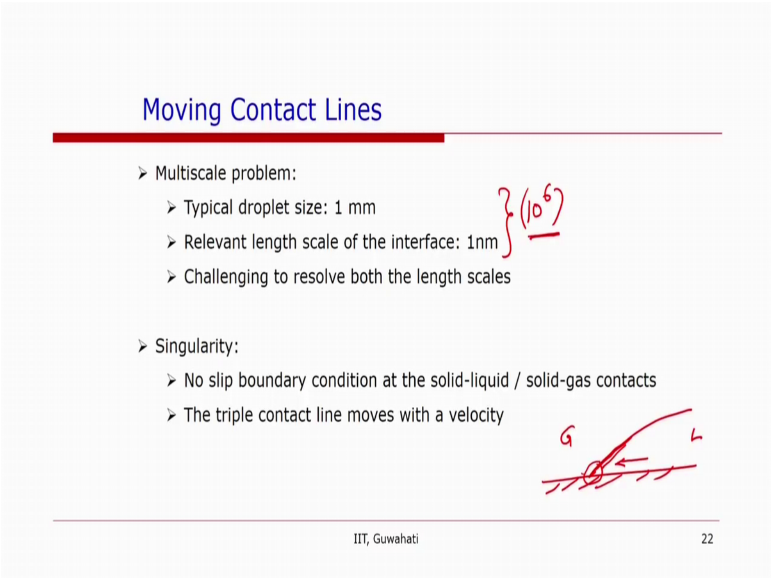
- Droplets on a moving train
- Droplet motion governed by the wetting dynamics of the contact line

Now, in the contact angle hysteresis we discussed about that the contact angle may move when the droplet is being post and the appropriate liquid ha has to made. Now all of us have seen that for example, when you are travelling on a train and it is raining outside.

then the droplets on the train they move and the moving of the droplet or the size of the droplet will depend on the speed of the train and so on and so forth. And you would have wondered that what moves these droplets and what controls the motion of this droplet, and this is governed by the wetting dynamics and the moving contact line.

So, in microfluidics because the size of the channels are small what we had seen the number of reflects when the size becomes a small to a push them to number one number of capillary effects that roportional to 1 over R, and when the size of the challenge becomes a small these effects become dominant ok or so, in microfluidics the very dynamics of the contact line also becomes important.

(Refer Slide Time: 69:14)



Moving Contact Lines

- Multiscale problem:
  - Typical droplet size: 1 mm
  - Relevant length scale of the interface: 1nm
  - Challenging to resolve both the length scales
- Singularity:
  - No slip boundary condition at the solid-liquid / solid-gas contacts
  - The triple contact line moves with a velocity

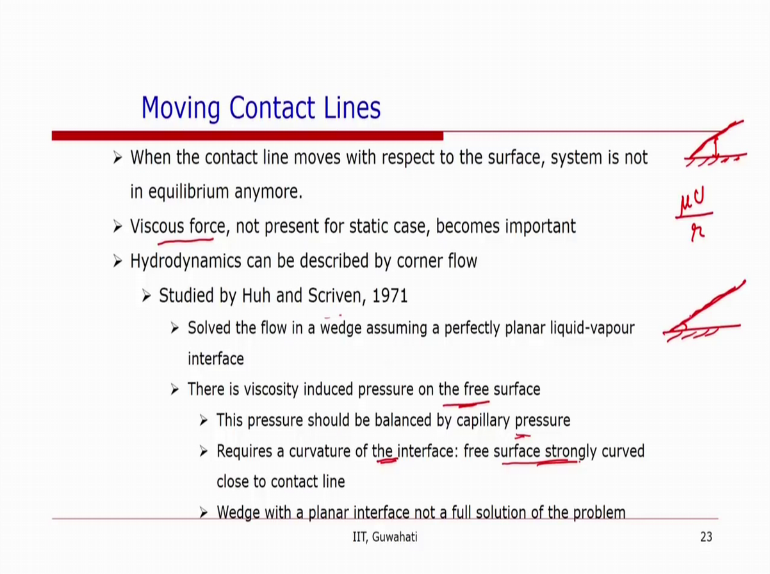
Now this is a multi speed problem; so, it involves the number of scales the largest scale for example, if we are talking about the droplet spreading on the surface, then the largest scale is say the capillary length scale which is about 1 mm. And the minimum scale is each element scale for the interface the molecular scale. So, which of the size 100 meter. So, we can see that this is very visible of of 10 decades.

So, in any study is difficult to dissolve both all all the length scales. it it is a challenging task. Now the other problem with the moving contact lines is which is called contact line singularity or contact line paradox. Now we apply all of us know that the no slip boundary condition has been found to be valid on the on solid bound.

So, if it is the movement of a solid solid liquid on a solid or movement of a gas on a solid we have the no sleep boundary condition which generally say that the fluid that is it contact with the wall will have the same velocity as the velocity of bond. So, effectively there is no um relative motion between the wall and the fluid over the wall ok. So, that is fine, now if we have a contact line. So, for example, on the solid surface we have a droplet of liquid gas a moment.

And this droplet is moving in this direction then the contact line moves. So, that means, there is motion in the near the contact line, then only this fluid can move. So, this is what the paradox says that the no slip boundary condition not valid or has a discontinuity here. So, we need to take this and of course, this is coming apart the phenomena that happens here is the molecular level and the no slip condition smarty arty are describing at macroscopic phenomena; which is or even that the continuum is here. So, there are different models that had been suggested to take into account this contact line singularity.

(Refer Slide Time: 72:02)



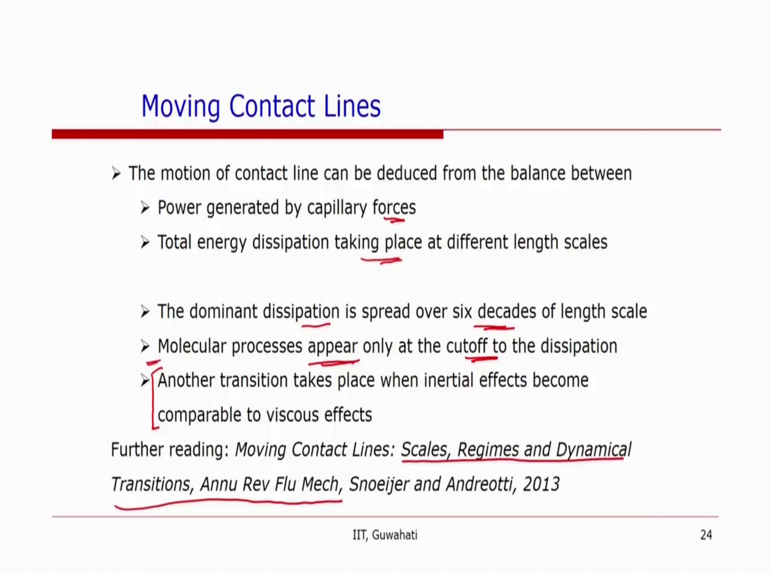
Moving Contact Lines

- When the contact line moves with respect to the surface, system is not in equilibrium anymore.
- Viscous force, not present for static case, becomes important
- Hydrodynamics can be described by corner flow
  - Studied by Huh and Scriven, 1971
    - Solved the flow in a wedge assuming a perfectly planar liquid-vapour interface
    - There is viscosity induced pressure on the free surface
      - This pressure should be balanced by capillary pressure
      - Requires a curvature of the interface: free surface strongly curved close to contact line
      - Wedge with a planar interface not a full solution of the problem

$\frac{\mu U}{h}$

So, we are not going to discuss those things in detail, and you are suggested to go through this paper, on moving contact lines in annual review fluid mechanics to understand more about it.

(Refer Slide Time: 72:14)



Moving Contact Lines

- The motion of contact line can be deduced from the balance between
  - Power generated by capillary forces
  - Total energy dissipation taking place at different length scales

  - The dominant dissipation is spread over six decades of length scale
  - Molecular processes appear only at the cutoff to the dissipation
  - Another transition takes place when inertial effects become comparable to viscous effects

Further reading: *Moving Contact Lines: Scales, Regimes and Dynamical Transitions, Annu Rev Flu Mech, Snoeijer and Andreotti, 2013*

And we will just summarize some of the things here, that when the contact line moves when we have a static contact angle, then the system is in equilibrium, but then the contact line is moving. And of course, the system is not in equilibrium anymore and in that static case because there is no velocity. So, there is no role of viscosity, but the viscosity becomes important in these cases. And as we move near the contact point the viscous forces that scale as mu u over R.

And then R if R is the distance between the contact line, and the solid surface then as we move towards the contact line this becomes very dominant force. So, this phenomena this was studied by huh and scriven by assuming a wedge kind of corner flow. So, he derived an analytical solution, for a planar liquid vapour interface. And then he showed that on the free surface there is a viscosity induced pressure on the free surface, and this pressure can only be balanced by the capillary pressure.

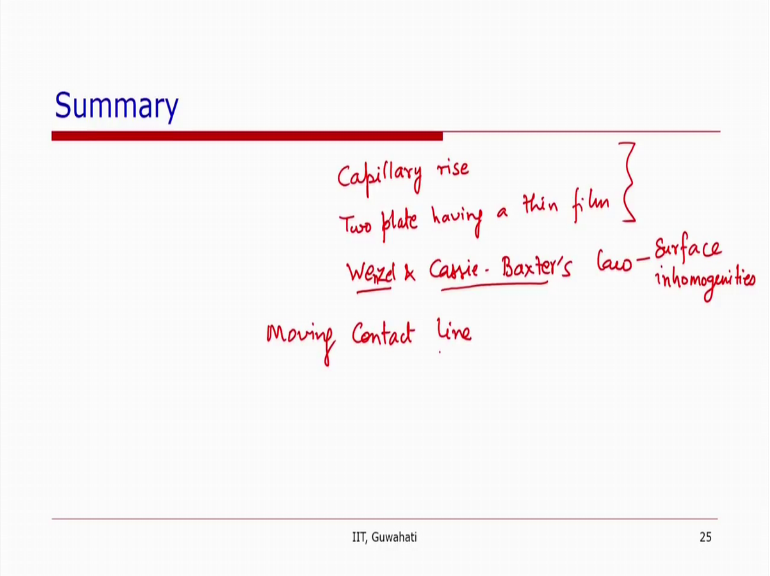
And when we have a capillary pressure, then we need that the interfaces carved, and the curvature is 0 then the capillary force will be 0. So, that means, that the free surface needs to be strongly curved close to the contact line. So, his assumption or generalises was limited only when the planar water the interface was cleaner. But it came out from the earth. And this is solution not full solution because when we need to take into account the curvature of the interface near the contact line.

So, one need to take different scales and clear from some of the conclusions from the vapour that the motion of contact line can be reduced by the balance between power generated by the capillary forces. And the energy dissipation that takes place at different length scales. Most of the time this dissipation is the viscous dissipation and it is spread over 5 to 6 order of different length scales from molecular from 1 nanometer to one millimeter length scale.

And the molecular processes they become important only at the cut off to dissipation only at the 5 nanometer length scale. Another phenomena that can be important unrelated to this h that; when inertia becomes important when the velocity of the contact line is very high. then then inertial effects become important, and they become to the comparable to the viscous effects.

So, in summery in today's lecture what we have studied is different phenomena of contact line.

(Refer Slide Time: 75:47)



Summary

Capillary rise
Two plate having a thin film }
Wezel & Cassie - Baxter's law – Surface inhomogenities

Moving Contact line

So, the capillaries rise and to plates having a thin film. So, we looked at the to a jump this where we applied that basement of capillary force to find the liquid rise effect. But then we also looked at the Wentzel. And Cassie Baxter's law, for the surface inhomogeneities; it may be chemical or physical. So, the Wenzel's law takes into account the physical inhomoginities of the surface and Cassie Baxter's law takes in to account the chemical inhomogeneities of the surface. Then we also looked at the briefly looked at the contact line when it is moving. So, we looked at moving contact line in this lecture to end.

Thank you.