Microfluidics

Dr. Ashis Kumar Sen
Department of Mechanical Engineering
Indian Institute of Technology – Madras

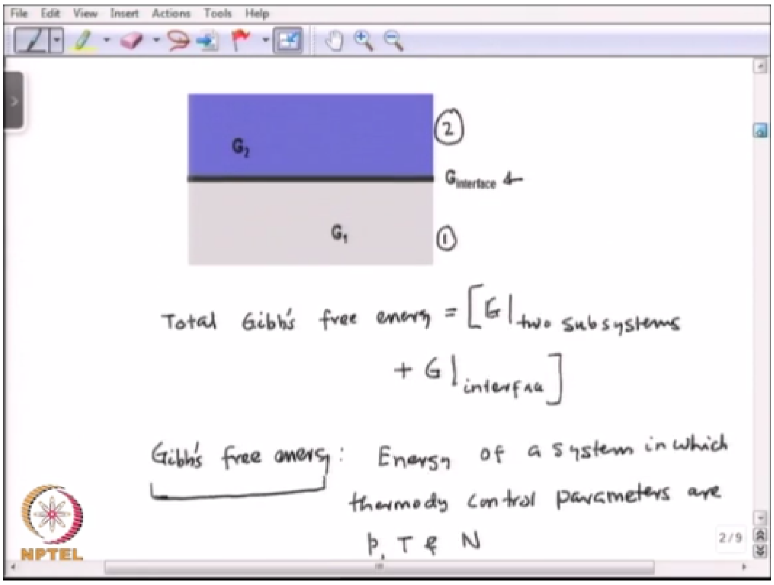
Lecture - 11

Capillary Flows

Okay, so we have been looking at Poiseuille flow, okay. So let us move on and start the next topic which is on Capillary flow, okay. So as I was telling you at micro scale because the large surface area to volume ratio, so surface force is become very important, okay and once such important surface force is capillary force, okay. Capillary the word comes from the Latin word capillaries which means hair, okay.

So when you are talking about flow in a capillary we are talking about flow in a channel that has size of the order of 50 to 100 microns, okay. Typical size of human hair, okay. So capillary flow is driven by basically because of the difference around the interface, interface between 2 different fluids, okay. And these capillary flows can be better understood with the help of the Gibb's free energy.

(Refer Slide Time: 01:21)



Total Gibb's free energy = $\left[G|_{\text{two subsystems}} + G|_{\text{interface}} \right]$

Gibb's free energy: Energy of a system in which thermody control parameters are p, T & N

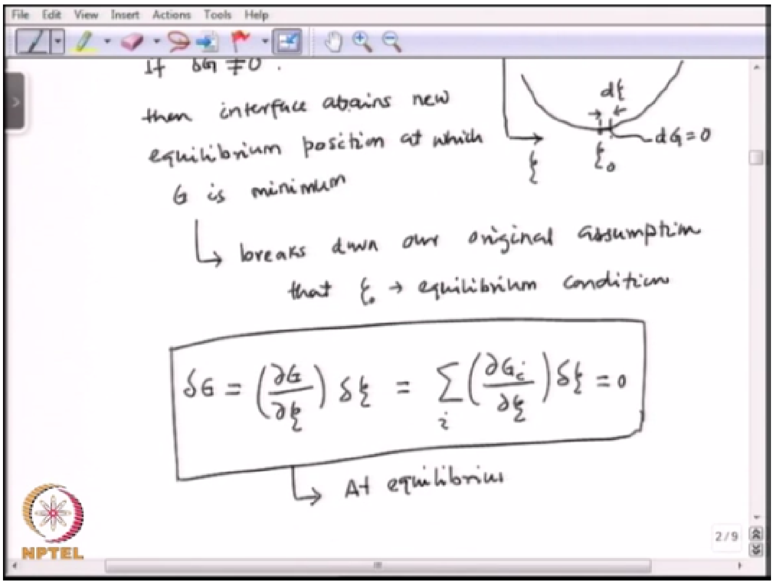
Here, we have a system that has got 2 different sub-systems, we have sub-system 1 and sub-system 2, okay and they are separated by an interface here, okay. So this is the interface. Now the total Gibb's free energy would the Gibb's free energy of 2 sub-systems + the Gibb's free energy of the interface, okay. So before we talk about that let us discuss what you mean by Gibb's free energy.

Gibb's free energy is the energy of a system where the controlling parameters are the thermo dynamic parameters meaning the temperature, pressure and the number density, okay. So these are 3 parameters if we have a system and it is specified by these 3 parameters then the energy of the system can be define in terms of Gibb's free energy, okay.

So Gibb's free energy is nothing but energy of system in which thermo dynamic control parameters are pressure, temperature and the number density, okay. So in that case you can call the system energy you can specify in terms of the Gibb's free energy. So in this particular system the total Gibb's free energy is submission of the Gibb's free energy for the 2 sub-systems 1and 2 and that of the interface.

If we assume that this system here is in equilibrium, okay. So if a system is in equilibrium the Gibb's free energy is minimum of that system, okay.

(Refer Slide Time: 04:10)



If $\delta G \neq 0$.

then interface attains new equilibrium position at which G is minimum

↳ breaks down our original assumption that $\xi_0 \rightarrow$ equilibrium condition

$$\boxed{\delta G = \left(\frac{\partial G}{\partial \xi}\right)\delta\xi = \sum_i \left(\frac{\partial G_i}{\partial \xi}\right)\delta\xi = 0}$$

↳ At equilibrium

So, for systems in equilibrium Gibb's free energy is minimum, okay. So now, let us say this interface here, okay this interface if we specify that the size, shape and the volume of the interface can be represented by a parameter xi then since we say that this system is already in equilibrium let us say the system is undergoing a perturbation let us say xi moves from xi + Del xi then for that Del xi perturbation of the system the Gibb's free energy changes, okay.

Then only we can say that the Gibb's free energy for xi or let us call it xi 0 as the equilibrium position is minimum, okay. So we say that the free surface defines by xi in terms of position, volume and shape, okay. So, xi is the quantity, the parameter that is defining the location or the position, the volume and the shape of the interface, okay. Now if so that let us call it at equilibrium let us call this value at xi 0, okay.

Now if you have a perturbation let us say we subject the interface to some kind of perturbation d xi, so the free surface quantity would become xi 0 + d xi, okay. Now this would, this perturbation d xi should result in vanishing free energy. So, the resulting delta c should be 0. This is because if you let say assume that this is the variation of let us say this is we are talking about in this axis G.

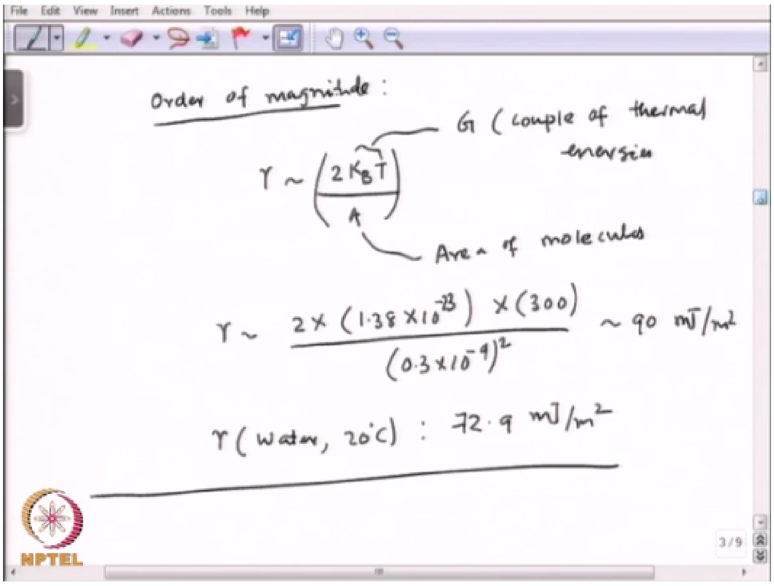
And here we are talking about some zeta and this is the minimum, this is the value of zeta 0 **at** system is at equilibrium and there the zeta is zeta 0, right and G is minimum. Now if you perturb the system by a small amount delta xi, okay. Let us call this as delta xi since this is the minimum the change in the free energy here should vanish, okay. So, dG should be = 0 and if dG is not 0 then what it means is that the system attains a new equilibrium position, okay.

So, our original assumption that zeta = zeta 0 is the equilibrium position is breaking down, okay. So, if delta **G** is not = 0 then the interface attains new equilibrium position at which the **G** is minimum, okay. So, this basically breaks down our original assumption that xi 0 is the equilibrium condition, right. So, in that case we can write delta G the change in the free energy as del **G** over del xi*delta xi, okay.

Which would be = we have a system of different subsystems, so we can say i*delta xi i over delta xi*delta xi, okay. And this change in the Gibb's free energy is going to be 0, right. So, this is the condition that should be valid at equilibrium, okay. So, what we learned from here is that if you have a system having different sub-systems and then the interface the sum of the Gibb's free energy leads to be 0 for that system to be in equilibrium, okay.

So, having said that next to move on and talk about surface tension. Surface tension is an important parameter when you talk about surface forces, okay or the physics of surfaces. The surface tension basically arises because of own balanced forces at the interface between 2 different fluids, okay.

(Refer Slide Time: 10:48)



Order of magnitude:

$$\gamma \sim \left(\frac{\overbrace{2K_BT}^{G\text{ (couple of thermal energies)}}}{\underbrace{A}_{\text{Area of molecules}}}\right)$$

$$\gamma \sim \frac{2 \times (1.38 \times 10^{-23}) \times (300)}{(0.3 \times 10^{-9})^2} \sim 90 \text{ mJ/m}^2$$

$$\gamma(\text{water}, 20^\circ C) : 72.9 \text{ mJ/m}^2$$

So, if you look at the surface here this is a surface between a liquid and a gas and if you will take a molecule somewhere at the bulk of the liquid, okay this molecule here it has interaction with the surrounding molecules equally, okay. So, the free energy of this molecule is minimum, okay.

So, then if you consider a molecule at the interface between a liquid and a gas we can see that it interacts with all the molecules liquid molecules, okay at the bottom sides but on the top it does not have the liquid molecules to interact with, okay. So, there is the molecule here is missing all those molecules at the top and what that provides is increased free energy of the system of molecules around the interface.

So that gives a tension force at the interface which is known as, which is basically the source behind surface tension. And what surface tension tries to do is tries to minimize the interfacial area, okay. So if you put a drop of liquid at a corner you can observe that the interface is going to be part of a sphere, okay because it tries to minimize the surface area. So we can define surface tension.

So surface tension can be defined as Gibb’s free energy per unit area and that is at fixed temperature and pressure, okay. So mathematically we can write surface tension is defined, is expressed as gamma = del G Gibb’s free energy divided by del A at constant pressure and temperature, okay. So, the unit of surface tension energy will be newton into meter, so divided by meter square, so the unit is going to be Newton meter, okay.

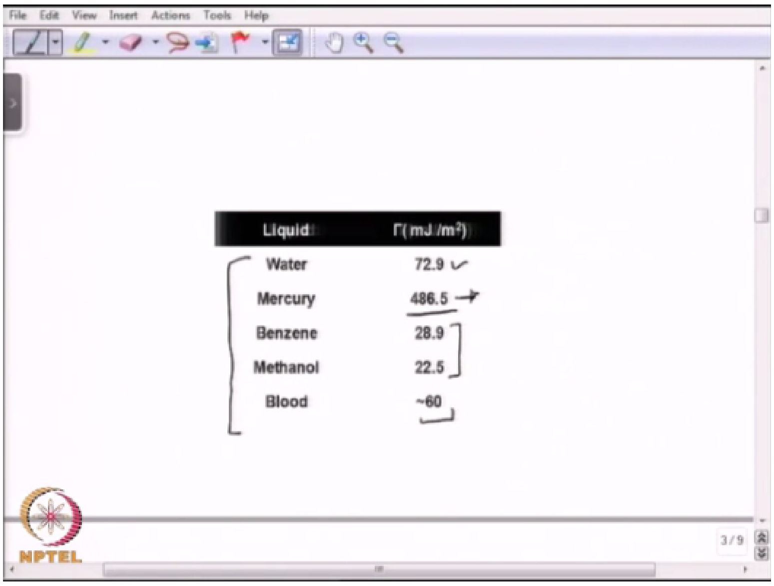
So, that is going to be the unit of the surface tension. Now if you do an order of magnitude, okay sorry this is Newton per meter not Newton meter. So gamma is the energy is Newton*meter area is meter squared, so you get Newton per meter as the unit of surface tension. Now let us look at the order of magnitude of surface tension, okay.

So, typically the gas molecules have size of liquid molecules or gas molecules they have size of the order of 0.3 nanometer that is what we have studied. So, the area will be of the order of 0.3 nanometer square and the interaction energy between the molecules is of the order of couple of thermal energies. Thermal energy will scale as the Boltzmann constant*temperature, okay.

So, considering that we have gamma will be equal to 2 KB*T over area, okay. Sorry, this would scale as, okay we are not determining the exact value. So, this term here is the Gibb's free energy which is couple of thermal energies, this is the area of molecules, okay. So, you can find gamma at the order 2*KB will be 1.38*10 to the power -3 into let us consider temperature as 300 degree Kelvin, right – 23 divided by area is 0.3 nanometer, right 0.3*10 to the power - 9 square, right.

So, if you calculate you will get this about 90 millijoule per meter square, okay and we know that the gamma of water at 20 degree centigrade has been found to be 72.9 millijoule per meter square. So, that gives you a scaling of the value of surface tension or liquid water and the 72.9 millijoule per meter square is what has been calculated, okay.

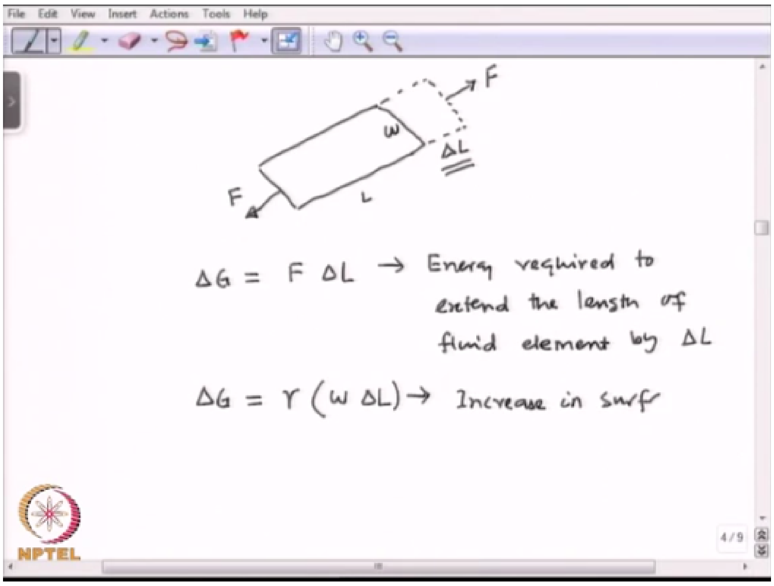
(Refer Slide Time: 17:08)



Liquid	Γ(mJ/m^2)
Water	72.9 ✓
Mercury	486.5 →
Benzene	28.9
Methanol	22.5
Blood	~60

So, here we look at the surface tension of different liquids, we have water which is 72.9 millijoule per meter square then mercury has got very high surface tension about 486.5, Benzene has about 28.9 lower than water also Methanol okay and blood has surface tension about that of water. So, 60 millijoule per meter square. Now let us try to express surface tension in terms of how it will scale by considering a fluidic element, okay of some length and some width, okay.

(Refer Slide Time: 18:03)



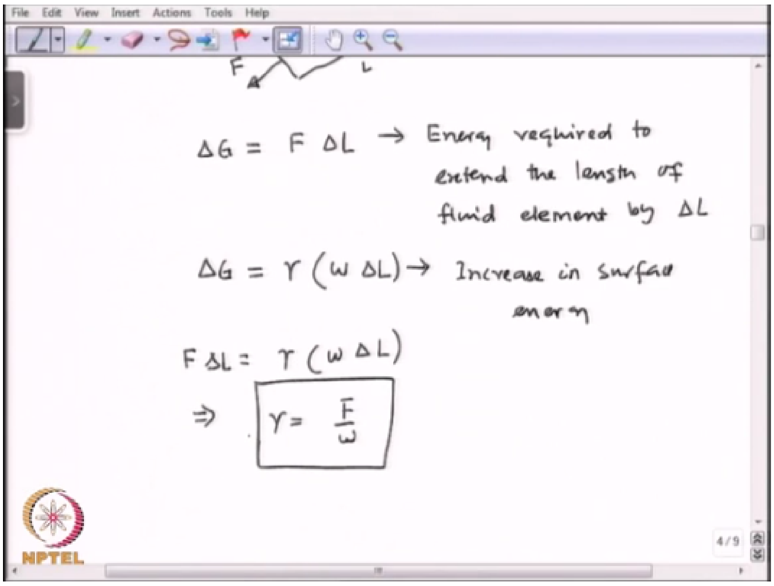
$\Delta G = F \Delta L \rightarrow$ Energy required to extend the length of fluid element by ΔL

$\Delta G = \gamma (w \Delta L) \rightarrow$ Increase in surf

So, let us consider this is the fluidic element, okay let us consider that we are applying a force here and because of the force the fluidic element undergoes an extension, right. So, this is F and this is L this is delta L and the width is w, okay. So, the amount of force that we required to apply that will cause a change in length delta L will be F, sorry the amount of energy that would be required to cause that change in length delta G will be = F*delta L, okay.

So, this is the energy required to extend the length of fluids element by delta L, okay. So, now if you extend the length of a fluidic element the surface tension is going to increase, right. So, the surface energy is going to increase. So, the surface energy, change in the surface energy delta G will be gamma*the area, right. So, increase in area which is w*delta L, so that is going to be the increase in surface energy.

(Refer Slide Time: 20:24)



$$\Delta G = F \, \Delta L$$ → Energy required to extend the length of fluid element by ΔL

$$\Delta G = \gamma \, (w \, \Delta L)$$ → Increase in surface energy

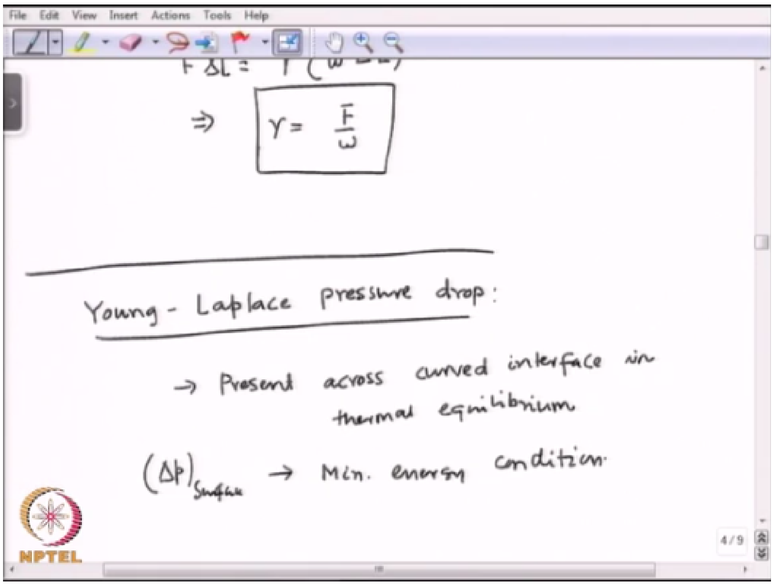
$$F \, \Delta L = \gamma \, (w \, \Delta L)$$

$$\Rightarrow \boxed{\gamma = \frac{F}{w}}$$

Now, if we equate these 2 F delta L is going to be gamma*w delta L then we get that surface tension gamma is going to be F over w, okay. So, it is the force per unit length that is acting on a fluidic element to extend it by some distance to enhance its surface energy. And as I was telling surface tensions behave the same way as the tension in a membrane which tries to always minimize the surface area, okay.

And the cause of capillary rise as I was discussing in the beginning is the Young Laplace pressure drop, okay which always exist across a curved interface. When the interface is flat they Young Laplace pressure drop vanishes, okay. So, we will try to derive an expression for Young Laplace pressure drop here.

(Refer Slide Time: 21:40)



$$F \, \Delta L =$$

$$\Rightarrow \boxed{\gamma = \frac{F}{w}}$$

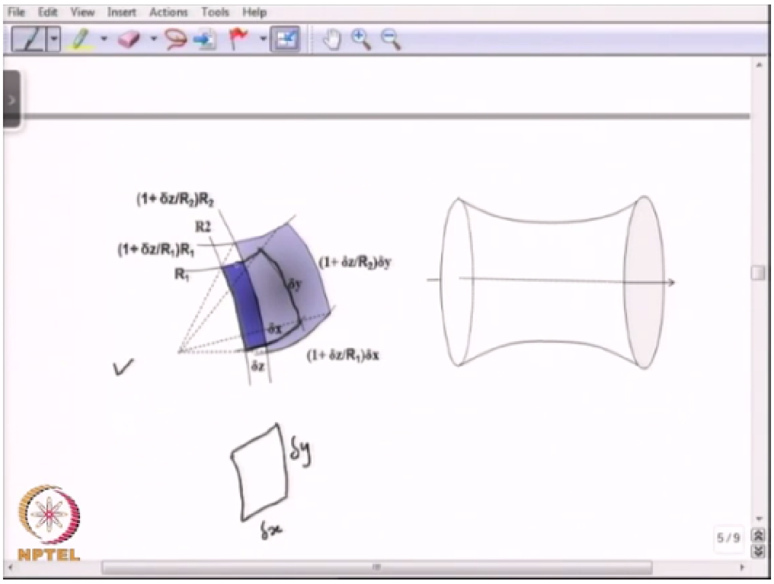
Young - Laplace pressure drop:

→ Present across curved interface in thermal equilibrium

$(\Delta p)_{\text{Surface}}$ → Min. energy condition.

So, let us try to derive an expression for Young Laplace pressure drop. So, Young Laplace pressure drop is present across curved interface in thermal equilibrium and we can derive the delta P surface the Young Laplace pressure drop using a minimum energy condition, okay.

(Refer Slide Time: 22:39)



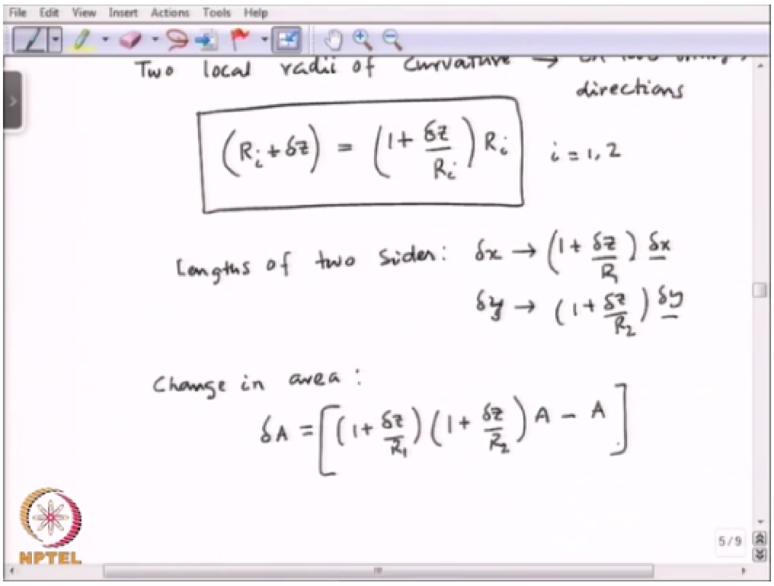
So, let us consider a fluidic element as you see it here, okay. So, this is the fluidic element. So, initially it has dimension in one-way delta X and the other way is delta Y. So, this is basically a fluidic element something like this, okay. And this dimension is delta X and this is delta Y, right what you see it here this across this, right. So, this is delta X and this is delta Y, right.

So, now this fluidic element expands by a length delta Z in the direction normal to this surface, okay. So, it expands by delta Z. So, this is the configuration after it expands, okay. This is the configuration after it expands. Now if you look at this surface we have 2 radius of curvature, one is R1, this original surface I am talking about delta X and delta Y. So, one radius of curvature is R1 and the other radius of curvature is R2, okay.

Now when this surface expands to this expanded surface the radius of curvature would change according to this high delta Z, right. So, this new radius of curvature here becomes 1 + delta Z over R1*R1, right. Similarly, this radius of curvature changes from R2 to 1 + delta Z over R2 to*R2, okay.

Accordingly, the lengths of the sides, okay from delta X it becomes 1 + delta Z over R1*delta X and this becomes 1 + delta Z over R 2*delta Y. This is geometry if you work out this what you get, okay.

(Refer Slide Time: 25:03)



Two local radii of curvature →

directions

$$\boxed{(R_i+\delta z) = \left(1+\frac{\delta z}{R_i}\right)R_i} \quad i=1,2$$

Lengths of two sides: $\delta x \rightarrow \left(1+\frac{\delta z}{R_1}\right)\underline{\delta x}$

$\delta y \rightarrow \left(1+\frac{\delta z}{R_2}\right)\underline{\delta y}$

Change in area :

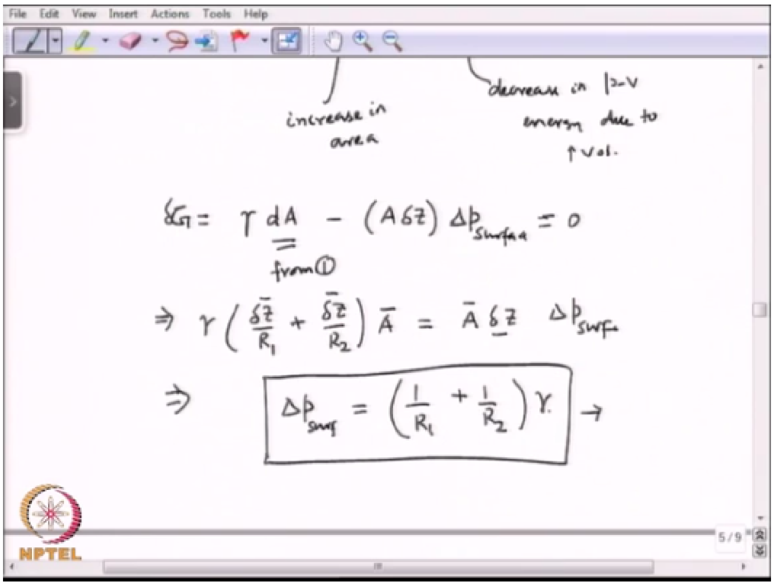
$$\delta A = \left[\left(1+\frac{\delta z}{R_1}\right)\left(1+\frac{\delta z}{R_2}\right)A - A\right]$$

So, now you can say that the 2 local radii of curvature in 2 orthogonal directions becomes R i + delta Z, okay will be = 1 + delta Z over R i*R i. So, it generalizes this, okay. So, 1 + delta Z over R1*R1, 1 + delta Z over R2*R2 where i = 1, 2 okay. Now here I should mention that for any curved liquid interface the radius of curvature is considered as positive if the center of that curvature lies within that medium, okay.

So that is very, that is a convention that is used, okay. So, here for example the radius of curvature is here and if it is within the fluid itself then it is considered as positive. Now, the lengths of 2 sides change from delta X to 1 + delta Z over R1*delta X and delta Y changes from delta Y to 1+ delta Z over R2*delta Y, right.

This is what we see it here. So, the change in the area, the change in surface area delta A could become 1 + delta Z over R1*1 + delta Z over R2*A, okay. So, delta X*delta Y will be A – A, okay. So, that is going to be the change in the area of that fluidic element.

(Refer Slide Time: 27:57)



increase in area

decrease in P-V energy due to ↑ vol.

$$\delta G = \gamma \underset{\text{from ①}}{\underline{\underline{dA}}} - (A\delta z)\,\Delta p_{\text{surface}} = 0$$

$$\Rightarrow \gamma\left(\frac{\bar{\delta z}}{R_1} + \frac{\bar{\delta z}}{R_2}\right)\bar{A} = \bar{A}\,\underline{\delta z}\,\Delta p_{\text{surf}}$$

$$\Rightarrow \boxed{\Delta p_{\text{surf}} = \left(\frac{1}{R_1} + \frac{1}{R_2}\right)\gamma} \rightarrow$$

Which will be nothing but, so you can write delta A as delta Z over R1 + delta Z over R2, okay into the area, right. Now here we have neglected higher order terms. We have neglected higher order terms, right okay. So, when the interface expands 2 things are happening. One is the surface energy is increasing and the other thing is the pressure volume energy is going to reduce because the volume is increasing and the pressure is reducing, okay.

So, the total energy of the system the change in the energy of the system the change in energy of the system delta G can be written as delta G surface + delta G pressure volume, okay. So, this is because of the increase in area and this is because of the decrease in pressure volume energy due to increase in volume, okay. So, we can write this, so delta G will be = gamma*d A.

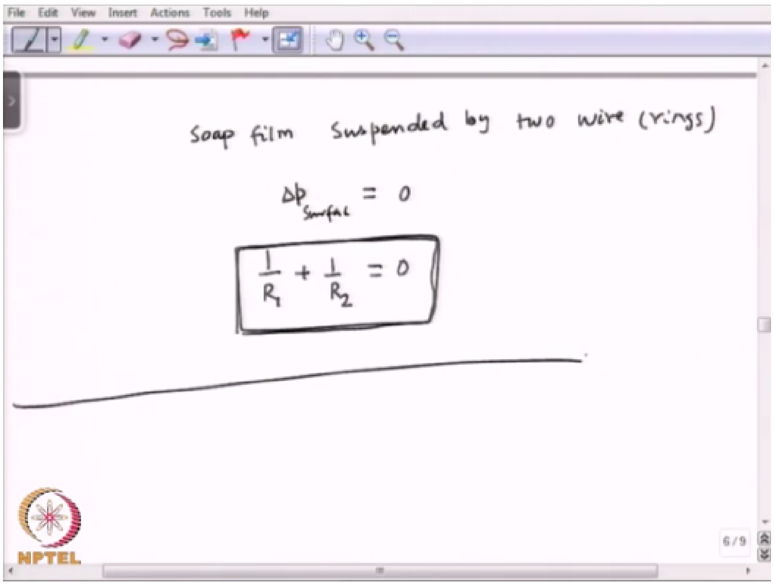
So, that is the surface energy – A*delta zeta is the change in the volume*delta P surface. Let us say we have a surface, we have a pressure delta p surface exist across this interface, okay. So, that becomes the pressure volume energy, right. So, if this is in equilibrium if the interface is in equilibrium then the change in the Gibb’s free energy will be 0, right. So, this will be 0.

Now if you substitute for d A from here, okay from 1 then you get gamma*delta zeta over R1 + delta zeta over R2*A is going to be A*delta zeta*delta P surface, okay. So, what we see here is delta P surface is going to be 1 over R1 + 1 over R2*gamma, okay, right. So, delta zeta, delta zeta will cancel area cancel. So, this is what we would get. Now so, here what you see delta P surface is 1 over R1 + 1 over R2*gamma.

So, the Young Laplace pressure drop acquires an interface would depend on its radius of curvature across 2 different we are talking about 2 different radius of curvature, in this case one and also its function of the surface tension gamma, okay. So, here now if you look at this image this is the image that you would see if you talk about a soap film suspended by 2 metal rings, okay.

This is 1 metal rings this is another metal ring and if you suspend a soap film this is the structure that you would see, okay. Now the soap film is suspended between the 2 wires, so the pressure across the film is the same. So, the Young Laplace pressure drop is going to be 0, right.

(Refer Slide Time: 33:15)



Soap film Suspended by two wire (rings)

$$\Delta p_{Surface} = 0$$

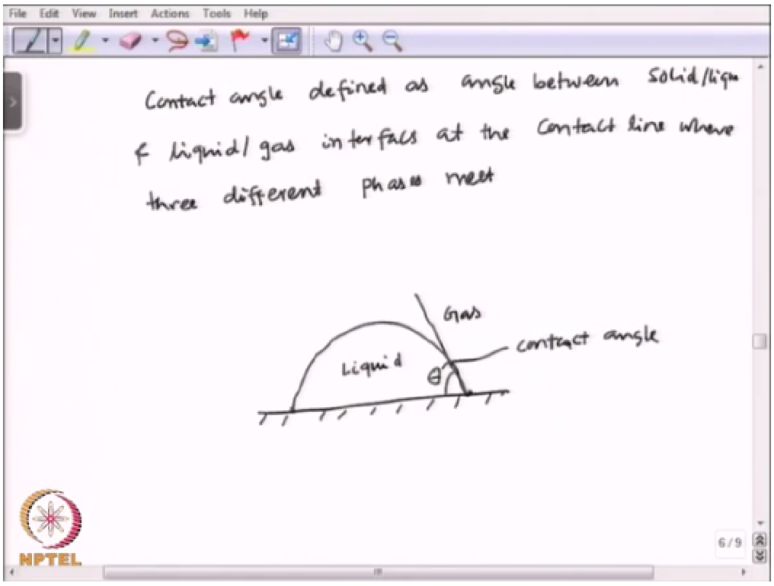
$$\boxed{\frac{1}{R_1} + \frac{1}{R_2} = 0}$$

So, we are talking about soap film suspended by 2 wires rings. So, delta P across the surface both are atmospheric, so is going to 0. Now from this equation from the equation on this equation you can say 1 over R1 + 1 over R2 is going to vanish, okay. Now how this is possible? It is going to be possible because here we are talking about 2 radii of curvature one is this radius, this we are talking about this R1 and the other is this radius of curvature which is R2, okay.

So, you can see here one, the center of 1 curvature lies within the liquid film and the other lies outside, okay. So, one is going to be positive the other one is going to be negative. So, that is there going to cancel each other and the net pressure drop is going to be 0, okay. So, with that let us move on and talk about another concept called contact angle, okay.

So, contact angle is another important property to be discussed when you talk about theory of surfaces. Contact angle is the angle between liquid gas and liquid solid interfaces, okay at the contact line. Contact line meaning when the solid, liquid and gas 3 different interfaces come together, okay.

(Refer Slide Time: 35:24)



Contact angle defined as angle between Solid/liqu

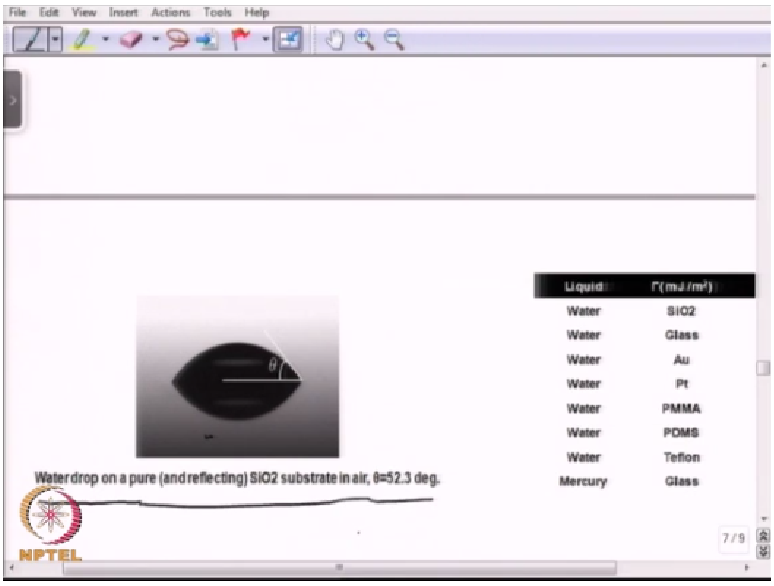
& liquid/gas interfaces at the contact line where

three different phases meet

So, we talk about contact angle and for this exist at, contact angle exist at contact line between solid wall and 2 immiscible fluids, okay. So, how do we define contact angle? So contact angle defined as angle between solid liquid and liquid gas interfaces at the contact line where 3 different phases meet, okay. So we can say, so this is the solid surface and we have a liquid film present here. So, this is liquid and this is gas.

So, the contact angle would be between the liquid gas interface and liquid solid interface. So, this would be called as the contact angle or theta, okay. So, this is the contact angle and it happens at the contact lines. So, this is the contact line which goes all around the perimeter where the liquid is in contact with the solid, okay. Now you can see an example here.

(Refer Slide Time: 37:46)



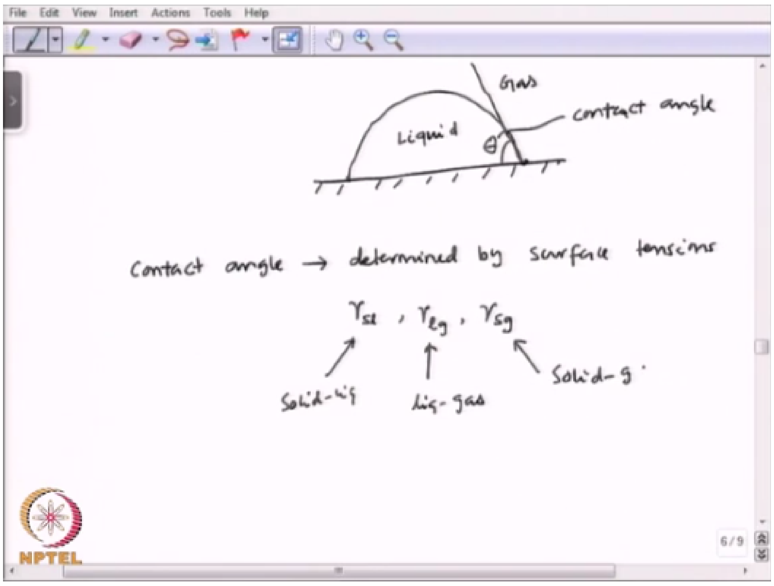
Liquid	Γ(mJ/m²)
Water	SiO2
Water	Glass
Water	Au
Water	Pt
Water	PMMA
Water	PDMS
Water	Teflon
Mercury	Glass

Water drop on a pure (and reflecting) SiO2 substrate in air, θ=52.3 deg.

If you look at here, this is the case where the water drop is present on a pure silicon dioxide substrate in air, okay. So, this is silicon water drop present on silicon dioxide surface and the contact angle is about 52.3 degrees which is the theta that is shown here. Now if you want to derive an expression for contact angle, it would depend on the surface tension between solid liquid between solid gas and liquid gas value, okay.

So, the contact angle would depend on 3 different values of surface tension.

(Refer Slide Time: 38:39)



Contact angle → determined by surface tensions

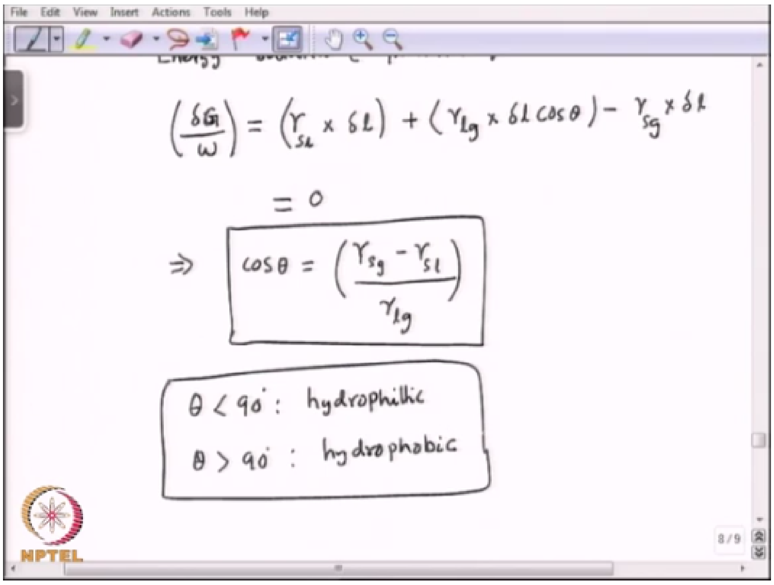
γ_{sl} , γ_{lg} , γ_{sg}

Solid-liq
liq-gas
Solid-g

So, the contact angle determined by surface tensions gamma solid liquid, gamma liquid gas and gamma solid gas. So this is for solid liquid, liquid gas and solid gas, okay. Now, if the liquid is stationary on a solid surface then we can very well define what is the value of the contact angle but if it is moving then the contact angle would have 2 different contact angles.

In some cases there will be different values of contact angle around the contact line between the liquid and solid. So, if let us say droplet is moving then the contact angle are the front surface, okay front end will be different as compared to at the backend, okay. So there will be 2 different contact angles in that case. So, let us try to derive the expression for contact angle.

(Refer Slide Time: 40:13)



$$\left(\frac{\delta G}{w}\right) = (\gamma_{sl} \times \delta l) + (\gamma_{lg} \times \delta l \cos\theta) - \gamma_{sg} \times \delta l$$

$$= 0$$

$$\Rightarrow \boxed{\cos\theta = \left(\frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}}\right)}$$

$\theta < 90^\circ$: hydrophillic

$\theta > 90^\circ$: hydrophobic

So for that let us consider a situation something like this, here we have a solid surface, okay and we have a liquid present in equilibrium, okay so this is the equilibrium interface, this is going to be the equilibrium interface and let us say we subject this interface between liquid and gas to a minor perturbation, okay. So this is the new interface for the liquid gas, okay.

This is the perturbed interface and when it does that this contact angle from here it stays the same when it attains a new position. Let us assume that we are really looking at microscopic we are taking a microscopic view at what happens of the contact line. So, in that case this interface at the contact line can be viewed almost constant almost linear, okay. So, the contact angle here is the same at the displaced position given that the displacement is elemental very small, okay.

So, this is the displaced liquid. So, in that case you can see that if you draw a normal from this point on to the gas liquid interface, okay this is the normal. So, there are because of the displacement of the liquid the interface between liquid gas, liquid solid and solid gas are going to change, okay. So, the changes in interfacial area, so the solid and liquid is going to be + delta l and the liquid and gas is going to be delta l cos theta and solid gas is going to be – delta l, okay.

So, this is going to be the changes in the interfacial area. Now if you look at thus if we represent the surface tensions at here we can say that we have gamma solid liquid and here we have gamma liquid gas and here we have gamma solid gas, okay. And this angle is theta here, okay. So what we can write here is we can do an energy balance at equilibrium and we can assume that the width of this film into the plain is W.

So, in that case we can say the change in the energy per unit width is going to be gamma solid liquid*delta l, okay what we see here + gamma liquid gas*delta l cos theta then -gamma solid gas*delta l. Because this delta is negative, so we have a negative sign there. So, this change in the free energy is going to be 0 if we consider that the film is at equilibrium initial, okay.

So, in that case we can write here cos theta is going to be gamma solid gas – gamma solid liquid divided by gamma liquid gas, okay. So, this is how we can express the contact angle. Now depending on the theta if the theta is < 90 degrees we call this as hydrophilic. So, the surface is hydrophilic if theta is > 90 then surface is hydrophobic, okay. So, this is the definition of hydrophilic and hydrophobic surfaces. So, with that lets us stop here.