**Instability and Patterning of Thin Polymer Films Prof. R. Mukherjee Department of Chemical Engineering Indian Institute of Technology, Kharagpur**

## **Module No. # 01 Lecture No. # 07 Rayleigh Instability**

Welcome back. As we told in the concluding minutes of the previous class or previous lecture that we will take up three particular settings or three particular examples.

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Which we are the capillary rise in a tube, the meniscus formation when a surface is dipped in a pool of liquid that is rise of liquid in a confined space and instability of a liquid cylinder that is Rayleigh instability

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So, capillary rise we all know probably it is something like this, you have a tube which is placed in a liquid pool and there is a rise. So, this is the central line of that tube. You have a liquid meniscus like this this makes an angle theta over here. So, the this is our coordinate system, tube radius is r this is z direction. So, let us say this is any point z this is the h or the height of the capillary and so here you have pg or the air side pressure and this if we regard that the tube diameter is narrow, then shape of meniscus is part of a sphere. If it is wide, what is going to happen over the central area, there is going to be flattening due to the effect of gravity or distortion due to gravity. We do not consider that effect. So, let us say this is r and this is the radius of curvature of the meniscus. So, please do not confuse this to be the tube diameter, tube diameter is R, small r is the radius of curvature. So, of the meniscus. So, let us say this is the centre and we sort of mark this angle to be five

Now we we have to assume or we know that in order to have a capillary rise theta has to be less than pi by 2 and we also regard that the external pressure is constant. In nature capillarity is a sort of extremely important it is we all know it is a passive mechanism for transport which is triggered. Now you understand that this mechanism out the its triggered by the surface energy or the balance of surface energy or the wettability of the surface and it is argued by many scientists that in very tall trees sort of water reaches to the to the different parts of the tress of the higher parts of the trees or the leaves through capillary forces. Of course, there is a contradicting view also that some people say that

the trees the plants sort of burn part of their metabolic energy to do that but it still dividable but we all know that capillarity is there.

So, let us look in to it how we can sort of proceed based on our concept we already have. So, what we have from this particular balance that if you are looking at p g, at any specific point that this is simple. So, what comes out that your p g minus p L is equal to. So, this is essentially the pressure difference delta p. So, this is the pressure at this particular point at the air side or the gaseous side this is the pressure p L plus rho L into g z at the liquid side and the difference between. So, these two are balanced. So, the their difference is the delta p right. So, what comes out from here is that z is.

Now let us look in to the young-Laplace equation and what we get is  $\frac{1}{18}$  (no audio 05:13) to 05:40) delta p. So, this is now turns out to be rho L g z. Now rho L g z is if we sort of mark this difference to be eta, it turns out to be rho L g h plus eta it is pretty logical to assume that eta is very very small compared to h. So, therefore, this is equal to rho  $L$  g into h and the.

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2 A + Z=h, x=0, Zx=0.  
\n
$$
At = R
$$
, tan $\theta = \frac{d\frac{x}{d}}{d\frac{y}{d}}$ .  
\n $\frac{2y \cos\theta}{f\perp g} = R (h + \frac{R}{3} - 0.1288 \frac{R^2}{h} + 0.1312 \frac{R^3}{h}$   
\n $\frac{2vtoth \text{ odd}}{f\perp g} \frac{\text{approximation}$   
\n $\frac{1}{2} = \frac{2y \cos\theta}{f\perp g R}$   
\nIn case we assume that  
\nmeniscus L part of a  
\nSphau.  $f = \frac{R}{G\perp g}$ .  
\n $\frac{Z}{dr} = \frac{2y}{G\perp g} r$ .  
\nNow AP = 3Lg<sup>2</sup> =  $\frac{2y^2}{r}$ .

So, this is the this is essentially gives the equation of the surface and the corresponding boundary conditions are it will become clear to you once you proceed. At z equal to h and x equal to 0, z x is equal to 0 and because its it refers to this particular point. So, it is. So, this is z as a function of x and the gradient here is horizontal for the slope is horizontal. So, z x is equal to 0 and the second boundary condition for the closure corresponds to the condition over here where it makes a finite equilibrium contact angle a finite angle and this angle is determined by the wettability of the solid by the liquid. So, this theta will match the equilibrium contact angle that comes from the **young Laplace** young's equation. So, we will have at x equal to r and tan theta is or del x del z tan of theta where theta will come from the young's equation, now once the first boundary condition is plugged in into the equation. You can have a analytical solution of this particular equation when which gives us that not going into the solution it is not needed but they are more interesting things to look at.

So, **zeroth order solution** zeroth order approximation gives. This you can try to do do yourself or may be some some of the subsequently lectures we might take it up. If we in case we assume, that part of a sphere. Therefore, then we get  $\overline{R}$  by cos theta therefore z in that case or you can write the delta p. So, this is fine but from the stand point of capillarity. The most important thing is the calculate the weight of total liquid within the column that can be sort of sustained due to a capillary motion. We all know that if you have tubes of different diameter having the same of the same material narrower is the diameter of the tube of the tube diameter the highest will the rise be. Essentially what comes out that based on the balance of the surface energies, the weight sort of becomes constant and. So, in in that case if you have a narrower tube diameter you can see higher capillary rise.

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**ECET** W =  $\int_{L}^{R} 2\pi x. z dx$ <br>  $Z = \frac{dP}{P_L g}$   $dP = \sqrt{\frac{2x}{(1+2x)^{N_2}} + \frac{2x}{x(1+2x)^{N_2}}}$  $W = 2\pi \int_{0}^{R} x \cdot \sqrt{\frac{z_{xx}}{(1 + z_x)^3/2} + \frac{z_{xx}}{x(1 + z)}}$ R<br>  $\begin{cases} \frac{x \cdot \overline{z} + x}{(1 + \overline{z}x)^{3/2}} + \frac{\overline{z}x}{(1 + \overline{z}x)^{3/2}} \end{cases}$  $x = Z_x = \frac{dZ}{dx}$ 

So, let us see, let us try to calculate the weight of the liquid that can be sort of sustained within the capillary, which turns out to be again if you look into the figure it will become clear. So, let us say we are considering over here at any z this is the axis of symmetry which is at a distance x from the surface. The width of it is d x, the height here z. So, the liquid the weight of the liquid or the volume of the liquid on that ring is 2 pi x into d x into z. The weight of these the liquid is this is multiplied by g multiplied by the liquid density. So, rho L into g and into 2 pi x z dx and if you want to find out the weight of the liquid along the entire meniscus well you have to integrate it in terms of x from zero to r. So, that is how you get to this expression. I hope it is its clear you look into the capillary meniscus like this this is the axis of symmetry. You pick up a point at a distance x which has an width del x. So, this is the area 2 pi x into dx. The this is the amount of liquid present in that 2 pi x dx into z and the weight of liquid is multiplied by rho l into g.

So, if you want to find out the weight of the entire the **capillary**? The the liquid that is present in which is forming this entire meniscus. You have to perform an integral over x from zero to r. Where, r corresponds to the tube diameter and so what you have here how young's Laplace young-Laplace equation comes into the picture is because of the fact that we have z is equal to delta p divided by rho L into g. And now, we have the expression of delta p equal to the this thing. So, your weight now becomes, this turns out to be little bit of mathematical manipulation. So, this is the very very simple. Now, let us define parameter just to sort of simplify the things or how to understand k to be equal to z x. Just a little bit of writing the things, little simple fashion.

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 $\begin{bmatrix} \n\text{CET} \\
\text{L.T. KGP}\n\end{bmatrix}$  $Z_{xxx} = \frac{dK}{dx} = \frac{dK}{dx} \cdot \frac{dZ}{dx} = K \frac{dR}{dx}$  $x \overline{z} x \overline{z} x$ <br>  $\overline{z} (1 + z_x^2)^3/2$ <br>  $= x \cdot \frac{d\overline{z}}{dx} \cdot \frac{d\overline{x}}{dz}$ <br>  $= x \cdot \frac{d\overline{z}}{dx} \cdot \frac{d\overline{x}}{dz}$ .  $W = 2n \times \int R$  $\left[ \frac{2 d k}{(1+k^2)^{3/2}} + \frac{k dx}{(1+k^2)^{1/2}} \right]$  $2\pi r \int A \left[ \frac{(xk)}{(1+k^2)^{1/2}} \right]$  $= 2\pi r \left[\frac{x k}{(1+k^2)^{1/2}}\right]^R$ 

So, what we have. So, this is k. So, you can write this to be know. Let us look into this first term, the first term is let us look into the numerator, this turns out to be we will look into it  $\frac{into}{into}$ , multiplied by this d x. So, we will look into this particular term which is inside the parenthesis before you integrate you sort of it  $\frac{1}{10}$  multiplied by d x. So, if we look into it. This particular term turns out to be x k d k del z into dx which turns out to be k. Now, you substitute in terms of del z del x into del k del z into dx and this eventually gives you x dk. If you look into it sort of del z del z and del x del x gets cancelled out. So, you are left with x d k. So now, if you look at the expression for w over here. So, what you have is that if I write it in this form.

So, this term as you can see corresponds to x d k. This term corresponds to k dx right. So, your expression for w now becomes two pi gamma to 0 to r x dk 1 by k square and if you look carefully this entire term, you can now write as it is just a little bit of not even manipulation you just compact the two  $two$  terms. So, you can write is as a differential of this particular thing. So, what turns out if, you now perform the integral. So, your w turns out to be two pi gamma into this whole thing between 0 to r, which is pretty neat.

Now, let us have a look. How the sort of boundary conditions get changed. So, what are the boundary conditions we had we had at z equal to h and x equal to  $0 \times x$  is equal to 0 now. So, the boundary condition sort of the turns out is that, here you get k equal to 0 and at x equal to r del x del z del x del z is tan theta. So, what it means that one by k is tan theta. So, at r k equal to cot theta. So, this is the modified boundary condition k at r is equal to cot theta. So, if you now substitute  $so$  essentially the modified boundary conditions are become at z equal to h, x equal to 0, k equal to 0 and at x equal to r, k at  $r$ is cot theta.

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So, if you know plug in the boundary conditions over there, you get w equal to 2 pi gamma.(no audio 19:05 to 19:30) No w we have seen that, at x equal to 0, k is equal to 0. So, this term goes to zero and what you are left with in this particular term is x at r is equal to r. Of course, this is cot theta and this can be further simplified to have 2 pi gamma into r divided by 1 plus again 1 plus tan square if ,you sort of substitute the square thing. So, what comes out is w is 2 pi into cos theta. So, this is this gives us an expression for the weight of the liquid column that can be sustained or sustained sustained within a capillary tube. So, you can see that, it depends on the radius of the tube. Of course, and it also depends on the contact angle or the equilibrium contact angle that you get from the young's equation. So, based on this you can find out.

So, if you if you sort of know the tube diameter and if you know the equilibrium contact angle the liquid is going to make on the **material** solid material of the tube. Then, you can find out the weight of the liquid that can be sustained sustained within the capillary. And this liquid rise is due to a flow, which is driven entirely by surface tension. You are not applying any external pressure or any other mechanism or there is a times you see that the the flow is actually in the in the direction opposite to the gravity. So, and this is the this sort of we can find out plugging the young-Laplace equation. We get an expression for the weight of the that can be sustained in a capillary tube.

 $\left[\begin{array}{c} \circ \\ 0 \text{ CET} \\ 11.1 \text{ KGP} \end{array}\right]$ Liquid in a Confined Space Rise ۰F cular Rod dipped w lig Pool.  $\overline{6}$ boundary Conditions  $R \rightarrow \infty$ Dip Coaling

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The second example, as I told we will take up is the rise of a liquid in a confined space. Essentially, we think of a rod dipped in a circular rod in a liquid pool. So, again if the material of the rod you are taking sort of allows a preferential weighting of the liquid column that is if, the value of theta e is less than pi by 2. In this particular  $\frac{1}{\ln \ln \ln \ln \cosh x}$  case, you will see a meniscus like this forming along the walls of the rod. So, here let's say this is the height up to which it can go up. So, this again is the surface that that that has formed which sort of any point can be represented as  $\frac{1}{\sqrt{a}}$  z x and so this is let us say x equal to 0. Let us say the diameter of the rod is R. This is the z direction, this is h and of course, you must understand that, here again the closure is this angle is theta or the equilibrium contact angle, what you get from young's equation for the combination of this liquid and this solid material.

The question to ask is, we can either find out h which is the height up to which the meniscus will rise or if h is known, we will be interested to find out the shape of the meniscus. So, essentially we would like to find out z as a function of x. The boundary condition here, at x equal to r tan theta is minus del x by del z which is here and well, what is the other boundary condition, you **you** sort of feel that at x equal to infinity asymptotically it goes to infinity. The meniscus sort of becomes  $((\ ) )$  matches with the the undisturbed interface of the liquid. So, it becomes horizontal. So, mathematically what it means that del z del x is equal to 0. Now, this particular if you if you want to solve the young-Laplace equation for the axis symmetric geometry for this particular boundary conditions. Then of course, it has to be solved numerically. Because you cannot proceed analytically but one limiting case on another asymptotic case of this particular setting can have an analytical solution.

So, that is this is if R tends to infinity. So, what does it mean, if R tends to infinity this tube sort of becomes extremely wide. So, eventually it represents to a setting where a flat slab is being dipped in the liquid. So, it is something like this and you have the liquid pool. So, here if sort of R tends to infinity this is the radius, we are talking about and this is. So, you have a meniscus like this which is forming and we will see that you can get an expression for that analytically. This is also more realistic and very important in a process which is known as dip coating where, typically a flat substrate is dipped and pulled out from a liquid meniscus. And of course, I will show you that here also the shape of the meniscus is governed by the young-Laplace equation.

So, let us define sort of x in that case this case is to be equal to R plus y. So, it is this is x equal to 0 ,this is the R diameter of the tube or in this case if it is tending to infinity, it sort of represents a flat slab which is like this this is the face of the slab was seen and this is sort of the meniscus distance. So, any point y, we are taking. So, x is equal to R plus y. From young-Laplace equation what we have.(no audio 27:02 to 27:28).

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 $\left[\begin{array}{c} \circ & \circ & \bullet \\ \circ & \circ & \bullet \\ \circ & \circ & \bullet \end{array}\right]$  $x \to \alpha$ .  $AP = \sqrt{\frac{Z_{XX}}{(1+Z_{X}^{2})^{3}/2}}$  $B_{L}g$   $\overline{z}$  =  $x = 0$   $Zx = \frac{d\alpha}{dx} = \frac{d\alpha}{dx}$ .<br>  $x = \frac{d\alpha}{dx} = \frac{d\alpha}{d\overline{z}} \cdot \frac{d\overline{z}}{dx} = \alpha \frac{d\alpha}{d\overline{z}} = \frac{1}{2} \frac{d}{d\overline{z}}(a^2)$ .

So, if R is tending to infinity, what it means that based on the expression of x, what we have taken x also tends to infinity. So, under this condition if x tends to infinity, this term tends to zero because x is in the denominator. Therefore, what we get is delta p, right. Now, delta p we know that its rho L g z. So, we have which is if you look at it has z x z and z x x. It is non-linear second order ode. Now again a little bit of just like the previous approach, we sort of define a dummy variable just to sort of simplify the thing. Lets define z x to be equal to something like an a. We also have z x primarily means its del z del x which is also del z del y looking at the expression of x is equal to r plus y y where, r is a constant. Therefore, z x x is equal to del a del x del a del z into del z del x turns out to be again a del a del z, which now turns out you can write as half of del z of a square. Therefore, if you substitute these things so, z x x and z x in terms of a.

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 $T_{\text{I.T. KGP}}$  $\int \frac{1}{2} \frac{d}{dz} (a^2) = \frac{\int \frac{\partial}{\partial y} \frac{dy}{dz}}{(1 + a^2)^{3/2}}$ <br>  $\Rightarrow \frac{1}{2} \int \frac{d(a^2)}{(1 + a^2)^{3/2}} = \int \frac{\int \frac{\partial}{\partial y} \frac{dy}{dz}}{y^2} dz$ <br>  $\Rightarrow - \left(1 + a^2\right)^{-1/2} = \left(\frac{\int \frac{\partial}{\partial y} \frac{dy}{dz}}{y^2} + C_1\right)$ <br>
at  $\frac{z}{z} = 0$ ,  $\frac{d^2 z}{dx} \Rightarrow 0 \Rightarrow \frac{a}{z}$ 

In this equation, what you get is half. Now, if you integrate it both sides plug in the boundary condition later. So, what you get of course, this comes to this side. So, it's you get minus half. Now, what are the boundary conditions, the boundary conditions are at z equal to 0, x equal to this z, z equal to 0. So, that is the surface the plane of the interface. So, at z equal to 0 we have del z del x is equal to 0 or tends to 0 which means that a equals to 0. So, if you plug in this expression what you will get, you will get c 1 equal to minus 1.

Now, use the **secondary boundary conditions** second boundary condition which says that at z equal to h d x del z is equal to minus tan theta which is one by a. So, if you plug that in. So, if you plug in the expression, if you plug in c 1 equal to minus 1. Your expression, this equation reduces to, let me write it here itself minus 1.

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 $T_{\text{I,I,KGP}}$  $Sin 0$ 

Now, plug in the secondary second boundary condition, what you get is minus 1 divided by under root of 1 plus cot square theta (no audio 32:38 to 33:08). So, here you have an expression for h which again turns out to be in terms of the equilibrium contact angle and the surface tension of the liquid. For a scenario, like this when if you have a flat plate which is dipped in a pool of liquid. So, what it gives its essentially you get an idea or measure of each that is going to form. Due to this surface forces or essentially capillarity. My only request is that, you just listen to this lectures and sort of rework the calculation yourself. Everything will fall in place because I am showing all the steps. So, that you understand how it comes and when when it is happening. So, it is in a video class you really have that advantage of pausing going back and seeing it again and again and do it. Do the calculations yourself on a sheet of paper. I am sure, you'll understand what happens.



Now, we come to the third example which is the stability of a liquid cylinder which is essentially, you have a free falling liquid cylinder. And these are the coordinate axis. It turns out that, this problem this particular problem can be better solved if we sort of define the other words you if you from the figure itself you can see, that the the surface of the liquid cylinder is better represented or will be better represented not as z equal to function of x. But it will be it the I mean sort of it is captured, if we write f as a function of z. So, that transformation of the coordinates is essentially necessary and we will see what we do. So, essentially we sort of test the. So, this is one of the foundations of what is an a very important topic. We we are going to cover and in the very first lecture we talked about it is the issue of linear stability analysis. So, essentially here we sort of give a perturbation to this surface. May be a perturbation that is periodic in space and we want to see whether that perturbation grows or sort of dampens out. So, if the perturbation grows you have a periodic perturbation over here if it grows. So, eventually the liquid column will disintegrate into isolated droplets. And this is one of the reason as I gave you the example in the last minutes of previous class. That, if you sort of have sort of close your tap nearly closed configuration a thin strip of liquid drop coming out. You see that, it is recently getting into drops very high falls. For example, you see lot of flashing lot of water drops coming out it is also partly attributed to Rayleigh instability in many cases it sort of breaks out. So, this is what is known as the set this this is the setting of Rayleigh instability. So, as it is called it is a very very important thing and a very classical instability and we will show how the radius of curvatures play crucial role in deciding or what are the condition under which you can have a Rayleigh instability

Now what we need to do is we need to do a transformation of the equation of the young-Laplace equation where we represent x as a function of z. So, later in order to achieve that, first we have to do a little bit of mathematics. So, what we do is let us define the del x del z is some del f del z. Therefore, del z del x is therefore, del 2z del x square is del del x of del z del x and this turns out to be del del x of del f del z inverse which is del del z of del f del z inverse into del z del x. And if you do it carefully what will come out is you will get a minus del f del z minus 2 into del f into del z del x. And this del del z del x you now substitute del f del z to the power minus one. So, eventually this will lead you to an expression of del f del z minus 3 into del 2 f del z square. So, and del f del z is nothing but del x del z.

So, this you can write as, minus del x del z cube into del 2x del z square. So, this is one of the important thing. So, del 2z del x square or the z x x it sort of transforms to minus del x del z cube into del 2x del z square this is one of the parameters. Of course, if we want to do the transformation all we have to do is we have to find out z x and z x x in terms of the x z, essentially that is the whole idea. So, our essential motivation is that we find out, why we are doing all this is these two terms we would like to get it in terms of these two that is the whole idea that is the mathematics we are doing.

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So, now we have 1 by r 1 which you now if you get back to your young laplace equation, which is z x x divided by 1 by z x square raise to the power 3 by 2. So, this now turns out be minus del x by del z minus 3 del 2x del z square divided by 1 plus del x del z minus 2 raise to the power 3 by 2. We have del z del x essentially defined as a this thing. So, del z del x is nothing but del x del z inverse. So, that is precisely what has been plugged in here and if you now do the necessary simplification, what you get is that (no audio 41:12 to 41:41) you just sort of take this out. So, there is a 3. So, its minus 3.

So, this actually cancels out now and what you are left with is del 2 x del z square divided by del x del z square plus q raise to the power 3 by 2. You can write as x z z divided by x z square plus 1 divide 2. **Sorry**, there is a minus sign that comes this is the 1.

Correspondingly, the 1 by r 2 term turns out to be z x divided by x into 1 by z x square raise to the power half and So this is 1 divided by del x by del z. And you have x into 1 plus del x by del z minus 2 raise to the power half you just take it out. So, what you are left with is 1 divided by, this cancels out. 1 divided by x plus del x del z square raise to the power half yeah. So, I will write it neatly it goes here as one divided by x into one plus del x del z square raise the power half . So, the important thing is that, when you do the change of the I mean you just do not blindly write x z in place of z x because of the simple fact that ,if you  $\frac{if}{y}$  you do that you just miss out this minus sign ok

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 $\left[ -\frac{\alpha z z}{(1+x^2)^{3/2}} + \frac{1}{\alpha(1+x^2)^{1/2}} \right]$ <br> $\frac{\alpha z z}{(1+x^2)^{3/2}}$ <br> $\frac{1}{R_2} = \frac{1}{\alpha(1+x^2)}$ 

So, you get del p now. So, where your 1 by r 1 turns out to be minus x z z by 1 plus x z square raise 3 by 2 and 1 by R 2 turns out to be 1 by x into 1 plus x z square raise to the power half now, let us sort of. So, this is the cylinder we have this is at x this is z direction now, let us perturb the surface. Let us say, this is the mean diameter of the surface to be h 0. So, how do we perturb the surface, we perturb the surface.