Soft Nano Technology
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Lecture – 11
Laplace Pressure

Now, we sort of look in to our last topic related to the fundamentals of surface tension is 1 of the consequences of this surface energy and inter facial energy, on a liquid meniscus, that is Laplace pressure.

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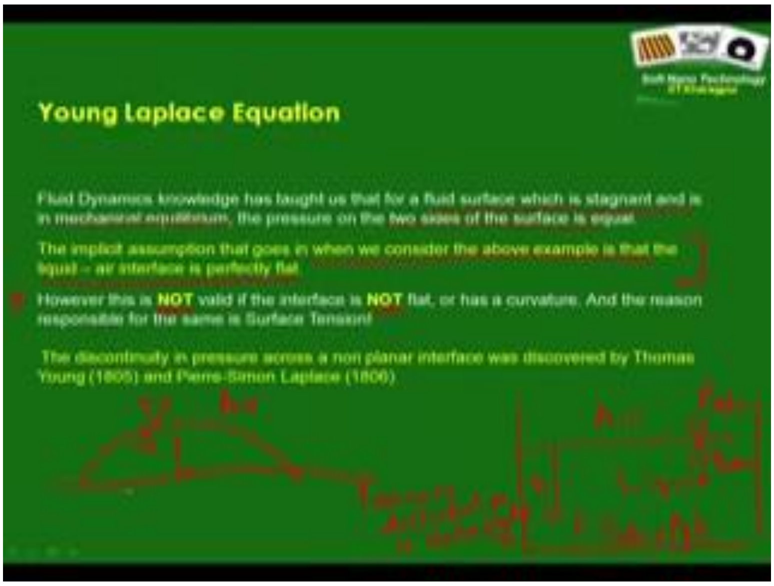

Young Laplace Equation

Fluid Dynamics knowledge has taught us that for a fluid surface which is stagnant and is in mechanical equilibrium, the pressure on the two sides of the surface is equal.

The implicit assumption that goes in when we consider the above example is that the liquid – air interface is perfectly flat.

However this is **NOT** valid if the interface is **NOT** flat, or has a curvature. And the reason responsible for the same is Surface Tension!

The discontinuity in pressure across a non planar interface was discovered by Thomas Young (1805) and Pierre-Simon Laplace (1806).

What we know from our basic fluid mechanics knowledge is that fluid surface, which is stagnant and is at mechanical equilibrium. The pressure on the 2 sides of the surface is equal. That is if you have a liquid surface this is let us say, it is exposed to air and you have liquid here and this is atmospheric pressure let us say.

What we know so far that the pressure at the interface both at the air side and at the liquid side is same and their atmospheres. So, if one is looking at a tank, open tank for example, pressure at any depth each is plus rho g h. So, one says that within the tank the pressure distribution is hydro static, purely hydro static. Now this we know, but what is increase it, in this knowledge is that the liquid air interface is perfectly flat. This is the implicit assumption that goes in.

However what turns out and we will soon realize that, when it is not. This is not valid if the interface is not flat and if the interface has a curvature, in fact, the pressure distributions. So, if this is the interface, this is liquid and this is let us says air. Just the way we drew the drop. For example, while considering Youngs equation, when the liquid is in fact exposed atmospheric pressure; however, we will soon see that though the pressure on the air side is P atmosphere it is not same on the liquid side. In fact, it is different. So, there is a pressure discontinuity and this discontinuity is in fact attributed to surface tension. Just because you can also correlate it like after all this curve shape of the meniscus is also due to surface tension, is the surface energy minimization that is responsible.

This phenomenon was discovered more than 200 years back by Young and Laplace and therefore, this pressure difference is called the Laplace pressure and the equation that governs Laplace pressure is called the Young Laplace equation.

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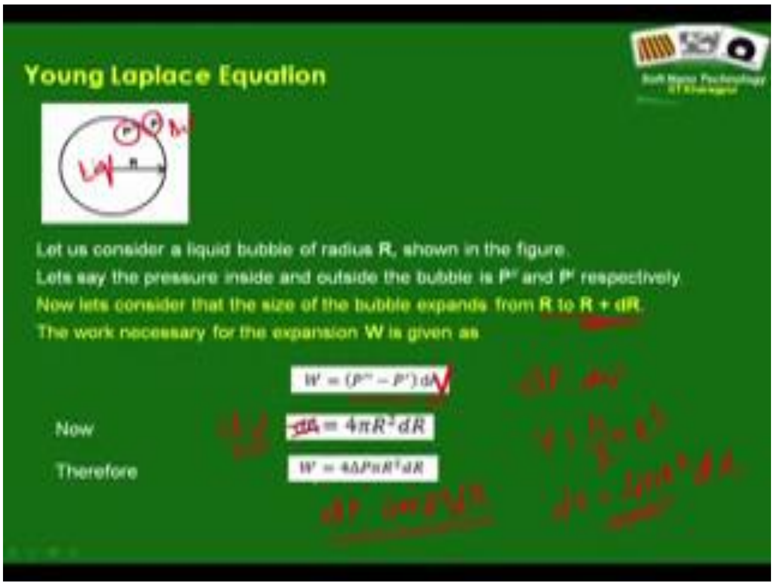

Young Laplace Equation

Let us consider a liquid bubble of radius R, shown in the figure.

Lets say the pressure inside and outside the bubble is P'' and P' respectively

Now lets consider that the size of the bubble expands from R to R + dR.

The work necessary for the expansion W is given as

$$W = (P'' - P')\,dA$$

Now $$dA = 4\pi R^2 dR$$

Therefore $$W = 4\Delta P \pi R^2 dR$$

Let us considered a very simple example; we have a liquid bubble with, let us say radius R. So, this is liquid and this is air, on this side. Let us say the pressure inside the drop is P double dash and outside is P dash. Now let us consider that the radius, initial radius of the bubble which is R sort of expands from R to R plus d R right. So, we know from our basic concept of thermodynamics that the. So, this is in fact wrong it is P d V. So, we know that the pressure required, the work done to achieve this is essentially the delta p.

That is actually the pressure, the (Refer Time: 04:23) pressure that is P double dash minus P dash into d V right. So, it is delta P into d V.

We typically consider, I will not talk about it, I will talk about something. I will just highlight something later. We have a tendency of when we draw a (Refer Time: 04:47) about considering it to be P d V. It considered to be P because we simply assume that the other side is open to atmospheric pressure and therefore, it is consider to be 1.

If we consider the gauge pressure, it is only the p. So, we know that again this is wrong unfortunately, it is d V. V is four-third pi R cube for a sphere therefore, d V is 4 pi R square. When I upload this PPT in the online material, I will correct this. This is a mistake, this is going to be d V and the expression it is not d A.

Therefore, the work done is you can see, it is a delta P times 4 this is d R will come here delta P times 4 pi R square d d R. This is expression of w. I just neatly write it down here.

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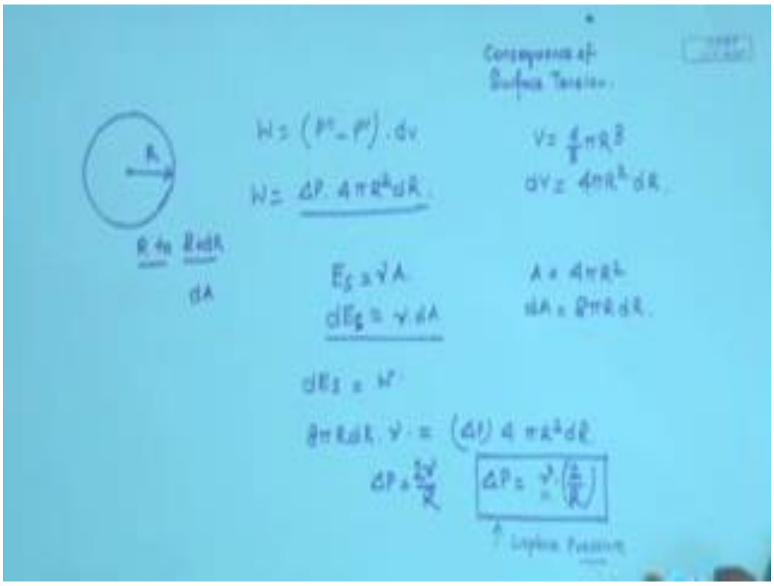

Work done is P double dash minus P dash into d V, V is four-third pi R cube therefore, d V is a 4 pi R square d R and therefore, the expression of w is delta P into 4 pi R square d R. Now what you need to understand is that, as the radius of the drop increases, from R to d R plus d R and you need to work for that, mechanical work of course not only does it lead to increase in the volume, but it also leads to increase in the surface area and what is the?

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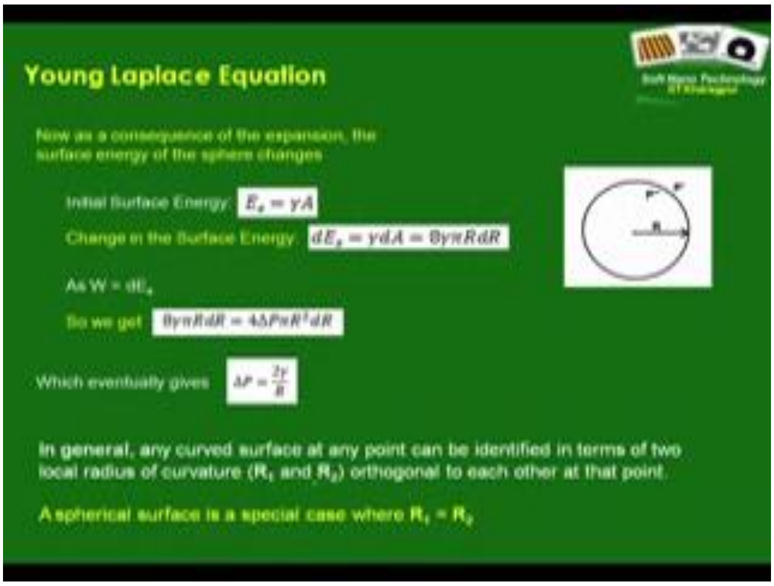

Young Laplace Equation

Now as a consequence of the expansion, the surface energy of the sphere changes

Initial Surface Energy: $E_s = \gamma A$

Change in the Surface Energy: $dE_s = \gamma dA = 8\gamma\pi R dR$

As $W = dE_s$

So we get $8\gamma\pi R dR = 4\Delta P\pi R^2 dR$

Which eventually gives $\Delta P = \frac{2\gamma}{R}$

In general, any curved surface at any point can be identified in terms of two local radius of curvature (R_1 and R_2) orthogonal to each other at that point.

A spherical surface is a special case where $R_1 = R_2$

As the surface area changes; so the let us say the surface area changes by an amount delta A. So, it also leads to a change in the total surface energy or the total energy that is described at the surface. So, let us say E s is the initial surface energy, it is gamma into A and upon expansion the d E s where, the energy of the work you have done is essentially manifested is gamma into d A.

Now, we know for a perfect sphere A is 4 pi R square therefore, d A is going to be 8 pi R d r. Therefore, what we get is the, what that you have done has essentially let to increase in the surface energy of the drop. So, we equate d E s as equal to the w. What you have got? And what we get? Is 8 pi R d R into gamma is equal to delta P into 4 pi R square d R or one gets delta P is 2 pi R into gamma.

You can see for a spherical draw. The delta P across the interface is 2 by R into gamma. What is more important, it is related to the radius of the drop and the surface energy right. So, this is important and this P is what is called as the Laplace pressure, but it is important to note that a spherical drop is a special case of an arbitrarily curved surface because in 3 d space any curvature can be represented by the 2 orthogonal curvatures R 1 and R 2 are, here 2 orthogonal radius of curvature R 1 and R 2 and a spherical surface is a special case.

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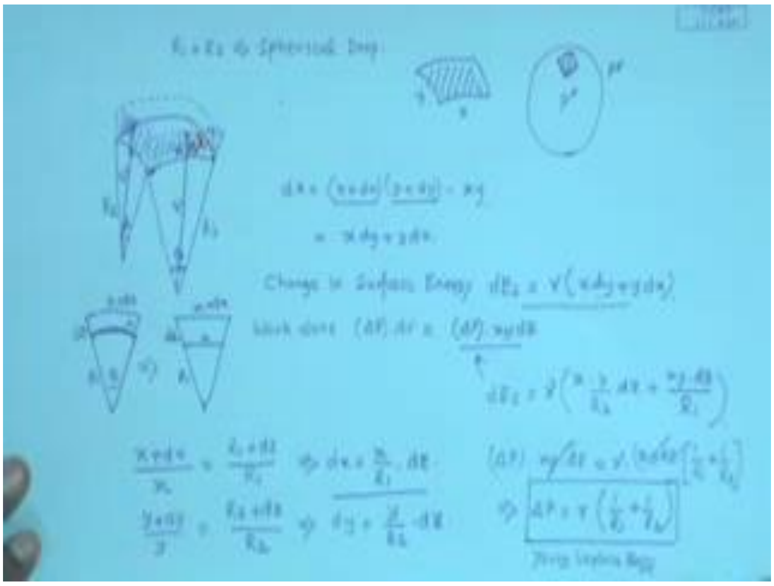

Where the 2 orthogonal radii of curvature R 1 is equal to R 2, it is the spherical drop. Let us look in to a more general situation. Let us consider a non spherical curve surface like this where, the 2 radii are let us say R 1 together some assumptions in this, but it is perfectly fine and we will see. Let us say the length, this length is x this is y. The angles obtained are theta here and alpha here. So, these are the 2 orthogonal radii of curvature, so if you just provide so just the way, in 3 d space unit, 3 co ordinates to be defined to identify a specific point in whatever cordial system you choose like. Similarly, we have essentially needs to define simply that 2 radii of curvature to generate a curve surface or a section of the curve surface.

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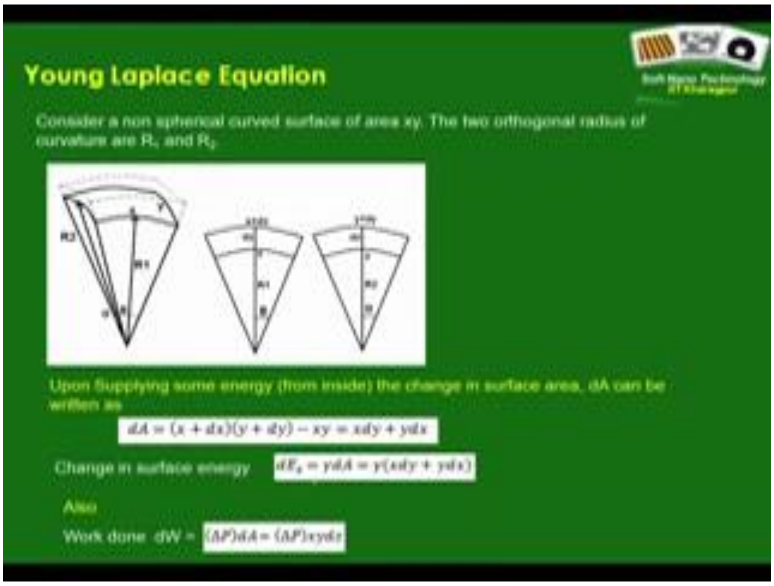

Young Laplace Equation

Consider a non spherical curved surface of area xy. The two orthogonal radius of curvature are R_1 and R_2

Upon Supplying some energy (from inside) the change in surface area, dA can be written as

$$dA = (x + dx)(y + dy) - xy = xdy + ydx$$

Change in surface energy $dE_s = \gamma dA = \gamma(xdy + ydx)$

Also

Work done dW = $(\Delta P)dA = (\Delta P)xydz$

If you want to so, what we do is that, we consider a curved object pretty similar consideration as the previous case, the pressure inside is P double dash, pressure outside is P dash instead of assuming it to be spherical, we now consider that it has 2 radii of curvature R 1 and R 2 and we are simply looking at a small section of it, of this thing. So, the length is x, this is y. So, we sort of look in to the 2 projection views. So, this is among 1 of the radius, the few take an along one of the radius are radius is R 1 and from other side it is R 2.

Now, the same thing, you do some mechanical work and this drop non spherical, but curve drops sort of expands and as a consequence of expansion the radius R 1 expands by an amount delta z, the radius active also expands by an amount delta z. So, this was the original location of surface and this is upon expansion. This is how the configuration takes like. So, this was R 2, this is delta z. This was R 1 and this is delta z. So, there is only one assumption and which is very logical that the expansion along both the radii is same. So, it is sort of an isotropic material, which is a very very common assumption to make.

As a consequence of this expansion, the change in the area surface d A, one can find a x plus d x into y plus d y minus x y. So, again there is a small assumption, that we are looking at very small values of theta and alpha and for those small values x and y can be considered to be linear. Therefore, the area of this segment we are considering, can be simply considered to be x y and then it expands to x plus delta x and y plus delta y and therefore, the increased area is x plus d x into y plus d y.

If you expand this will turn out to be, this neglecting the term containing d x and d y assuming to be very very small and the term x y gets canceled now. Therefore, the change in the surface energy is gamma times and the work done is delta P into d V and which is in fact, delta P into x y d z, that is the change in the volume that has taken place. This is volume by which it has expanded right.

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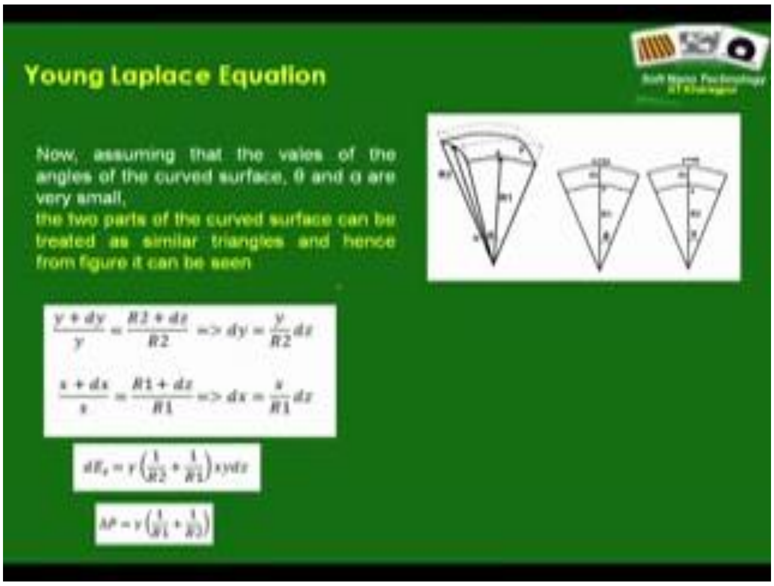

Young Laplace Equation

Now, assuming that the vales of the angles of the curved surface, θ and α are very small,
the two parts of the curved surface can be treated as similar triangles and hence from figure it can be seen

$$\frac{y+dy}{y} = \frac{R2+dz}{R2} \Rightarrow dy = \frac{y}{R2}dz$$

$$\frac{x+dx}{x} = \frac{R1+dz}{R1} \Rightarrow dx = \frac{x}{R1}dz$$

$$dE_s = \gamma\left(\frac{1}{R2}+\frac{1}{R1}\right)xydz$$

$$\Delta P = \gamma\left(\frac{1}{R1}+\frac{1}{R2}\right)$$

We can equate them, but before we do that, we just do a very small geometric maneuver. So, let us look in to these individual segments. We have already assumed that for very small values of theta this segment is linear. So, if we consider that this in fact turns out to be 2 similar triangles and what we get is from the properties of similar tangle; the x plus is d x by x is equal to R 1 plus d z divided by R 1 and from here what we get, is d x is equal to by R 1 into d z. Similarly, considering from the other side, we will get y plus d y divided by y is equal to R 2 plus d z divided by R 2 and this gives us d y to y plus y by R 2 into d z.

Now simply equating these 2; so what we get is we get d E s is equal to gamma we simply replace d y with this expression what we have got here; x into y by R 2 d z and here again we replace d x with the expression we got here. So, x y into d z by R 2 and these as we have all ready argues equates with delta P into x y into d z. So, here also on the right on side, you find gamma into x y d z comes out as common and you are left with 1 by R 1 plus 1 by R 2, you can write to 1 by R 2 plus R 1 does not matter.

These terms cancels out and you get is a fairy neat equation, which is known as Young Laplace equation. So, you now see that there is some pressure difference across a liquid meniscus because of the effect of the surface tension and for an arbitrarily curve surface with; at any given point the 2 orthogonal radius, if the 2 orthogonal radius an R 1 and R 2 Young Laplace equation. In fact, correlates the delta P, with the surface tension and the local radius of curvature.

These are very very useful equation. In fact, it can be used in many cases. It is important; I will just talk about few examples very quickly. One quick example, we will use it later, but the take home very important message is that, the movement there is a curvature over on a liquid surface. In fact, there is a additional pressure effects that come in and these effect are attributed to surface tension.

That sort of brings us to the end of over initial discussion on surface tension. We can just a couple of minutes to sort of find out what are the things we have learned in this particular text we started to understand the important about surface tension or understand what is surface tension and primarily we understood that surface tension is the energy that you need to spend to create some surface per unit area. So, typically surface tension is energy per unit area and it is the amount of energy.

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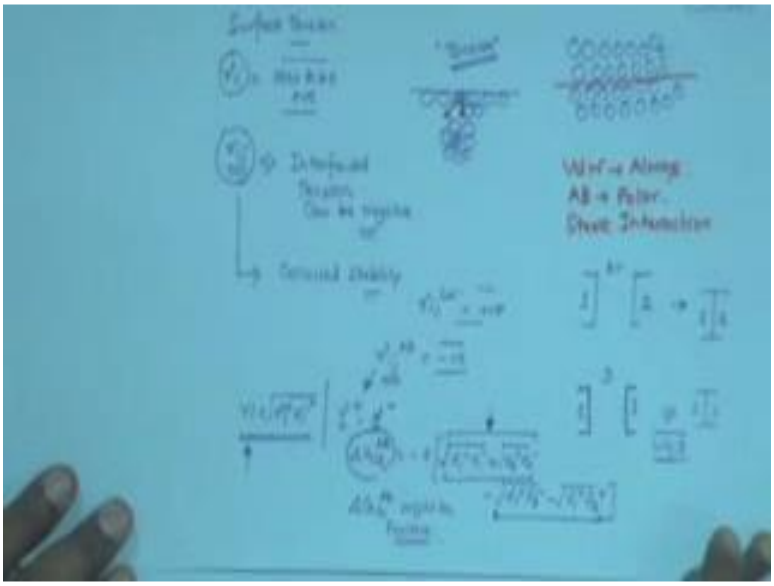

That you need to spend to create unite area of a particular material surface. Why do you needs to spend the energy? You need to spend the energy essentially to. Suppose this is a bulk and you have this molecules, there is some interaction between this molecules of course, omnipresent or always present or always present is Van Der Waals interaction.

Now if you would like to there can be other type of interaction like polar interactions. So, Van Der Waal is always present and then depending on the material, nature of the material you can have polar interaction, you can have Steric interaction etcetera. So, these are individual molecules, they are all interacting with each other within the bulk, the coordination number of all the molecules are lastly the same. So, the net interaction force acting on a molecule is almost 0.

Now, you want to create a surface here. So, what you actually have to do is, you have to supply adequate energy. So, that you can overcome the interaction of all the molecules along which you would like to create the surface. So, this is the energy that you need to actually spend to create your surface; which is fine, but once the surface has been created then, additionally what you see that the surface molecules are in a under coordinate state as compared to the bulk molecules. So, the net interaction on a surface molecules is no longer 0, it is always subjected to a net inward interaction by due to the presents of the molecules ones on side, but there is no net interaction on the other side.

This is manifested is this case can be the other way of looking in to what is surface tension and also the what tension because as if the surface molecules are sort of pulled inward by the molecules of the bulk. Very important thing to note, surface tension has to be positive. We have already understood and we now also understood what is the difference between gamma i and gamma i j; gamma i is typically surface tension of course, it is an inter face, but it is the inter face of a condensed phase with the non condensed phase, gamma i j is inter facial tension.

It is the inter face of one condensed phase with another condense face right and we subsequently started to look a more detail molecular level picture of surface tension and inter facial tension and then we realized that inter facial tension. In fact can be negative, this is very interesting observation and we also realized that this is responsible for colloidal stability and we started to look in to the various components of surface tension and inter facial tension and then we came up, with an understanding that gamma i j L w. Inter facial tension due to Van Der Waals interaction is always positive.

In fact, this implies that in both the cases addition between 1 and 2, these similar surfaces in here or addition between 2 similar surfaces in a liquid B for a polar material is always going to happen. So, you cannot have a constable collide of a polar particles in a polar liquid and what is going to cause the problem is the Van Der Waals component of inter facial tension? You can have if you have polar interaction in your system, depending on the relative strength of the individual components. That is the first you say is the relative magnitude of the cohesive and the adhesive components of the polar components of the individual components.

You can have a positive or negative value of inter facial tension. In order to mathematically represent the polar components of inter facial tension, we sort of introduced to semi empirical parameters; gamma minus and gamma plus, which represents or talk about the acid given, the electron given and electron accepting conjugate parameters, we have discussed it in great detail.

We also had come up with a, some sort of a relation it is a geometric mean to represent the polar component of an individual, a polar component of surface tension of an individual materials. So, this relation and we also had come up with a relation that talks about the free energy change, when 2 objects both having polarity come in contact with each other and the relation that we wrote is something like this where you.

In fact, notice that these are the 2 adhesive components, these are the 2 cohesive components of the polar interaction within a material and this is the polar interaction or the cohesive component of polar interaction between the 2 materials one and 2 and depending on the relative magnitude of these 2, it may be possible that delta G 1 2 A B might be positive and which is necessary to have collidal stability.

1 more interesting example I would like to give. So, these are the things we have sort of done in the last few lectures and I would request you to go through them some sort of again and then I think this recapitulation that, what we are doing would really help. The last thing that we came up is surface tension also manifest. So, leads to a pressure discontinuity or some sort of an additional pressure difference.

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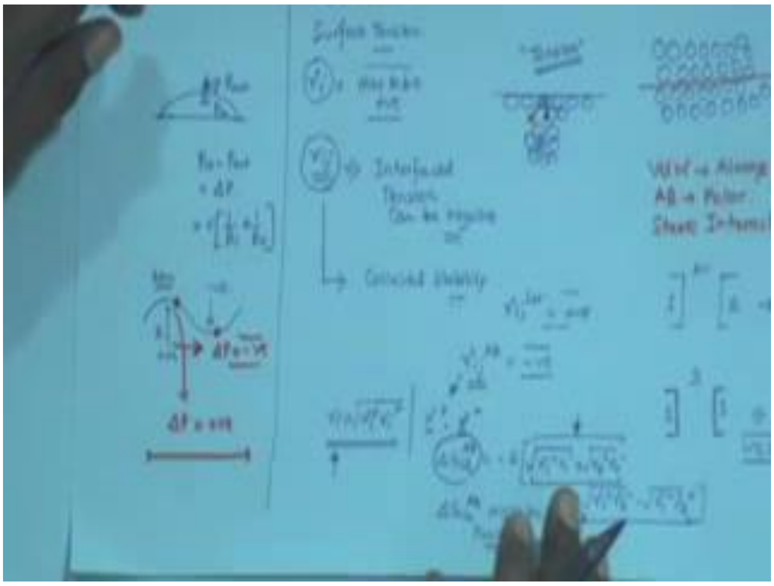

Even across a liquid surface which is act mechanically equilibrium; however, if it is not flat, it has a curvature there exists a difference in pressure between the inside and outside and this delta P is related to surface tension by the Young Laplace equation and you can also now understand this is something that we will use significantly later. That if you have a curvature like this, since the R 1 in this case is positive and this case is negative the nature of delta P, let us assume this is exposed to atmosphere

The nature of delta P is going to vary from this point to this point. So, here delta P is going to be positive and here delta P is going to be negative. What it means that outside pressure remaining constant in both the cases? The pressure inside pressure at this point is going to be higher than the inside pressure here. We always know that if there is a pressure difference it triggers flow.

You can expect an undulating surface like this to have some stabilizing flow from this point to this point and the level should flatten down which is of course, valid because a flat level for a film or liquid represents a lower surface area configuration. I think this I will take up in greater detail. This particular concept I will take up in greater detail when I discussed in thing full means stability, but this flow is triggered by the difference in the Laplace pressure at the 2 points.

I will stop here this particular lecture. We are pretty much done with, what I wanted to discuss on surface tension; the basic concepts. And from the next class we will move on to the second aspects that, we have discussed in the content part and that is the patterning part and we get started with photolithography.

Thank you.