Instability and Patterning of Thin Polymer Films

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Lecture No. # 06
Young Laplace Equation

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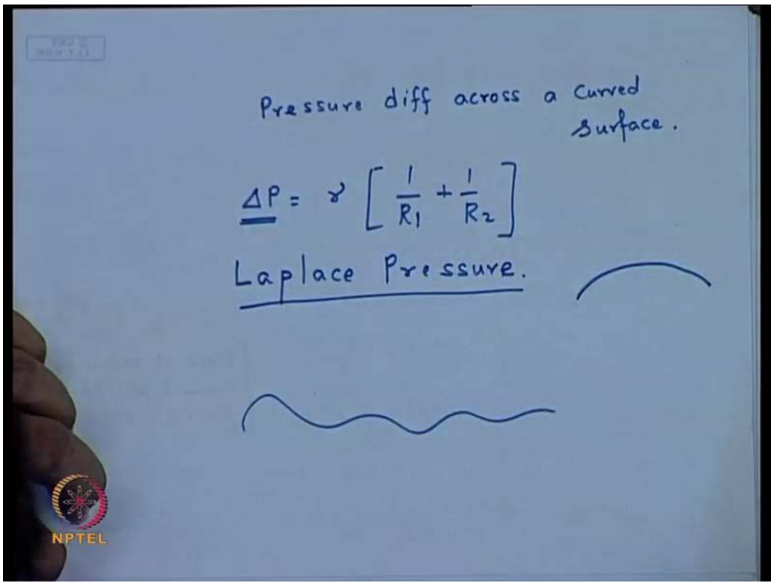

Welcome back, if you recall we just discussed about we have discussed about the existence of a pressure difference or a pressure gradient across a curved surface, which has let us to the concept of what is known as the Laplace Pressure, which is this particular pressure gradient. And for an arbitrarily curved surface which has two orthogonal curvatures, which can be expressed in terms of two orthogonal curvatures in 3 D space R 1 and R 2. The young laplace equation takes a very simple form which is gamma times 1 by R 1 plus 1 by R 2. We further started talking, I mean though the simple equation looks very simple the reality is for a perhaps randomly curved surface like this at every point knowing the values of R 1 and R 2 becomes a problem. So, in very rare cases you can find an expression - analytical expression, and one such case is the axi-symmetric surfaces.

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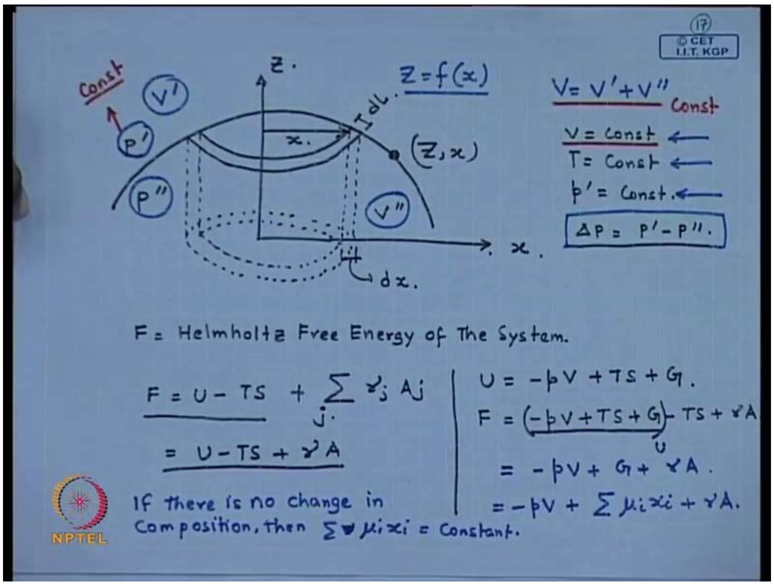

So, we just briefly introduced what exactly is an axi-symmetric surface and if you remember we were looking at this particular figure; where essentially this is an axi-symmetric surface, this is the axis of the symmetry. And axi-symmetric surface essentially allows you to write the equation of the surface in terms of one special coordinate that is x. If you just quickly recall we looked at the Helmholtz free energy of this particular surface which has on the, let us say this is a liquid or internally has a pressure of P double dash. This is the external pressure, which in many cases can be the atmospheric pressure, which is P dash.

The volume of the first phase is V dash, volume of second phase is V double dash. The total volume of the system is constant, it is an isothermal process; P dash is taken to be constant, delta P look at the way, it is defined it is P dash minus P double dash. And we took an expression for the Helmholtz free energy of the entire system, and we also talked about why we are considering Helmholtz free energy and not Gibbs free energy.

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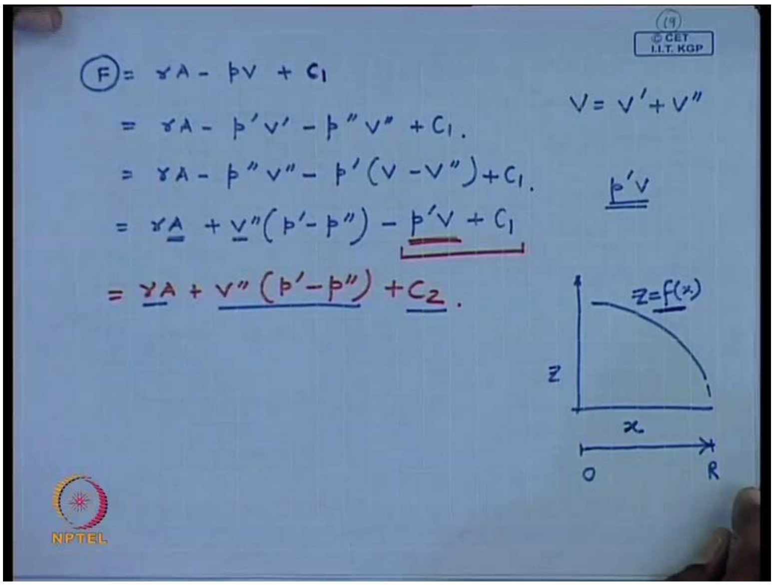

So, finally what we have is that the Helmholtz free energy of the system takes the form like this. Now, what we want to do is that we would like to look into the energy of the surface as a function of its shape. In particular, our intention is to find out a specific shape that corresponds to the optima of energy; so that, I mean it is the equilibrium configuration. In most cases it is the minimum surface energy configuration, that is why an equilibrium is attend, but we would, the way we will be proceeding we would like to find out the optima or let us say the minima of the energy that corresponds to a specific shape.

So, in order to do that we need to really express, if in terms of this which contains the area of the surface and the volume of the particular surface; so, this has to be correlated in terms of the special variable x. And since we are taking an axi-symmetric surface, so what we know that this curve, which by rotating by an angle of 360 degree around the axis of symmetry you generate the surface. On this particular curve, because of the axis symmetry, the equation of the curve can be expressed in as a function of x only. So, this is the coordinate system, let me just repeat; so this is the z axis and the x axis. So essentially let us say, if we can sort of have the expression as an integral of over x from 0 to R. And if we can incorporate the geometry of the surface properly into this expression, then we can have the expression of F as a function of x. And eventually then our problem becomes to minimize or to find out the condition of optima of this particular energy associated with the surface to find out; so that we get the equilibrium configuration.

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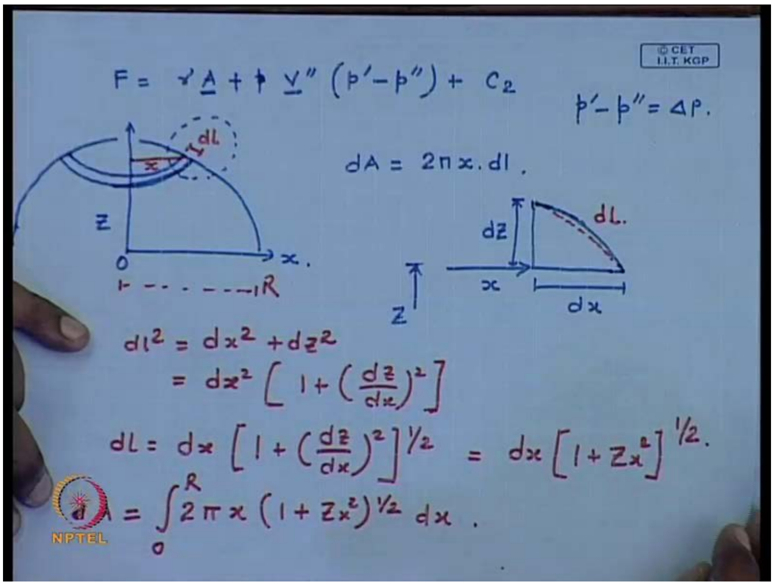

Now, in order to sort of look at the surface the geometry of the surface, let us look into the expression of A; so, what we have is gamma A minus or like that we put it some constants C 2, where your P dash minus P double dash is essentially the delta P. Now, let us try to figure out the area and the volumes of this particular surface. So, let us look into the drawing again or construction of the figure again; so, here is a surface axi-symmetric surface, you have considered, you consider a thin strip on the surface; it was nicely drawn in the previous drawing, but let me try to do it again, so that you follow the drawing and you get an idea, what I am doing.

So, what you have here is this is at a, let us say at a distance x and let us say this particular thing is del L; so, del L is the thickness of the strip or the width of the strip on the surface. So, what we have the area of this element del A is twice pi x into dl. Now, let us look into detail over this particular area. So, what we have here? This is the actual surface and up to here is x; so essentially this is your dx, up to here from the origin, let us say this is the origin is Z. So, this length is del z. And if you assume that this area is very very smaller, the length is very very small and can sort of regard this to be a part of a straight line instead of a curved surface; so, it is something an approximation you are doing like this. Then essentially, if you regard del l to be a straight line, then you can conveniently apply the Pythagoras theorem to get eventually you can do a little bit of simplification. This gives you or you can write in a compact form.

Therefore, the area dA turns out to be 2 pi x into 1 plus z x is squared half dx. And this now, if you look into it, the infinitesimal area dA is now expressed in terms of one independent special variable dx. Therefore, in order to find out the entire area what you need to do? You need to perform an integral, but the limits of the integrals will be the limits of x. So, if you perform an integral from 0 to R let us say, you essentially get the entire area. Therefore, what you can write is your area dA or A is an integral of 0 to R over this particular expression. So, this is one of the important expressions we will be needing.

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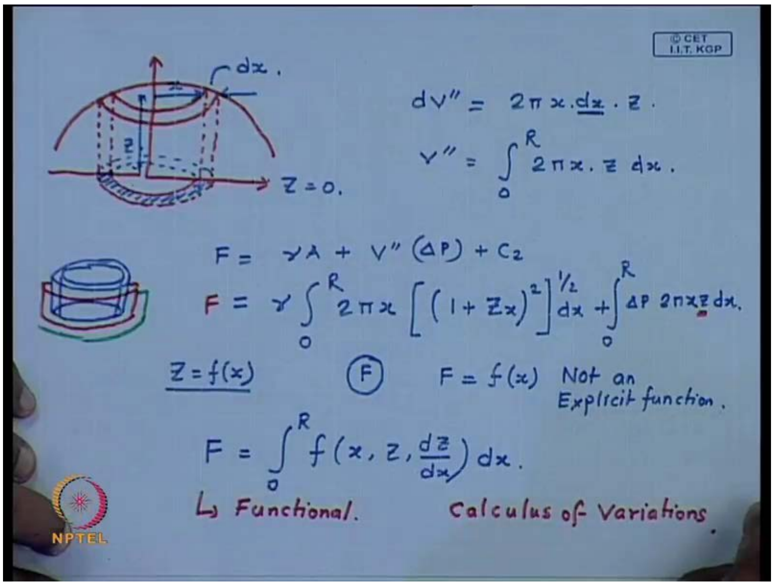

Now, let us look at the expression for volume. So, again let us quickly draw that particular figure. So, this is the surface you have; now we would like to find out the incremental area or the infinitesimal volume. So, what do you do about it? You are essentially, so you want to get the full volume. So, let me show you how to pick up the area the incremental volume; this is the strip of area we have considered, so, along with that you can consider a volume element like this. So, what are the parameters you have? You have this is x, so this is delta x; this is at any height let us say z, and this is at z equal to zero. Therefore, your dv double dash, v double dash is the volume of this particular phase is essentially 2 pi x into dx into z. 2 pi x into dx gives the area of this particular strip; and then you multiply it with the volume z, with the height of the at that particular area z, so you get this volume.

Now the issue is, if you go on integrating or adding the volume of all such elements starting from here right up to here, then you can eventually get to the total volume. Therefore, the total volume again you see here the only special coordinates is the independent special variable is dx; so, it turns out to be integral of 0 to R 2 pi x z dx. So, I hope this contraction is clear to you; this is an axi-symmetric surface you pick up a thin strip of area on the surface, correspondingly its projection at the bottom plane you can say is this. So, 2 pi x into dx corresponds to the area not this, but this entire area. And if you sort of multiply it with z at this particular point, you get the area of this cylindrical element.

And now, if you go on adding all such cylinders, so one is this, the subsequent one is something like this. The one next to that is this, if you go on adding the volume of all such cylindrical areas, you eventually get the volume of the entire entity of the object. So therefore, what we have at this point of time is that you can express your F, which is gamma A plus V double dash into delta P plus C 2, as sort of gamma into integral 0 to R 2 pi x.

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So, now as I have told you that we are interested to evaluate the value of F as a function of its shape; that is essentially we would like to find out an F as a function of x, which corresponds to the optimum. Now, you can see here that as the surface is axis symmetric, we have Z as a function of x. However, the function we want to sort of optimize; F, this is the function we want to optimize and from the basic concepts of let us say optimization or maximum minimum, we have the necessary and the sufficiency conditions. But if you look carefully, this F is we would like to optimize it with respect to x, the independent variable of the system, independent special variable for the system. However, F is not an explicit function of x; rather, if you look carefully F is of the form.

See in the expression of F you have an integral between 0 to R you have del x, you have z x or del z del x, you have x and you also have z; so, it is of this form. And this is what is known essentially as a functional. Without, I would not go into the details of this, this particular aspect of evaluating the maxima or the optimum of a functional, forms into their class of separate class of mathematics, which is calculus of variations and interested listener, if there are any might actually looking to some standard mathematics text book to find out more about calculus of variation.

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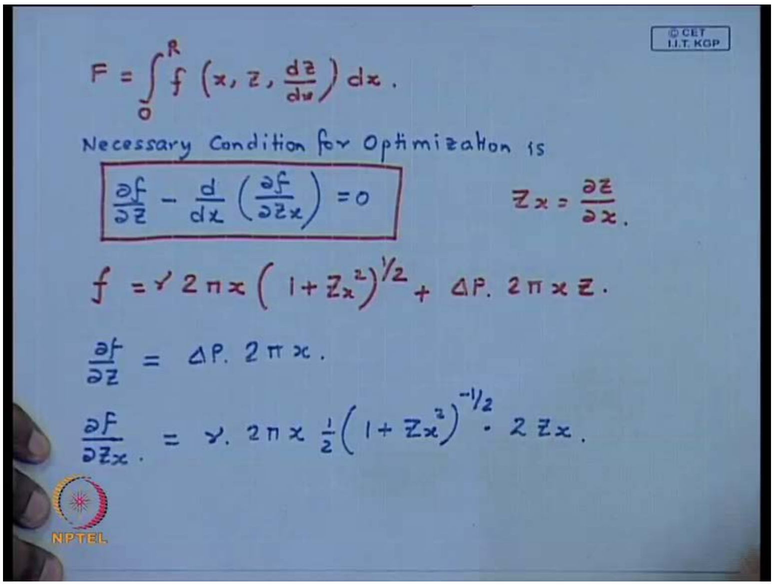

But what I will pick up here is that if you have a functional of the form, then the necessary condition for the optimization is. For the context of this particular course, you might just take this particular expression for granted without going into too much of the details. Where, I have already pointed out Z x is a particular partial derivative. Now, we have if we relook that at the expression of F, we have this is the expression of F; and we have defined the functional F, please this is general form of the functional, we have for simplicity kept this as capital F as well, but here we were looking at the free energy. So anyway, if you look at the general forms, so we define a sort of a function f small f which is within the integrals and is sort of which is going to be integrated over dx. So, from here we can pick out that in our case, f is.

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So, this is f, now this is the, if you multiply this with dx and integrate over 0 to R you get capital F, which is the expression for the energy of the surface of this particular element. So, this is the functional we have. Now, we need to sort of look into the mathematical expression for each of or of each of these mathematical expressions to find out the optimum. So, let us find out the del f del z first. This turns out to be, what we have here that z is a in the first term, we have z is to be a function of x. And this is del z del x, so this anyway is not a function of z. So, none of the terms in the first expression are functions of z. So, what you get as del f del z is simply.

Now, let us look at thus other term we will be needing, which is del z del F of del z x. And this turns out to be. So, here if you see in the second term now, none of the terms are functions of z x; z is a function of x, but none of the terms are functions of z x. So, if you have, so this is sort of if you try to find out a partial derivative with respect to this z x, this does not contribute. So, what contributes is this particular term, and so the expression eventually turns out to be. So, these are the two terms we will be needing.

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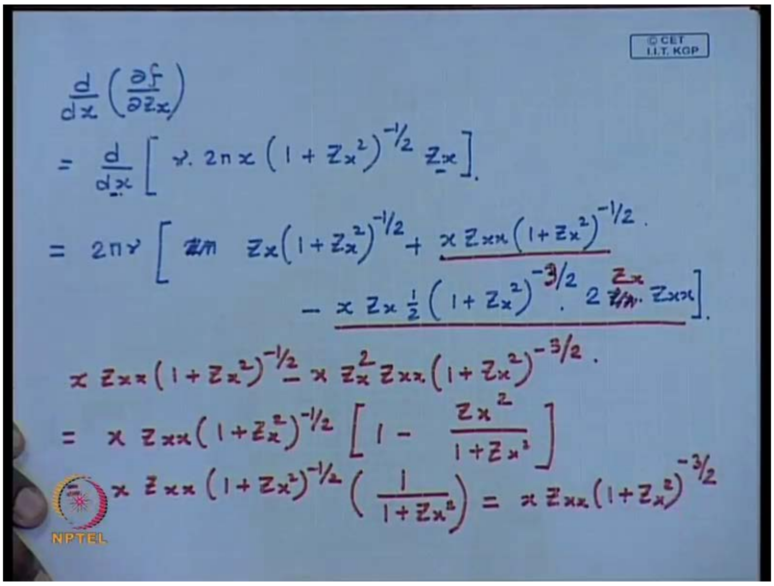

And now, we have to find out looking at the expression, we need to evaluate this entire term. So, del del x of this whatever we have got. So eventually, we now need to find out.

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If you just sort of expand it term by term, so what are the things you get, you can conveniently take out 2 pi gamma outside, the parentheses, so if you just look at this del del x of with ray of this x, you get, this is when this thing is operating only on this one. And when it is operating on this particular term what you get. Now, if you sort of look at these two terms, this one, and this one.

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This is three. So, what you can do is, no I am sorry, this one remains; just take out this as the common. So, what you are left with is.

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So, eventually these two terms contribute to or combine to become, it looks a little big. So, let us sort of write down the terms carefully or sort of in a compact form.

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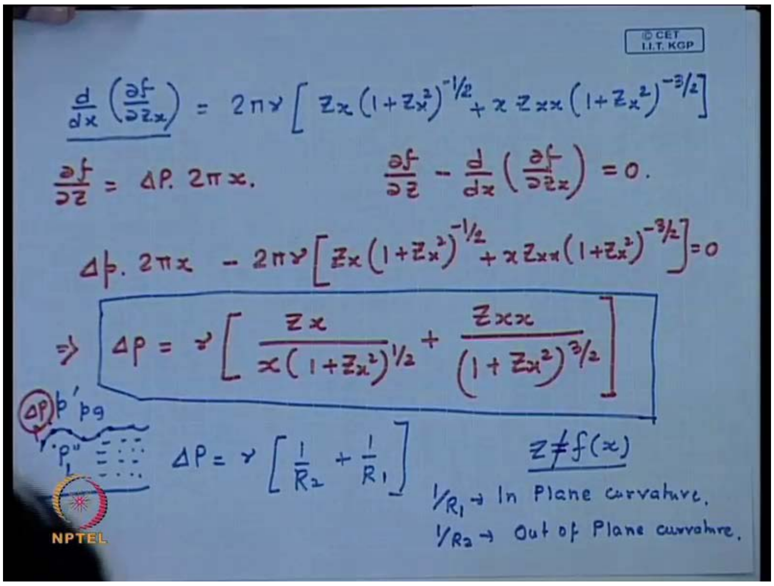

So, what you get?

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I have given all the steps, so, just do them once and you will eventually be able to find out how it is coming. So, let me quickly repeat, I mean we get an expression for del f del z x, which turns out to be this, we have now taken the del del x of this particular term, we have expanded term by term. If you combine the second and the third term, you eventually can simplify the combination of those two terms in terms of this particular term; so, your final form of this particular term is this. Now, we look at our relook and we also have del f del z to be equal to delta P into twice pi x. Now, we relook at the condition for the optimum which I we have already written which turns out to be, and if you substitute the respective terms here you get.

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So eventually, with a little bit of simplification which turns out to be delta P was gamma.

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So now, if you look at the expression this is of the form. So, essentially these two terms these two rather jumbo looking terms, essentially gives you the two curvatures or the two orthogonal curvatures. However this particular definition looks rather big, but reality is for an axi-symmetric surface, you can express z as a function of x. So eventually, if you can implicitly express this which is valid for an orthogonal surface; you ideally know z, you ideally know z x and z x x. So, from that you can calculate the delta P or in other words the more realistic setting can be that you have a liquid meniscus let us say; so, this is the second phase of the liquid phase, this is the gaseous phase which can be open to atmosphere.

So, what you can do? If you know the outside pressure of the P dash, you can solve the governing equation for a liquid that is the navier stokes equation it is of course, with some numerical methods by some computational fluid dynamic technique; and eventually you can get the pressure of the liquid side at the liquid side at every point on the interface. So eventually at every point, you sort of have now the node the delta p. So, based on that you can find out, you can sort of solve this ordinary differential equation non linear o d e to get z as f(x) at every point. So in that process, you sort of can find out the shape of the actual shape of the interface.

Now, the thing we need to understand is we will go into some critical discussion on the individual terms and how it shapes up with some classical example of this young Laplace equation for an axi-symmetric surface. So couple of things to remember, this is the general form of the young Laplace equation. For an axi-symmetric surface, the moment you have a non-axi-symmetric surface, you can no longer have this particular form, because of the fact that is for, if the axial symmetry is not there, you cannot express it express z in terms of x, and so eventually this expression becomes redundant.

Now typically, this choice of. So, the second question to ask is there a physical significance of the individual terms like z. So, one of the two terms is sort of is referred to as the 1 by R 1 term, the second term is referred to as the 1 by R 2 term, if you simply draw a sort of equivalence between the two expressions. Now, the question is that based on what or is there any convention of picking up R 1 and R 2 or you can just randomly select it. So, we will see the choice of R 1 and R 2, I mean what you define as R 1 and what you define as R 2 is more based on convention. So typically, the 1 by R 1 term is referred to as the in plane curvature, and 1 by R 2 is the out of plane curvature, but what it means, we will see with a very simple example. Now, let us pick up a few simple cases where we can sort of see a manifestation or see or understand the utility of this particular equation for an axi-symmetric surface in greater detail.

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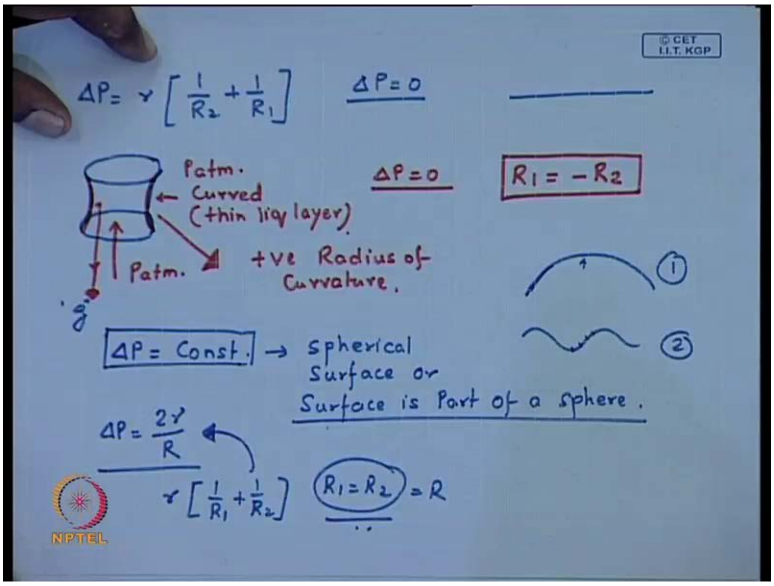

Let us pick up the simplest example of, let us take the general form itself. If we have delta P equal to 0, what does it mean? What can be the likely consequences? Of course, we know that delta P refers to the Laplace pressure, the origin of which is when you have a curved surface. So, one of that trivial solution of delta P equal to 0 is when you have a flat surface, which essentially is a trivial solution. So, the there is of course, a delta P is equal to 0.

Because of the fact that if you have a flat surface in both x and y direction, the R 1 and R 2 tends to infinity; therefore, 1 by R 1 and 1 by R 2 are both 0, so infinite radius of curvature in both the directions. But can there be any other examples, well there are actually lots of examples where you, I will give you an example where you can see that you have a curved surface, but still delta P can be 0. It is a very simple experiment you can do as children’s sometime we use to sort of do it. If you take two ware loops and sort of dip them together in a surfactant solution and now detach them.

You will see in many cases, if your detach rate is not too high that the surfactant solution is making a meniscus like this between the two ware loops. So this surface is curved, it is actually a thin liquid layer right; however, you have it is open to atmosphere on this side, as well as its open to atmosphere on this side. So, what you have is delta P equal to zero, but you still have a curved surface.

So, what it implies that what eventually you get mathematically is, of course, very very simple you get R 1 is equal to minus R 2, that is also a condition at which you can get delta P equal to zero. So, what does it mean really minus R 1 is equal to minus R 2. Well, if you look at now the essentially, again this is partly convention and partly it is a physics also; see this surface from this side is actually concave and from this side it is convex. So, you eventually can sort of define that a concave surface or let us say this is the concave, so this has the positive radius of curvature. So consequently, this side will have a negative radius of curvature and these two radius of curvatures match here and you get delta P equal to zero for this particular setting.

Now, this is a real life setting where you can do this experiment, and after sometime the meniscus might break, you may also see that. So, let me just add a minute on that what happens is, with prolong time there might be some gravity drainage. So, if you now refer to your or think of your basic fluid dynamics, the body force triggered by the effect of gravity is acting on this liquid meniscus, so there might be a slow gravity drainage; and if the liquid sort of drains of this meniscus might rupture. Now, your navier stokes equation or your viscosity of the system will essentially give you the time for this flow. So, if you have a higher viscosity liquid, this flow will be slow at, so the chances or the probability of the rupture or the time taken for this meniscus to rupture will sort of be slower, as compared to a lower viscosity liquid.

The second setting can be when delta P is constant. Now delta P is constant, so you have a curved surface, but everywhere your delta P is constant. Now think of this scenario compare these two, if you have the surface of the type two and the surface of the type. One, can you have delta P to be constant in the second case, because in the second case from every point to point the value of R 1 and R 2 are changing. So, it is very unlikely that your change will be in such a fashion that the change of the in plane curvature is sort of equally compensated by the out of plane curvature. So, if you have a surface like this there is every possibility that delta P will not remain constant.

So, in case you have delta P to be equal to constant, that means, that the curvature does not vary from point to point. And that is possible, we will shortly see with the mathematical expression also, but a firsthand guess would be if you have a curved surface; if you have a curved surface, which is part of a sphere, so it is a spherical surface, we will immediately see this. So, this is possible, only when you have a spherical surface or surface is part of a sphere.

So, these are some of the simple examples of our some special settings, I would say not exactly simple examples. Two special settings or what is a consequence the equivalent, I mean the corresponding consequence of the young Laplace equation. So, one specific example we took up was, if delta P is equal to zero, so you can have one of the possibilities is that you have a perfectly flat interface, so there is no Laplace pressure; and therefore, delta P is equal to zero, but you can also have the R 1 is equal to minus of R 2 and therefore, delta P is equal to zero. So mathematically in one case, R 1 is equal to minus R 2, where you can lead to delta P equal to zero, or in the other case, both R 1 and R 2 tends to infinity, which corresponds to a perfectly flat surface .

Now, as we sort of talk about a spherical surface, so even in the fundamental derivation or the first derivation of the young Laplace equation, a couple of lectures back we took; we actually showed that if you took a spherical surface, you get delta P equal to 2 gamma by R. And then we sort of looked into a surface which two arbitrarily curvatures, and we came up with the fact that delta P is equal to 1 by R into gamma into 1 by R 1 plus 1 by R 2. So essentially, in the case R 1 equal to R 2 equal to R, if this collapses to this form and which we have argued that which, we have argued sort of qualitatively as of now that is the case where it is a part of the sphere.

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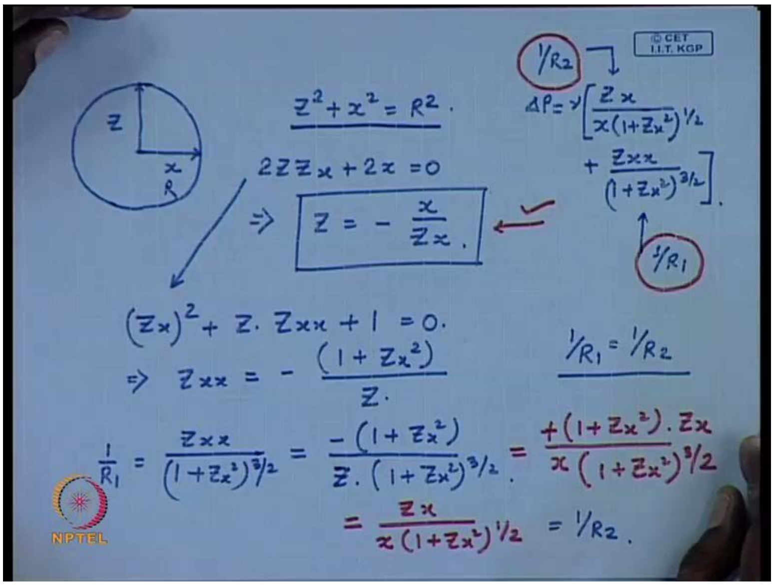

So, can we verify it mathematically. So, let us have a quick look at it. So, suppose we have a what we start off with, we have a surface which is spherical, and this is the way we have derived. So, let us say the radius of the sphere is R. So, this is an axi-symmetric surface, so the equation of this particulars z 2 is… If we want to take or look at the generalized expression for the axi-symmetric surface, which we will eventually look at, so let us have the equation here; this is the first term and this is the second term. So, we differentiate it with respect to x, x this equation of this circle, we sort of differentiate it with respect to x to get. So, this from this what we eventually can get is an expression of z. In order to find out z x x, we again differentiate it, so what we get is that. So, we get an expression of z x x to be equal to minus 1 by…

So, now we have the expression of z x and z x x both. So, let us look at 1 by R 1, we have defined the way we have compared So, far is the this is the term we have marked as one by R 1, this is the term we have marked it as one by R 2. As I have already told that these are more based on conventions rather than anything else, but it has a physical meaning, I mean these two curvatures; so, we will come to it. So, if we now look at the expression of 1 by R 1, which is z x x by 1 by z x square raised to the power 3 by 2, simply plug in the expressions so you have. And now, substitute this z over here, in terms of this expression.

So, if you do that you will get, then you simplify it to get there is a minus sign also here which comes from here, so it becomes overall a plus sign positive sign; so, you get z x divided by x into; which now you look is the expression for the other term, so it is 1 by R 2. So, you can. So, all we assumed here is the axi-symmetric surface is part of a sphere; therefore, we had this expression which is exactly the equation of a circle. And from the young Laplace equation, you can see here that it is possibly, when you have a surface like this, it turns out it indeed turns out that 1 by R 1 is equal to 1 by R 2. So, it is sort of verified from the young Laplace equation for a general asymmetric axi-symmetric surface; that if you have a spherical surface or a surface which is part of the sphere, then the two radius of curvatures sort of match with each other or they become identical.

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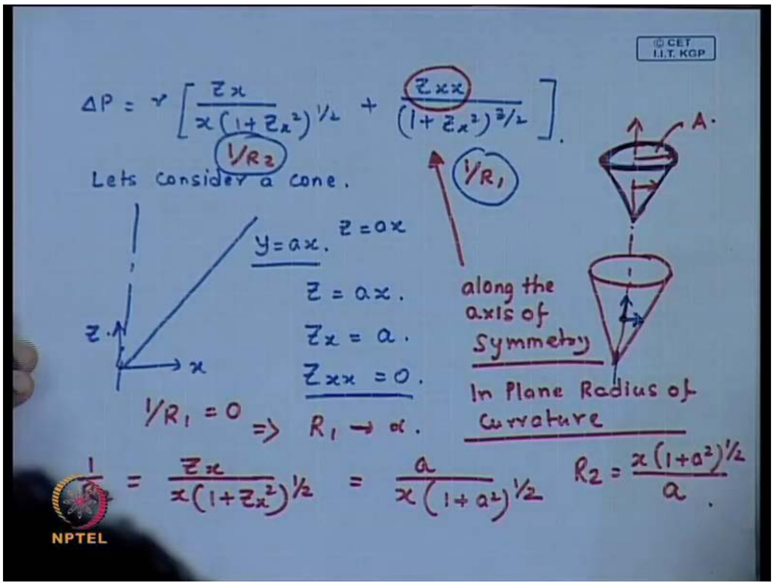

Now, let us physically understand what or what exactly these two terms R 1 and R 2 refer to or what sort of curvature we are talking about; so, this is the equation. Now, let us consider a cone; this is the axis of symmetry, let us say, this is the simple line we are considering y equal to ax simple equation, it is a straight line. So, you rotate it by 360 degrees, you get a conical surface like this. Now, if I ask you what are the radius of curvatures of this particular surface. Well, you will say that you can define this surface by two radius of curvature; one is the radius of curvature along the axis of the symmetry, and the other is here.

So, this varies that is why you have ax, so as the value of x changes the radius sort of goes on increasing you can see. So, over here a is equal to zero, so radius is equal to zero, here let us say a is some capital A. So, the radius is capital A, in between it varies from all values of zero to A. So, you have two radius of curvatures. So, this has a finite value, the radius in this particular direction, but what about this direction? What is the radius curvature along the axis of symmetry? The radius of a curvature in this particular direction, of course you can understand that its infinity.

So, let us have a look. So, our intension now is to look into the expression of these two terms and find out that with so, if the radius of curvature is tending to infinity, so essentially what it means? So, these are as we have marked that this is 1 by R 1 and this is 1 by R 2. So, we need to test or we need to figure out, if which of these two term is giving us, the term is going to zero. So, if one of the terms is going to zero then the corresponding radius of curvature is infinity. So, immediately we can then indentify which one is R 1, and which one is R 2. So, this is the simple concept, so I will repeat. So, suppose we have a conical surface or we have a cone, so you can clearly understand from the figure I will redraw it; so, that it becomes clearer to you, so this is a cone.

So, at any given height, if I ask you what are the two radius of curvatures, how sort of you define this surface. So, you have one radius of curvature is this, the other radius of curvature is this. This one in the along the axis is infinite, this is non zero right, so this has a finite value. So, now our intention is based on the equation of the cone, to find out y equal to fx or let us say z equal to ax that is what the coordinate system we are taking. To find out, which of these two terms contribute to the infinite radius of curvature. Now so, it is very very simple actually you have z equal to ax, so therefore.

So immediately, you can see the term which contains this double derivative contributes to it becomes zero for a cone. So, you now understand that for a setting like this, this term refers to the radius of curvature, which is along the axis of symmetry or which we have referred so far as the in plane radius of curvature. So, therefore for a conical surface, this is the term which gives this particular radius in this direction, and this is the term which gives the radius of curvature in this direction. Now therefore, what we have is 1 by R 2 now. So, 1 by R 1 is equal to zero, which implies that R 1 is infinity; 1 by R 2 it turns out to be and if you substitute it. So from here, what you can get is that R 2.

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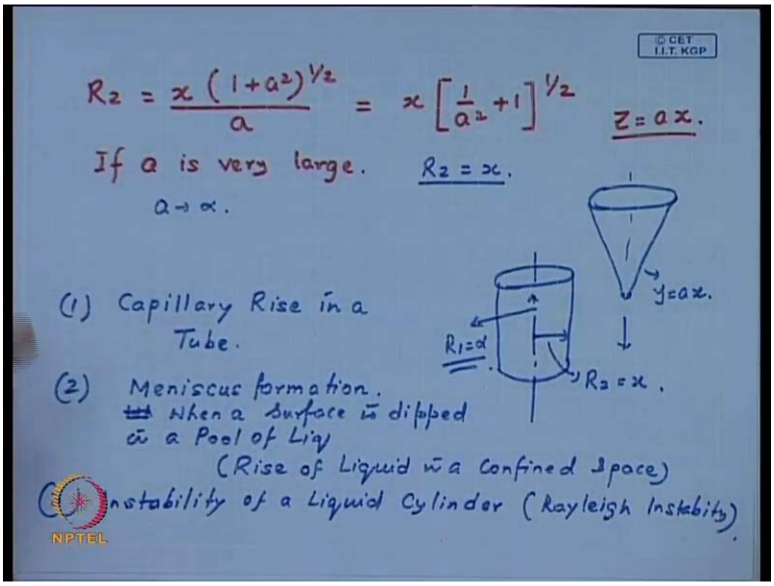

Or we can further same write it here, which we can further simplify or write as we just take this a inside the parameter. So, you can see that we had taken the expression of the surface to be z equal to ax. So, here you can again see that the radius of the curvature indeed is x multiplied by some constant after all if a is constant, so this is again a constant. Now, if a is very large, now what happens? If a is very large then this particular term, the first term can sort of be neglected in sort of comparison to the second term; so, what you get is, R 2 is x. Now, we have taken a conic, the equation of which is y equal to let us say ax.

Now what exactly a very large a or a tending to infinity mean, it sort of it is a limiting case where eventually this line becomes almost parallel to the z axis in this particular case. So eventually, it prefers to a cylinder. And so, now you can see for a cylinder, you have one radius which is equal to the x, and the other radius of the curvature is infinity. So, the only intention of showing this example is to impress upon you that while we can term anyone of these terms as R 1 or R 2. Physically or geometrically the individual terms have distinct or different roles to play.

For a conical surface for example, we can we know that one of the radius of curvatures is infinite, the other one is finite or non zero. And you can see that out of these two terms, only this particular term can correspond to this radius. So, the take home message is whether you sort of define or describe this one as R 1 or R 2 really does not matter, but when you look at the mathematical expression, it is this radius of curvature along the axis of symmetry which will always be referred to by this particular term that you have to stick. Conventionally, we term it as the in plane curvature or R 1, and the other one we term as the out of plane curvature or R 2.

So, this is the another example what we had. And now, I will take up three distinct examples, where the young Laplace equation or the Laplace equation or the Laplace pressure becomes critically important. the first one of that again we all know is the capillary rise in a tube; the second one is the meniscus formation, when a surface is dipped in a pool of liquid or essentially this is also referred to as rise of liquid in a confined space. And the third one is the instability of a liquid cylinder which is often referred to as the Rayleigh instability. So, before we sort of start looking into the details of mathematically of each of the settings, let us have a quick look at what are the scenarios, we are talking about.

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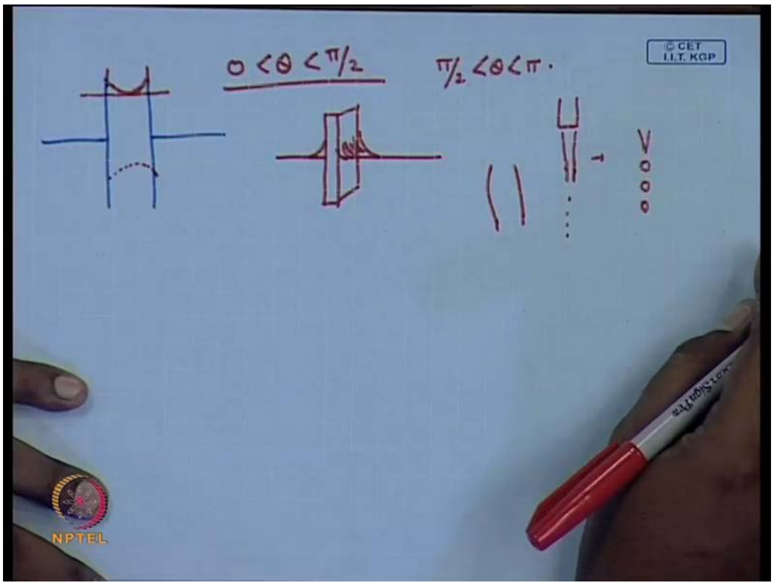

Capillary rise, we all know that you take a very narrow tube you dip it, in some cases you see a liquid rise of the liquid meniscus. We now have a, had some discussion on the relative magnitude of surface energy, and hydrophobicity, and hydrophilicity, and things like that. So, first thing you have to understand that if you want to see a capillary rise, the material of that tube should be such that on the surface the equilibrium contact angle lies between 0 to pi by 2. So it will, even if it is partially waiting, it has to be preferentially waiting. If you have a scenario, where theta lies between pi by 2 and pi, you would not actually see a capillary rise, but you will see a capillary depression; and in that case the shape of the meniscus will be like this.

So, this is something we have been told taught right in our school days, so where we started to look at the parallax error etcetera etcetera. So, if you remember correctly you have to take this to be the height of the liquid meniscus and not what it is climbing up to the wall, because this additional rise is not exactly due to the hydrostatic pressure difference, but is that additional movement because of the capillarity. The second case refers to the, so rise of a liquid meniscus is something like that if you have a pool of liquid and you dip a surface which can be a wire or a rectangular glass slide maybe. You see that if there is a preferential waiting, it forms a meniscus like this. So, we will look into that.

The third thing is that it is a very simple example; so, if you have a very narrow, long, thin cylinder of liquid, you see that it eventually breaks down. This is something you can actually try out in your own home or hostel or wherever; if you sort of have a tap and you have a high flow, then probably you see the a sort of a stream of liquid jet falling. But if you sort of gradually turn off the tap or sort of merely close it and you have a very thin sort of narrow stream of liquid coming out, in many cases you might see that before it falls on the floor, it sort of breaks down into isolated droplets. So, this you can just try it out, if you can see or you can correlate it to real life situations with what you are studying here, but this as we will discuss in the next class, is due to what is known as the Rayleigh instability.