Instability and Patterning of Thin Polymer Films

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Lecture No. #05
Effect Surface Tension: Laplace Pressure

Welcome back, in this particular lecture, we will start talking about the concept of Laplace pressure, but before that let us quickly look at an extension of what we did in the previous lecture.

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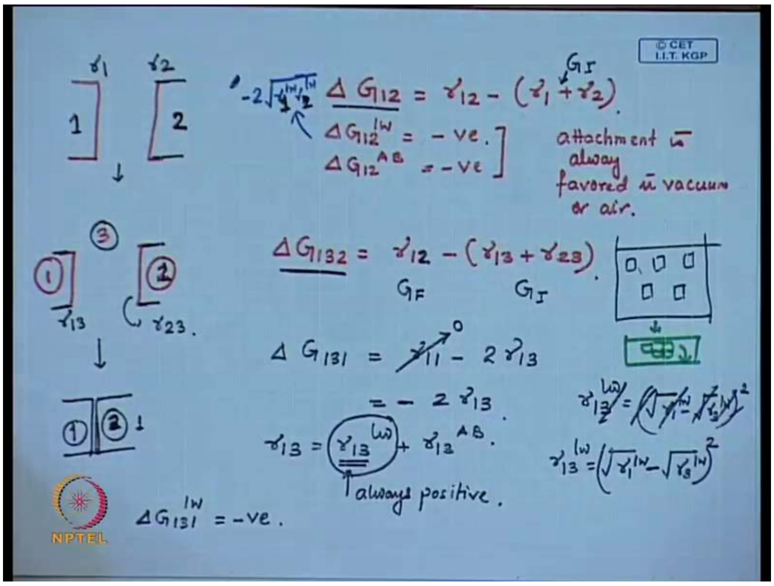

$-2\sqrt{\gamma_1^{lw}\gamma_2^{lw}}$

$\underline{\Delta G_{12}} = \gamma_{12} - (\gamma_1 + \gamma_2)$. G_I

$\Delta G_{12}^{lw} = -ve.$

$\Delta G_{12}^{AB} = -ve$

attachment is always favored in vacuum or air.

$\underline{\Delta G_{132}} = \gamma_{12} - (\gamma_{13} + \gamma_{23})$.

G_F G_I

$\Delta G_{131} = \cancel{\gamma_{11}}^{0} - 2\gamma_{13}$

$= -2\gamma_{13}$.

$\gamma_{13} = \underline{\underline{\gamma_{13}^{lw}}} + \gamma_{12}^{AB}$.

always positive.

~~$\gamma_{13}^{lw} = (\sqrt{\gamma_1^{lw}} - \sqrt{\gamma_3^{lw}})^2$~~

$\gamma_{13}^{lw} = (\sqrt{\gamma_1^{lw}} - \sqrt{\gamma_3^{lw}})^2$

$\Delta G_{131}^{lw} = -ve.$

So, here is the scenario you we have talked in detail about two surfaces of 1 and 2, which are coming in contact with each other in a non-condense medium of air or vacuum. So, we have looked at the delta G 1 2, the expression for which is gamma 1 2 minus gamma 1 plus gamma 2. Now, delta G 1 2 l w, this is the expression we have seen that it is negative. The way we have defined delta G 1 2 AB, this is also negative. So, what it implies that delta G 1 2 is always negative, when two surfaces are coming in contact in a non-condense medium. So, this is always negative and what it implies is that attachment is always favoured in vacuum or air.

Now, let us talk of a more realistic scenario that you have two surfaces 1 and 2, which are sort of dispersed in a or in a medium or dispersed in a medium 3. Let us say 1 and 2 are two solid surfaces in a medium in a liquid medium 3 which are trying to come in contact with each other. So, what is the key difference? Here, you had the two surface tensions acting gamma 1 and gamma 2, however here you do not have the plane surface, so here you have gamma 1 3 and gamma 2 3.

So correspondingly, your delta G 1 3 2 changes is now has the expression of gamma 1 2 minus; so, this corresponds to the G F, is the final configuration, where 1 and 2 are come in intimate contact. But G initial is no longer gamma 1 plus gamma 2, at as it was here in the case of the two surfaces exposed to non condensed phase or gas or vacuum non gas or vacuum. Here, the G I comprises of a summation of gamma 1 3 plus gamma 2 3. Of course, you can understand we are limiting our discussion to at a per unit area basis; so here, how does one pretty, what is going to be the magnitude or the sign of delta G 1 3 2.

Now, let say that we have, let us say 1 and 2 are same materials. So, you have two, let us say blocks of sugar which are coming in contact with each other, in say a liquid medium let us say water. So, what you have is gamma 1 1 minus twice gamma 1 3. Now, this is obviously zero, because two materials coming in contact there is going to be no surface, so it is minus 2 gamma 1 3. Now, this is interesting. we have delta G 1 3 1 to be equal to minus 2 gamma 1 3, we know that gamma 1 3 is gamma 1 3 l w plus gamma 1 3 A B. We also know that gamma 1 3 l w will have the form of gamma 1, I think I will rewrite it; gamma 1 3 l w it is gamma 1 under root gamma 1 l w minus under root gamma 3 l w square. So, this is always positive.

What does it mean? That if it always positive delta G 1 3 1 based on or the vanderwaals component of delta G 1 3 1 will always be negative. So, delta G 1 3 1 l w will always be negative. In other words, what it means that based on the only the vanderwaals part of the interaction two surfaces will still prefer to attach to each other even in a liquid medium. Now, if two surfaces attach in a liquid medium, what you eventually leading to is a scenario; suppose, you have lots of particles which are dispersed in a liquid medium. So, if they all attach to each other what you are going to get? You are going to get a huge chunk of material, which will eventually fall down. Probably the picture is not very clear I am sorry about it, so I will redraw it.

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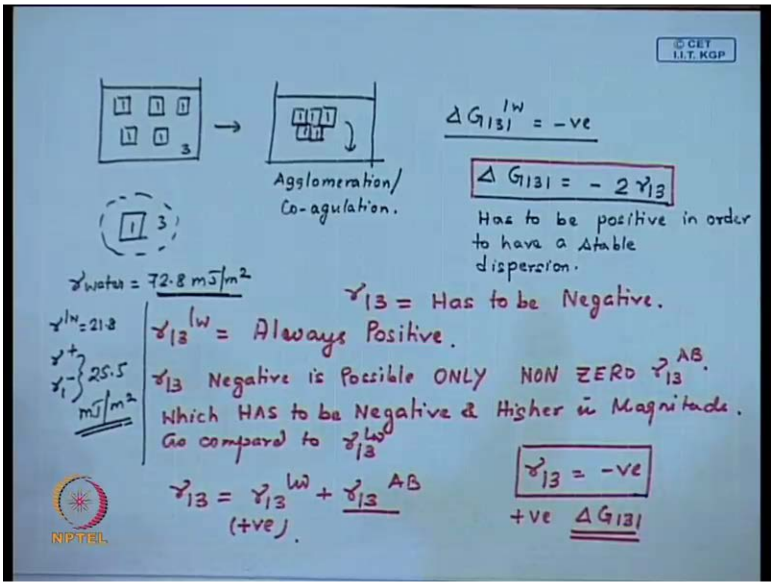

Agglomeration/ Co-agulation.

$\Delta G_{131}^{lw} = -ve$

$\boxed{\Delta G_{131} = -2\gamma_{13}}$

Has to be positive in order to have a stable dispersion.

$\gamma_{water} = \underline{72.8\ mJ/m^2}$

$\gamma^{lw} = 21.8$

$\left.\begin{matrix}\gamma^{+} \\ \gamma_1^{-}\end{matrix}\right\} 25.5$

$\underline{\underline{mJ/m^2}}$

γ_{13} = Has to be Negative.

γ_{13}^{lw} = Always Positive.

γ_{13} Negative is Possible ONLY NON ZERO γ_{13}^{AB}.

Which HAS to be Negative & Higher in Magnitude.

As compared to γ_{13}^{lw}

$\gamma_{13} = \underset{(+ve)}{\gamma_{13}^{lw}} + \underline{\gamma_{13}^{AB}}$.

$\boxed{\gamma_{13} = -ve}$

+ve $\underline{\underline{\Delta G_{131}}}$

NPTEL

So, here suppose you have lots of particles of 1. And if they all tend to attach with each other what will happen? So, they will all attach at one point, the size becomes large; so the gravity effect of gravity will be stronger, it may settle down. So, this is a situation where you have agglomeration or co-agulation. Now, so vanderwaals, if you have only vanderwaals interaction active or delta G 1 3 1 l w is negative. So, it always refers to a scenario, where if you have multiple surfaces in a liquid medium, let us say you will always have agglomeration or coagulation. So, how can you really have a stable dispersion? In order to have a stable dispersion, your attachment should not be favoured. Or in other words, the expression that delta G 1 3 1 is twice gamma 1 3; this has to be the delta G 1 3 1 has to be positive, in order to have a stable dispersion.

What it means? that if the two particles let us say of 1 and 1 come in contact with each other, there will higher penaled energy associated with that as compared to if they remain dispersed in the liquid 3. So, they then even if they come close to each other they will not prefer to adhere to each other and they will prefer to be surrounded with the liquid 3. So in that way, you will have a stable dispersion, where the particles sort of have a have sort of repulsive interaction between them. Now, looking at this expression, so mathematically we understand that is possible only when delta G 1 3 1 is positive. And in order to have that to be positive, the only way it is possible that gamma 1 3 has to be negative.

We understand that gamma 13 l w is always positive. So, the key message that emerges out that you can have, however you can still have gamma 1 3 to be negative, only if negative is possible, only when you have non zero, gamma 1 3 AB which has to be negative and higher in magnitude as compared to gamma 1 3 l w, because of the fact that gamma 1 3 is gamma 1 3 l w plus gamma 1 3 AB, this is always negative. So in order to make the whole thing, this is always positive; so, in order to make the whole thing negative, the only way it is possible is that this term has to be negative and it is numerical magnitude has to be higher than this particular term.

Only under that particular case, you can have gamma 1 3 to be negative, which will result in a positive delta G 1 3 1, which means that a stable dispersion is going to be possible. So, it eventually it shows that in order to have a stable dispersion or dissolution having polar interaction is mandatory. And if you correlate, I mean let me tell you one thing, which we will revisit in one of our subsequent lectures that water is a liquid, which has lots of polar interaction, it is a strong polarity.

And in probably in your school days, in some course, chemistry course probably you have come across this term that water is an extremely polar solvent. Now here it is, because water has a significant polar interactions or polar component of surface tension; incidentally, you may want to note down that surface tension of water is 72.8 milli joule per metre square, and it is gamma l w is roughly 21.8, it is gamma plus and gamma minus both are 25.5 milli joule per metre square. Water is pretty high, as far as the surface tension is pretty high and that is contributed or attributed to the presence of the non zero polar component of it is surface tension.

So, water has a significantly high polar component of surface tension; this sort of allows water to sort of have a stable dispersion or dissolution of ah many many materials; so, water is a good solvent for many materials. Now, one thing you need to understand that until and unless you are able to disperse the solute molecules into the solvent, it is not possible that the solute goes into a solution, it is just not possible. Because if there is an agglomeration, it is sort of forms vagulates and it settle down settles down, it is not going to solve. So, these are certain very basic things which you can understand from the stand point of surface and interfacial tension.

We will be revisiting some of these concepts later, which are very very critical, but one thing you are already understanding that surface tension has is made up of different types of interaction. Or the molecular level interaction is sort of manifested or lumped as surface tension. It is the primary interactions we have considered so far is the acid base type interaction or the polar interaction and the induced dipole induced dipole type interaction or the vanderwaals interaction. And simply based on the surface and interfacial tensions, you can look into the changes in the free energy scenario, to say or to conclude whether two surfaces in a third medium; whether they will prefer to come in contact with each other, get attached to each other or will or they will prefer to sort of remain dispersed. Of course, you also understand that in a vacuum or a non-condense phase, two surfaces based on both the types of interaction; whether the polar interaction is present or absent, they will try to attach with each other.

And the other thing to remember of course, is the polar interaction is more specific, I mean it may be present may not be present, but the vanderwaals interaction or the induced dipole type interaction is more generic and it is present in all settings. So, we now understand some of the basic concepts or at least the constituents of surface tension. Now, let us look into another specific aspect or contribution of surface tension. Again which we all know in various areas, we have read it probably right from our early school days that a, if you have if you are looking at the capillary rise.

For example, there is a liquid meniscus or water meniscus that forms within the tube and you need to worry about the parallax error, where you have to measure the thickness, etcetera, etcetera. Now, a question to ask is what exactly forms this meniscus? And probably most of you by now realized that the formation of a meniscus within a tube or the spherical shape of a droplet of a liquid resting on a solid surface is attributed to surface tension. Now, what is it is implication in terms of the pressure at the surface. This is something very, very important; we will show that surface tension on a liquid surface particularly results in a pressure imbalance.

So, this is what we are going to take up now, effect of surface tension across a non-planner liquid surface. So, this is something what we all understand.

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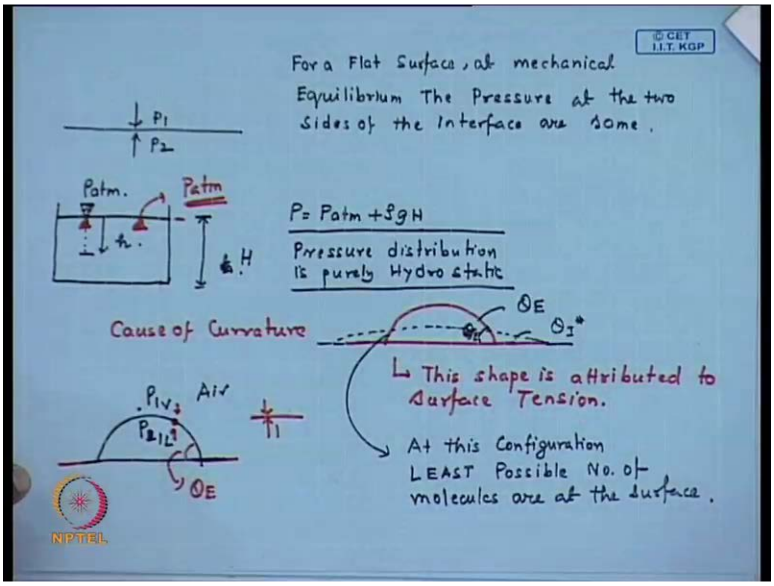

For a Flat Surface, at mechanical Equilibrium The Pressure at the two sides of the Interface are same.

$P = P_{atm} + \rho g H$

Pressure distribution is purely Hydro static

Cause of Curvature

This shape is attributed to Surface Tension.

At this Configuration LEAST Possible No. of molecules are at the surface.

For a flat surface, at mechanical equilibrium, the pressure at the two sides of the interface are same. So, if you have let us say p 1 and p 2 they are same, it is a, if it is a flat surface. The classic example engineering example, I would say the pressure distribution inside a tank, let us say full of water having depth h. So here, we all know that the pressure at the top surface is P atmosphere. And as you go deeper, your let us say this is the height of the tank, it gets sort of the actual pressure at any it is P atmosphere. So, here at the bottom of the surface the pressure is rho G H. This is a scenario, where you say that the pressure distribution within the tank or within the storage vessel is purely hydrostatic.

I am sure this concept you all know from your basic fluid dynamics course, which you have attended. So in other words, what it means? That at this that the first layer of liquid of the liquid surface over here, the pressure is equal to P atmosphere, because of the fact that at this line h is equal to zero. So, there is no contribution from this term, so pressure is equal to the atmospheric pressure. Or in other words, what we have written here, that is sort of validated. So for a flat surface, at mechanical equilibrium the pressure at the two sides of the interface are same. Now, however for a curve surface, there is a pressure imbalance. Now for a non condensed liquid phase, the curvature is caused.

Now, you have to understand what is the cause of this curvature. And as I tell you, thus this effect is more pronounced in a liquid. So, we were happy to draw, while considering young’s equation, a liquid shape like this. We understand that this is actually attributed to surface tension, as it tries to minimize the number of molecules which are present on the surface to the minimum possible extent and therefore, you get to this curvature. Now, so there is essentially an inward resultant or effective attraction the sorts of the molecules reorganize themselves and this reorganization is based on energy minimization. So, I gave you the example the other day, so you dispense some water on your table or something like that; and you spread with your hand, you see that the water is retracting back to form a spherical droplet.

Of course, on a on a dirty table or a bench top, it might not form a spherical droplet, because there might be defects in the form of dust particles or similar things, but ideally it should form a spherical droplet. So, what exactly happens? What happens is, so this is the young’s configuration, you have an equilibrium contact angle; you understand that it is a balance between the horizontal component of surface and interfacial tensions.

So by way of spreading it with your hand, what you do is you sort of flatten the liquid. So, this intrinsic contact angle sort of is lower than the equilibrium contact angle. Or in other words, there is now an imbalance in the horizontal component of the surface and interfacial tension. So, the liquid retracts back, till it attains theta E, the equilibrium contact angle is attain back. But the other picture to, the other way to looking to this problem is that by spreading, you have actually created more surface area for this liquid drop.

So, you are exposing more number of surface molecules than the minimum possible number of surface molecules, that can be exposed to the surface or that can remain at the surface for this particular volume of the liquid drop. So, the liquid tries to sort of minimize retract it forming a meniscus or a shape, which corresponds to we call it the minimum surface energy configuration. But the reality is, at this configuration least number possible number of molecules are at the surface. Because you understand, because of the under coordination of the surface molecules, there is an energy penalty associated with each molecule that goes to the surface; lower is the number of molecules at the surface lower will be the energy penalty. So, thermodynamically it will be the favoured configuration.

Now, it is time we need to consider; now here whether the pressure across this interface let us say or let us say are same; suppose, this is a liquid drop, which is exposed to air. So at this particular point, whether the pressure inside and the pressure outside are the same. Had it been a flat surface, of course we have seen that these two pressures would have been equal. So, this is a drop which is sort of in a thermodynamic equilibrium once it has attained it is equilibrium contact angle value. So now, we are going to critically evaluate whether the two sides or two pressures are same. And let me tell you that these pressure is not same; that there is a pressure imbalance, due to this energy associated at the surface or the energy that you need to consume at the surface, which leads to a pressure imbalance across a curved interface. And let us look into the physical origin, as well as the expression for that.

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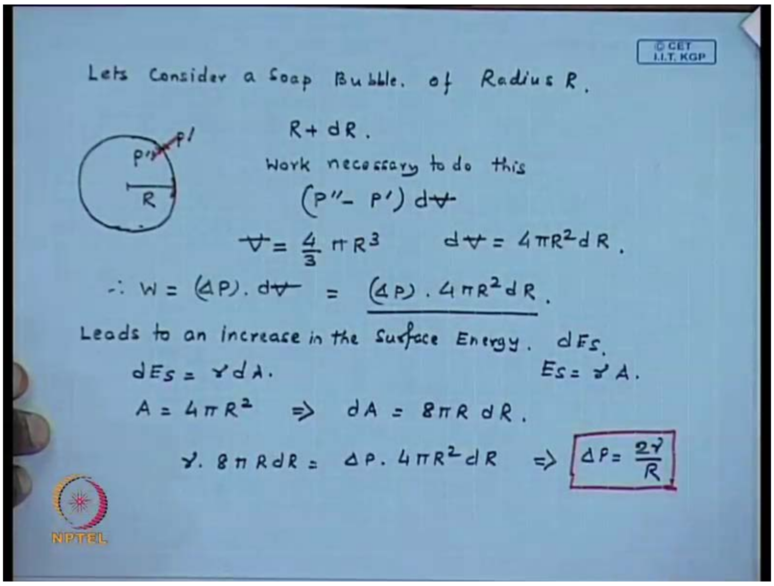

Lets Consider a Soap Bubble. of Radius R.

R + dR.

Work necessary to do this

$(P'' - P')\, d\bar{V}$

$\bar{V} = \frac{4}{3}\pi R^3 \qquad d\bar{V} = 4\pi R^2 dR.$

$\therefore W = (\Delta P).d\bar{V} = \underline{(\Delta P).4\pi R^2 dR}.$

Leads to an increase in the Surface Energy. dE_s.

$dE_s = \gamma\, dA. \qquad E_s = \gamma A.$

$A = 4\pi R^2 \Rightarrow dA = 8\pi R\, dR.$

$\gamma . 8\pi R dR = \Delta P . 4\pi R^2 dR \Rightarrow \boxed{\Delta P = \frac{2\gamma}{R}}$

The easiest example to consider in this regard is, let us consider a soap bubble of radius R. So, this is the radius R. let us say the pressure inside is P double dash, pressure outside is P dash. And suppose, it is expanding and it has expanded to a radius of R plus delta R. So, the work necessary to do this, so this is expanding against a pressure of P dash is dv bar, where dv bar is the change in the volume. The volume of a sphere, we know is four third pi r cube. So, dv bar is 4 pi R square dR. Therefore, the work done is pressure difference into delta v, which is delta P into 4 pi R square into dR.

Now, what exactly this work leads to, or what is the manifestation of this work? The manifestation of this work is essentially as it expands the radius the associated surface area also changes. Now, we know that if the surface was area was A, the total energy ascribed to the surface was gamma times into A, where gamma is the surface tension. Now, let us say the surface area changes from A to A plus delta A. Therefore, the energy ascribed to the surface also changes from gamma A to gamma into A plus delta A. So, the manifestation of this work is, it leads to an increase in the surface energy. Let us say dES, we have we can term ES as surface energy total energy ascribed to the surface to be gamma A. Now, gamma is constant therefore, you have d ES to be gamma into dA. Now for a spherical object, A is 4 pi R square; therefore, dA is 8 pi R dR.

Now, as we have discussed that this work is leading to this enhancement in the surface energy is due to this work you have performed. So, if you consider the equality between the two components what you get is gamma times 8 pi R dR equal to delta P into 4 pi R square dR, which gives you delta P equal to 2 gamma divided by R. So, first thing to note is delta P is non zero and for a spherical thing, it is 2 gamma divided by R. So therefore, even at a mechanical equilibrium across a curved surface the pressure, there is a pressure gradient or the pressure inside a or the pressure within the meniscus or within the liquid and outside the liquid right on the other phase is not same; this is the first thing you to understand. Now, let us consider so this is a soap bubble or a spherical bubble, we have considered a spherical object, where the it has only one I mean you can define it in terms of one radius. Let us consider any general surface, general curved surface.

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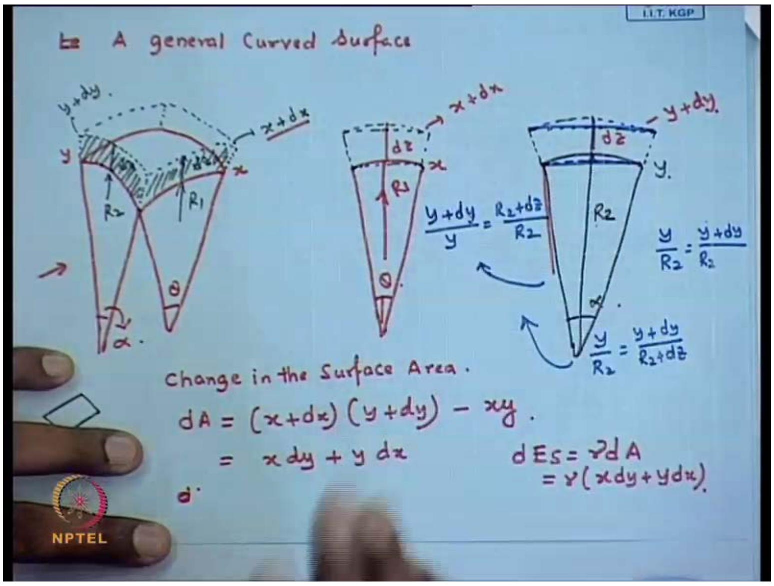

A general Curved Surface

Change in the Surface Area.

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

$$= x\,dy + y\,dx$$

$$dE_s = \gamma\,dA$$

$$= \gamma(x\,dy + y\,dx).$$

$$\frac{y+dy}{y} = \frac{R_2+dz}{R_2}$$

$$\frac{y}{R_2} = \frac{y+dy}{R_2}$$

$$\frac{y}{R_2} = \frac{y+dy}{R_2+dz}$$

Now, in order to define a point in 3 D space, you need to define, if you are if you need to define 3 coordinates. If it is cartesian, you need to define x, y and zee. If it is R theta z coordinate, you need to define R theta and z. Similarly, in order to define a curved surface in a 3 D space, you need to actually define two curvatures that will give you the geometry of the general curved surface. So, let us say we are sort of considering a curved surface like this; I will make the drawing clear to you. So, this is let us say x and this is y. And so, if you look from this particular side, let us say this subtends an angle theta, this subtends an angle alpha over here. So, what you have here is theta and this is x. So, this is the radius R 1 and from this particular side, if you view now what you will have? You have y and this radius is R 2. So, you have defined a surface in terms of two curvatures R 1 and R 2.

Now, exactly similar to what we have discussed in the previous case. So, this is part of a enclosed object which has this type of a curvature at any given location, one side is x, the other side is y, and subtends an angle theta here alpha here. So, the curvature in or the radius of curvature here is R 1 the radius of curvature here is R 2. You can sort of imagine it that R 1 is the sort of in planed curvature along the plane of this paper; for example, and arc 2 is the curvature at a plane perpendicular to the plane of the paper, because this is a 3 D object, which has been sort of drawn artificially on a 2 D surface. Now, we again do a pressure volume type work here. So, what it results? It sort of expands the surface.

And this is, let us say a new configuration. If we assume that the expansion is isotropic, then what happens is that this is delta z, let us say this is also delta z, this new area is x plus delta x let us say, this is y plus delta y. So, here we had x this figure will look like this from here. So, this is dz, this is also dz, this is x plus del x, this is y plus del y. So, the change in the surface area d A, what is the change in the surface area? What is the new surface area? New surface area is x plus del x into y plus del y. And what was the earlier surface area? It was simply xy. So, it turns out to be x dy plus y dx. If you neglect the term del x into del y to be very very small. Therefore, the corresponding d ES, which is gamma dA turns out to be gamma x dy plus y dx.

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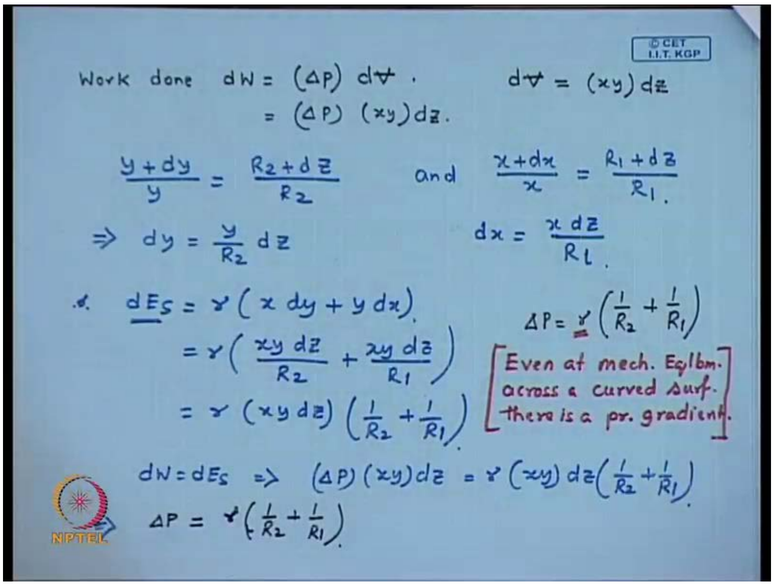

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Work done $dW = (\Delta P)\, d\forall.$ $\quad d\forall = (xy)\, dz$

$$= (\Delta P)\,(xy)\,dz.$$

$$\frac{y+dy}{y} = \frac{R_2+dz}{R_2} \quad \text{and} \quad \frac{x+dx}{x} = \frac{R_1+dz}{R_1}.$$

$$\Rightarrow dy = \frac{y}{R_2}\,dz \qquad dx = \frac{x\,dz}{R_1}.$$

$$\therefore \underline{dE_S} = \gamma(x\,dy + y\,dx).$$
$$= \gamma\left(\frac{xy\,dz}{R_2} + \frac{xy\,dz}{R_1}\right)$$
$$= \gamma\,(xy\,dz)\left(\frac{1}{R_2}+\frac{1}{R_1}\right).$$

$$\Delta P = \underline{\gamma}\left(\frac{1}{R_2}+\frac{1}{R_1}\right)$$

[Even at mech. Eqlbm. across a curved surf. there is a pr. gradient.]

$$dW = dE_S \Rightarrow (\Delta P)(xy)\,dz = \gamma\,(xy)\,dz\left(\frac{1}{R_2}+\frac{1}{R_1}\right).$$

$$\Rightarrow \Delta P = \gamma\left(\frac{1}{R_2}+\frac{1}{R_1}\right).$$

Now, the work done to achieve this expansion is dw is equal to delta P into dv. Which in this particular case is the change in the volume and if you look into the figure carefully, this is actually xy into delta z. So, this is the change in the volume, you have achieved over here. So, it is xy into sort of delta z. Of course, we are assuming that that the curvature at the, at this particular point is negligible; so, therefore, the surface area is xy ideally that would have been the case had the surface been flat, but we are doing that approximation it is perfectly fine. So, you have delta P is xy into dz. Now, from the concept of similarity triangles, so here you can assure you can see you can regard, if you regard these to be straight lines what we have already done when we consider that the surfaces are surface area is xy.

If you consider these two these to the similar triangles, what you can come up with is y plus dy by y equal to R 2 plus dz by R 2 from this triangle. Clear, a something very very simple y plus dy divided by y is R 2 plus dz divided by R 2. This you can, I guess you all understand how it comes? It comes from the concept of similar triangle; you just assume that these are essentially straight lines. So your, so you what comes out exactly is y by R 2 is y plus dy divided by R 2 y by R 2 is y plus dy divided by R 2 plus dz; you do a little bit of reorganization, you get to this thing this setting. So, from one of the similar triangles we get y plus dy by y equal to R 2 plus dz by R 2. From the other one, we get x plus dx by x R 1 plus dz by R 1. Therefore from here, we get dy is equal to y by R 2 into dz; here we get, dx is equal to x into dz by R 1. If we substitute these two expressions, in the expression we have already got for dES which is gamma times x dy plus y dx, we get that this is gamma into xy dz by R 2 plus xy dz by R 1, this turns out to be gamma into xy dz into 1 by R 2 plus 1 by R 1.

Now, doing exactly in the same way the delta d ES is essentially a manifestation of dw. So, that these two energies are same. So, if we do that, we get delta P xy dz is gamma xy dz 1 by R 2 plus 1 by R 1, which turns out to be delta P is equal to gamma into 1 by R 2 plus 1 by R 1. So, you see the pressure difference across the interface of any arbitrarily curved surface which can be represented with the two orthogonal curvatures R 1 and R 2 can be obtained in terms of the respective curvatures, radius of curvatures and is multiplied by the surface tension. So the, so the two key things that emerge essentially are. Firstly, even at mechanical equilibrium across a curved surface, there is a pressure gradient. This is the first major thing to understand which comes out and second thing is that this pressure gradient is correlated to two entities; one is the surface tension and the other thing is the two respective curvatures. So, important thing to note is that if you have two liquid meniscuses of the same shape, which means that the R 1and R 2 are the same. And in that case, the pressure difference across the interface will be higher for the liquid which has higher surface tension, because of the fact that delta P it is a function of 1 by R 1 plus one by R 2, but that gets multiplied with gamma.

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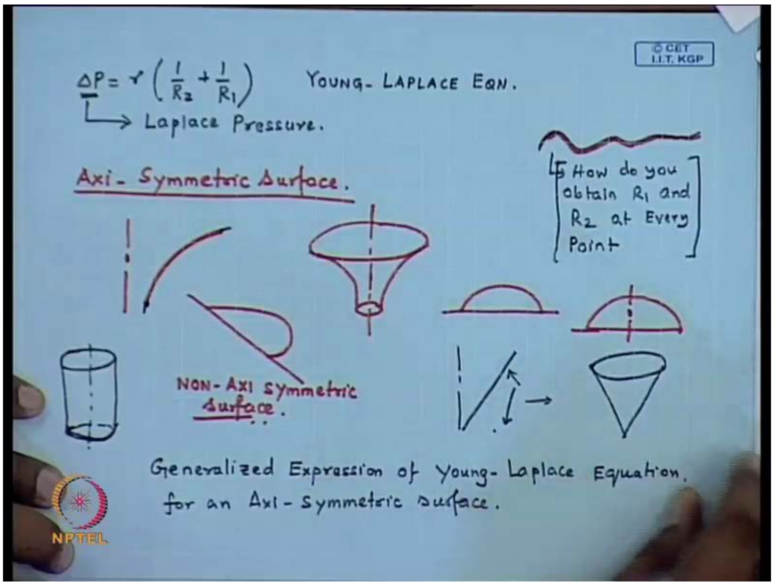

$\Delta P = \gamma \left(\frac{1}{R_2} + \frac{1}{R_1} \right)$ YOUNG- LAPLACE EQN.

$\hookrightarrow$ Laplace Pressure.

Axi- Symmetric Surface.

How do you obtain R_1 and R_2 at Every Point

NON- AXI Symmetric Surface.

Generalized Expression of Young- Laplace Equation, for an Axi - Symmetric surface.

Now, the critical thing is that need to be we need to understand is that how do we get for arbitrarily curved surface, the magnitude of R 1and R 2. So, it might be very simple the equation the I just did not mention that this equation is very, very well known and it goes by the name young Laplace equation. And this pressure difference or delta P that generates or that is engendered, due to the curvature and the surface tension effect is known as the Laplace pressure. Now, this equation looks very simple and rather manageable in a rather manageable form. But if you sort of look at an arbitrarily curved surface in 3 D, the biggest problem is how do you obtain R 1and R 2 at every point. Because it is obvious or you should be able to understand that along this curved surface, the thing that is occurring that at every point there is a variation of R 1and R 2. So, consequently the Laplace pressure at every point varies.

Now, if you want to find out the Laplace pressure at every point, you need to know the radius of curvatures at every point, but then how do you measure it? It is not that easy, I mean the equation is very, very simple, but measuring the radius of curvature is not going to be that simple. Therefore, in order to overcome this difficulty not exactly to overcome, so there are some specific cases, where one can correlate the radius of curvature to other geometric properties of the system. And one such example is the so called axi-symmetric surfaces. So, what exactly is an axi-symmetric surface? there can be a classical definition, but it is very, very simple; any surface that has an axis of symmetry or in other words, if you have any arbitrarily curved surface and you sort of route it around a line the surface you will get.

Suppose, you have this curved curvature or curved line and this is sort of an axis around which you want to rotate it, what will you get? You will actually get a conical hold like this. And this is the axis of symmetry around which it has been rotated. So similarly, if you look at a liquid drop which is perfectly spherical it is also an axi-symmetric surface, because you can obtain that by taking a curved line like this and simply rotating it by this axis. So, you rotate it by 360 degree and you will get to this type of a surface. So, this is also an axi-symmetric surface, but if you consider the same liquid drop, what we talked about a little bit before in one of our previous classes about when we were talking about the contact angle hysteresis. For example, it takes a shape like this; you remember that. Now, this you see you do not have an axis of symmetry. So, this is a non axi-symmetric surface.

Now, what subsequently we are going to take up. So, I guess you briefly understand what exactly is an axi-symmetric surface, it is not the really that tough that difficult to understand. So, you sort of take any curved line and sort of, if you have a specific axis, if you rotate it by all 360 degrees around that axis, whatever you get is an axi-symmetric surface. So, instead of a curvature if you sort of have a line, if you rotate it you will get this is very simple you will get a cone. So, this is also an axi-symmetric surface. There is no mandatory requirement that this has to be a curved thing, curved line or something like that it can be a straight line also under a limiting case. So, this is an axi-symmetric surface, a cone can be axi-symmetric surface. You also understand that a cylinder is also going to be an axi-symmetric surface following the same logic. So, what we are going to do now is looking to the generalized expression of young Laplace equation for an axi-symmetric surface.

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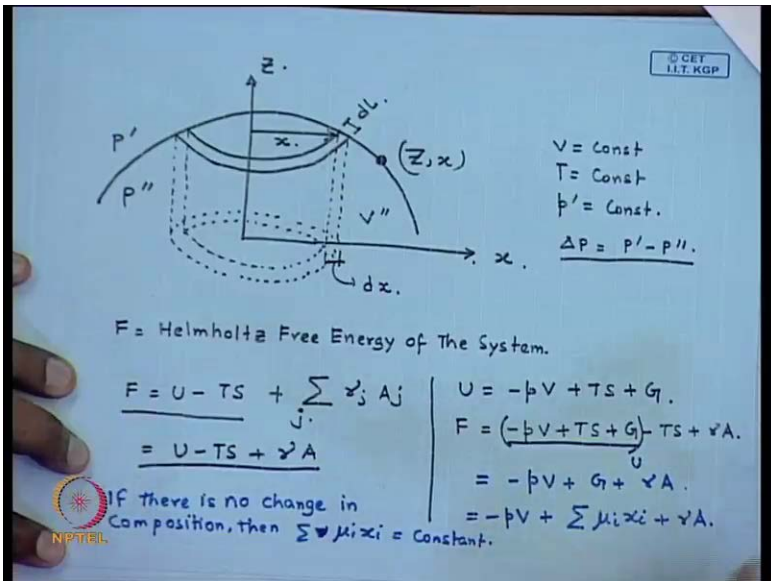

$V = \text{Const}$
$T = \text{Const}$
$p' = \text{Const}.$
$\Delta P = P' - P''.$

F = Helmholtz Free Energy of The System.

$$F = U - TS + \sum_{j} \gamma_j A_j$$
$$= U - TS + \gamma A$$

If there is no change in Composition, then $\sum \mu_i x_i$ = Constant.

$$U = -pV + TS + G.$$
$$F = \underbrace{(-pV + TS + G)}_{U} - TS + \gamma A.$$
$$= -pV + G + \gamma A.$$
$$= -pV + \sum \mu_i x_i + \gamma A.$$

So, for this purpose what we do, follow the construction carefully, it will make things very simple for you. Let’s say we consider a surface like this, this is the axis of the symmetry. And we take a area or strip of area on the surface. Let us say this width is dL, this is the x axis. So, this point is at a distance x from the origin. So if you draw the projection at the base, it looks something like this. So this is the projection at the base. So projection at the base and this is essentially dx. Now, so any point on the surface will be represented as a function of let us say z and x.

If we are considering two coordinate axis to be z and x. Let us say the pressure inside this curved domain is P double dash, pressure outside is P dash, which let us say it is exposed to atmosphere. And you have a volume is constant, temperature is also constant, and P dash is constant. Therefore delta P is by definition it is P dash minus, P double dash it is by definition. So, look at the convention or delta P its delta P outside minus inside.

Now if we consider, so what we want to do? We want to actually look at the variation of the energy as a function of P double dash. So, V double dash is the volume of this curved object. You would like to look at the energy as a function of the volume, which corresponds to which corresponds to the minimum energy configuration; which we will we want to actually have look at the variation of energy f, as a function as V double dash is essentially changed with the total volume remaining constant. This is what we want to look at.

And what we would like to figure out is what is the shape that corresponds the equilibrium or what is in other words the equilibrium shape or corresponds to the minimum energy configuration. Now in order to do that, let us consider the Helmholtz free energy of the system. Now, I am sure all of you know what exactly Helmholtz free energy is.

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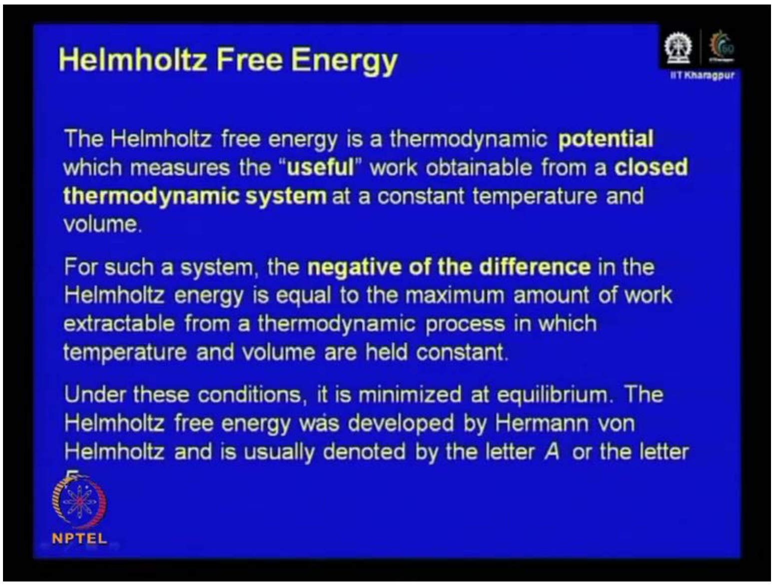

Helmholtz Free Energy

The Helmholtz free energy is a thermodynamic **potential** which measures the "**useful**" work obtainable from a **closed thermodynamic system** at a constant temperature and volume.

For such a system, the **negative of the difference** in the Helmholtz energy is equal to the maximum amount of work extractable from a thermodynamic process in which temperature and volume are held constant.

Under these conditions, it is minimized at equilibrium. The Helmholtz free energy was developed by Hermann von Helmholtz and is usually denoted by the letter *A* or the letter *F*

A Helmholtz free energy is the thermodynamic potential, which measures the useful work obtainable from a closed thermodynamic system at a constant temperature and constant volume. For such a system, the negative of the difference in the Helmholtz energy is equal to the maximum amount of work extractable from a thermodynamic process in which temperature and volume are held constant. Under these conditions, it is minimized at equilibrium and it was invented by or developed the formation or the formulation was first proposed by Hermann von Helmholtz and it is typically denoted by the letter A or F.

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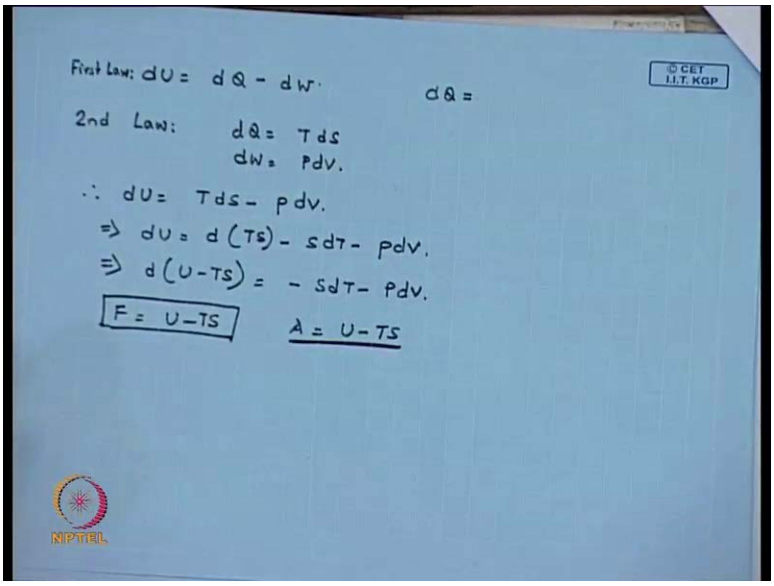

First Law: $dU = dQ - dW.$ $\quad dQ =$

2nd Law: $dQ = Tds$

$dW = Pdv.$

$\therefore dU = Tds - pdv.$

$\Rightarrow dU = d(TS) - SdT - pdv.$

$\Rightarrow d(U-TS) = -SdT - pdv.$

$\boxed{F = U-TS}$ $\quad \underline{A = U-TS}$

This is something that I am sure you have read in your basic thermodynamics. So, if you look want to look at the mathematical expression, the first law from the first law of thermodynamics what you get is dU is del Q minus del W. del Q is the energy externally energy added, del W is the work done by the system. Now, from the second law, so this is what comes from the first law. From the second law, what comes out is dQ is TdS and dW is pdv therefore, del U is TdS minus pdv or del U is del TS minus SdT minus pdv or U minus TS is minus SdT minus pdv. Now, F you may all recall is defined as F U minus TS. In many of the standard text books it is also referred to as A, so this is the Helmholtz free energy. I am sure you have also come across the other very popular or well known free energy; you must understand what is the difference, which is the Gibbs free energy.

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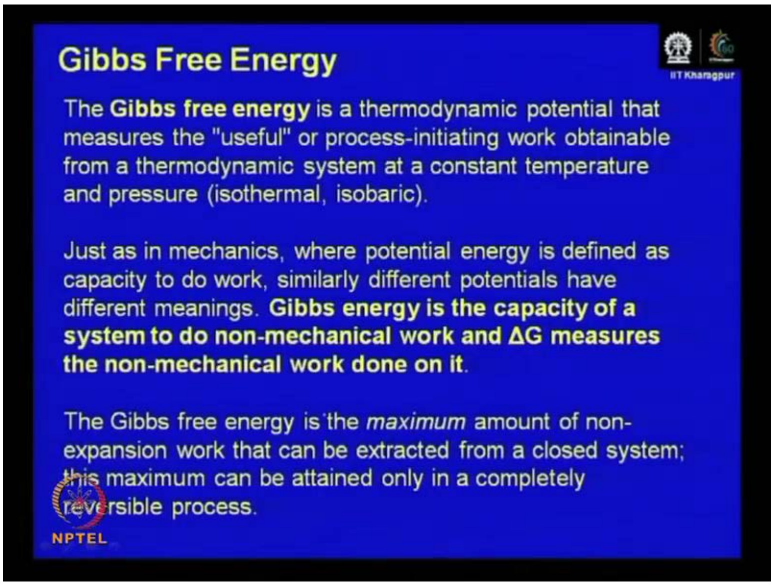

Gibbs Free Energy

The **Gibbs free energy** is a thermodynamic potential that measures the "useful" or process-initiating work obtainable from a thermodynamic system at a constant temperature and pressure (isothermal, isobaric).

Just as in mechanics, where potential energy is defined as capacity to do work, similarly different potentials have different meanings. **Gibbs energy is the capacity of a system to do non-mechanical work and ΔG measures the non-mechanical work done on it**.

The Gibbs free energy is the *maximum* amount of non-expansion work that can be extracted from a closed system; this maximum can be attained only in a completely reversible process.

Now, Gibbs free energy is the thermodynamic potential that measures the useful or process initiating work obtainable from a thermodynamic system at a constant temperature and pressure. So, it is essentially isothermal and isobaric. Just as in mechanics, where potential energy is defined as the capacity to do work. Similarly, different potentials have different meanings. Gibbs free energy is the capacity of a system to do non mechanical work; this is important, it is a non mechanical work and delta G measures the non mechanical work done on it. So, delta G is a measure of the non mechanical work done on it. And the Gibb's free energy is maximum amount of non expansion work that can be extracted from a closed system. More important, this is important it is a non expansion work which can be extracted from a closed system. And the maximum can be attained only in a completely reversible process; I am sure all of you know it.

Now, let us took a. So, you understand that since we are looking at the mechanical work it is a expansion type of work. So, we have to consider the free energy based on the Helmholtz free energy, a Gibbs energy formulation will not suffice. So, if you look at the total Helmholtz energy of the system, you have U minus TS plus. Now, typically in a thermodynamics text book the expression you come across is F equal to U minus TS. So, you might want to argue that what is this additional term I am adding, this is nothing I mean out of place, this is actually the surface energy terms we are adding.

So, j is the number of interfaces present and for a system like this it, it will simply get replaced by a term like, because what you have? You have one interface and where the surface tension at one surface, where the surface tension is gamma. Please do not confuse this j with the number of components present in the system. j here refers to the number of interfaces present in a particular system. So, this is going to be the final form of the Helmholtz free energy, we are going to talk about. Now, we know from basic thermodynamics that U is minus pV plus TS plus G. And F is therefore, U minus TS; so, it is essentially minus pV plus TS plus G minus TS plus gamma A, the expression of F. So, this is what we have replaced for U and U minus TS plus gamma A. So, this eventually turns out to be minus pV plus G plus gamma A. G is the Gibbs free energy, which we all know can be written in terms of chemical potential as mu i x i into gamma A. Now, if the composition does not change, then if there is no change in composition, then this term remains constant.

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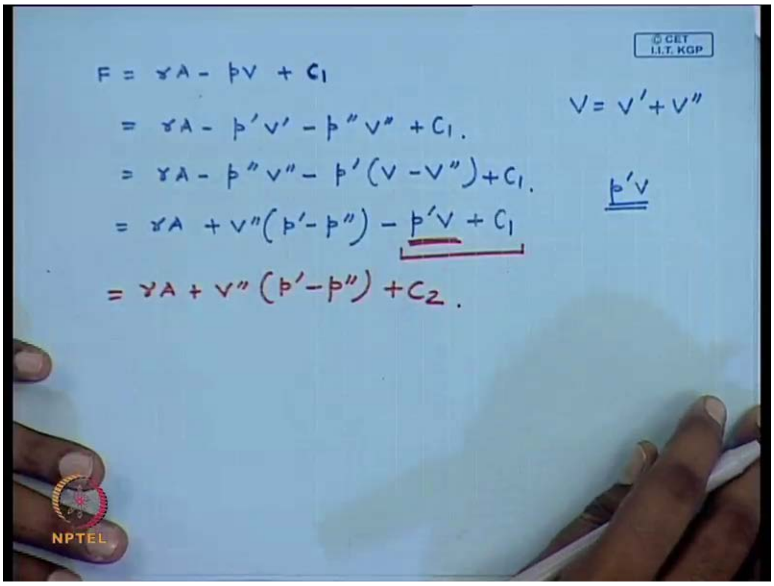

$$
\begin{aligned}
F &= \gamma A - pV + C_1 \\
&= \gamma A - p'V' - p''V'' + C_1. \\
&= \gamma A - p''V'' - p'(V - V'') + C_1. \\
&= \gamma A + V''(p' - p'') - \underline{p'V + C_1} \\
&= \gamma A + V''(p' - p'') + C_2.
\end{aligned}
$$

$V = V' + V''$

$\underline{p'V}$

So, what we eventually get is that F is gamma A minus pV plus, let us says A constant C 1, which now has sort of the Gibbs free energy term based on the chemical potential is included into it. Now, what exactly is pV here, pV you have the pressure for the two phases as P dash and P double dash and the respective volumes are V dash and V double dash. So, this is the pressure of this phase volume and what we know that V is constant; so, V is essentially V dash plus V double dash. So, what you can write is F is gamma A minus P dash V dash minus P double dash V double dash plus C 1.

What turns out that you can sort of, since we have V is V dash plus V double dash, you can conveniently write that. Now, with reorganization what you can write is that. Now looking to this term P dash into V, we have considered that P dash is sort of the atmospheric pressure. So, this is constant and V is the total volume. So, that is also constant. So, what it means that this term is also constant. So, this sort of you can augment within this constant to write something like gamma A. I will stop here.