Instability & Patterning of Thin Polymer Films

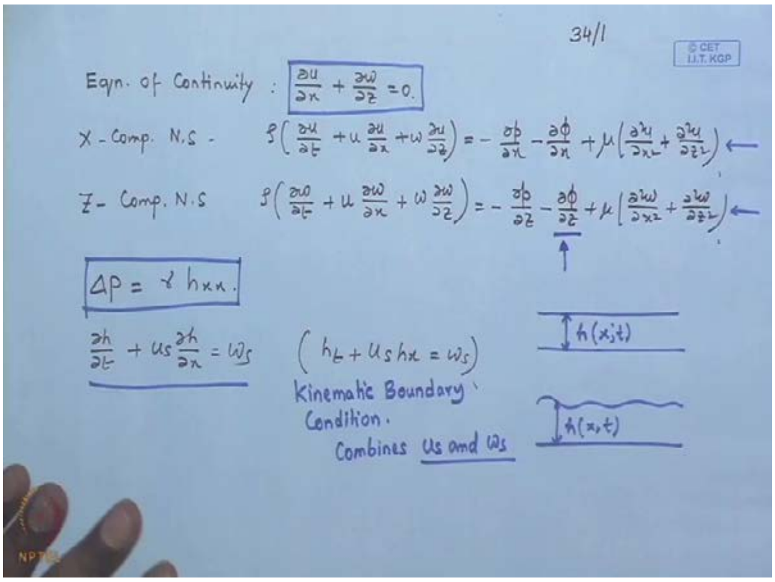
Prof. R.s Mukherjee
Department of Chemical Engineering
Indian Institute Of Technology, Kharagpur

Lecture No. # 34

Spontaneous Instability & Dewetting of Thin Polymer Film- IV

Welcome back, we just got started off started to look at the mathematical formulation of the spontaneous instability of an ultra thin film which is coated on a on a on a rigid or a solid substrate.

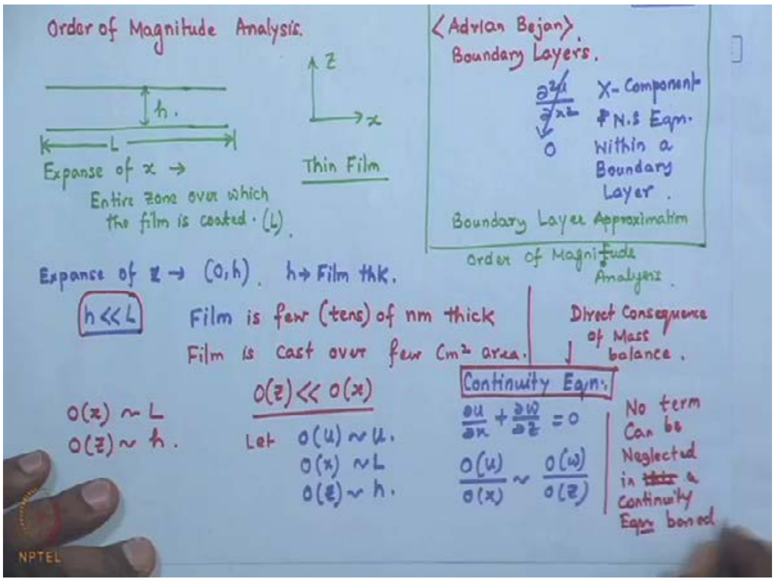
(Refer Slide Time: 00:28)



The film thickness is h, h is a function of x and t and so, essentially we are talking about a film like this where the thickness can vary specially as well as temporarily. The continuity equation we have seen is this, we have talked about in in detail, the governing equation based on the force balance remains to be the Navier-Stokes equations for x and z components which are given here, only additional term that what has come in is the effective interface potential which we have considered.

Because of the non planarity of the top surface, we have assumed the axisymmetric fluctuations at the surface and that gives results to the Laplace pressure which is taken care by the long wave long wave approximated young Laplace equation which has this particular form. And we additionally have the kinematic boundary condition (No audio from 1:35 to 1:44) which sort of correlates the components of velocity at the liquefy surface that is it it combines u s and w s.

(Refer Slide Time: 02:32)



So, these are the all the equations that we will need to understand the, a mathematically or to distinguish how the instability of a thin film can be sort of used, or can be understood. The next thing that we will do is what is known as order of magnitude analysis, this is a very common practice (No audio from 2:32 to 2:41) that is done in sort of which gives an idea about the scaling or the orders and it is very common in heat transfer and as well as in fluid dynamics.

So, if you I am sure you have done order of magnitude analysis in some setting or the other, if you have not done it just go through it from some text book of let us say fluid dynamics like, or heat transfer like Adrian Bejan for example, that if you look at the chapter on boundary layers in your fluid dynamics or in your heat transfer, I am sure you will come across this concept of order of magnitude analysis. Because, what you regard as the boundary layer approximated Navier-Stokes equation, where if you were talking about a 2 D flow, you preferentially neglect one of the terms, if you remember carefully, this term is neglected from the x component, it has nothing to do with our derivation; this term is neglected from the x component, Navier-Stokes equation within a (No audio from 03:58 to 04:06) boundary layer.

And if you try to understand the origin, what this some chemical engineering text books, of course refer to this as the boundary layer approximation. But if you look carefully, this whole concept of the so called boundary layer approximation comes from nowhere rather than order of magnitude analysis.

So, in other words, this sort of this analysis gives a relative scale of different variables. So, let us say we, I will also make your concepts give you some simple concepts, we have a film like this and this is our coordinate system we have chosen, x and z, we have identified that the film thickness is h (Refer Slide Time: 4:53). Of course, you have created the film, the film can be very very thin, because we are talking about a thin film where we have the interfacial interaction to be active. Therefore, there is no doubt the film thickness is very very low, but the film can be spread over a large area, because you (()) coding. So, you cannot create it over a few nanometer area, you are taking a macroscopic object over the entire area the film is nicely coated.

So, what it means that the expanse of x is much higher than the expanse of z in your system. So, your x sort of stretches (No audio from 5:48 to 5:55) is the entire zone over which the film is coated; let us say this is of the order of L, L is some sort of a length, let us say this is L (Refer Slide Time: 6:15).

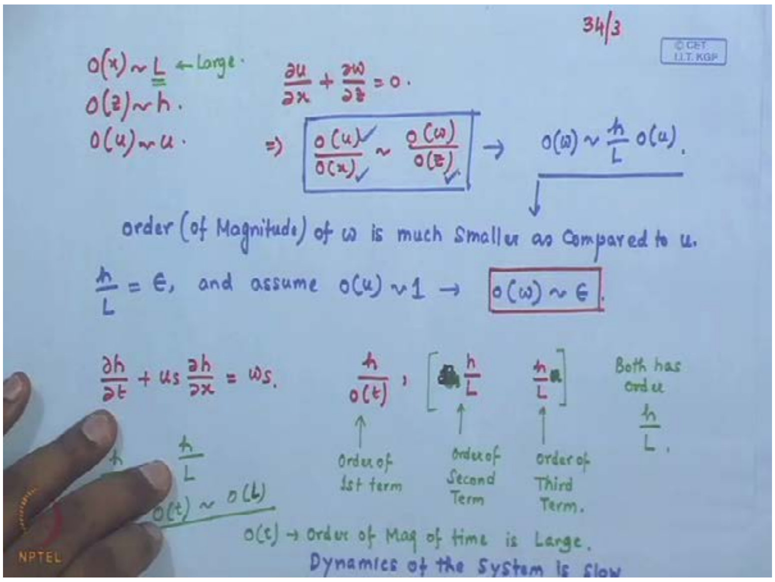
In contrast, your expanse of z is z stretches from only 0 to h, and h is the film thickness. So, from the physics of the system, what you can say is that, first thing you can say that h is of course much much smaller than L. Because you are talking about a film, why you say this, this is this comes from the basic system configuration, film is film may be tens of nanometer thick, in contrast the film is cast over few centimeter square area.

So, what it implies that the lateral dimension x is much much larger as compared to the vertical dimension h. So, we can write the order of x that is how it is written, o x that is the order of x is that of L and the order of z is that of h. Therefore, immediately what you can say that order of z is much much smaller than order of x.

So, this is how a typically an order of a magnitude analysis would be proceeding. So, let us assume that, but this is a some sort of a very approximate approach to sort of get a qualitative idea about the magnitude of the scale of different systems. But still it works remarkably well for systems, for unknown systems, or to identify the important of different terms in a particular system, and that is why we will discuss the order of magnitude analysis.

Now, let us assume that the order of u v that of u, and we also have the order of x to be L, order of z to be h. Now, if you look at the continuity equation which is del u del x plus del w del z is equal to 0, that is order of u by order of x is of the order of order of w divided by order of z, do not have to worry about the sign and all that, this is just a qualitative order, do not forget one thing, this is a simple rule of thumb, that is a continuity equation which is direct consequence of (No audio from 9:25 to 9:34) of mass balance.

(Refer Slide Time: 10:25)



So, no term can be neglected in this, in in a continuity equation based on order of magnitude analysis, but what it gives is this, use a fresh page, what we have is order of x is that of L, order of z is that of h, order of u we have are both assumed it to be the order of u, and then we have this is our continuity equation, therefore we get order of u by, now out of the four orders that are involved here in this equation, you see that three are known that is x, z and u are known (Refer Slide Time: 10:25).

So, if you plug in those orders what you can get, the order of w is h by L times order of u, which means that, what does is the significant of mathematical statement, it means that the magnitude of w is much much smaller or the order of magnitude of w is much smaller as compared to u.

So, if we are, if we assume h by L to be equal to epsilon, and further assume order of u to be equal to 1, what we get, order of w is of the order of epsilon. Now, after obtaining the order of w from the continuity equation, let us investigate the kinematic boundary condition with the order of magnitude analysis.

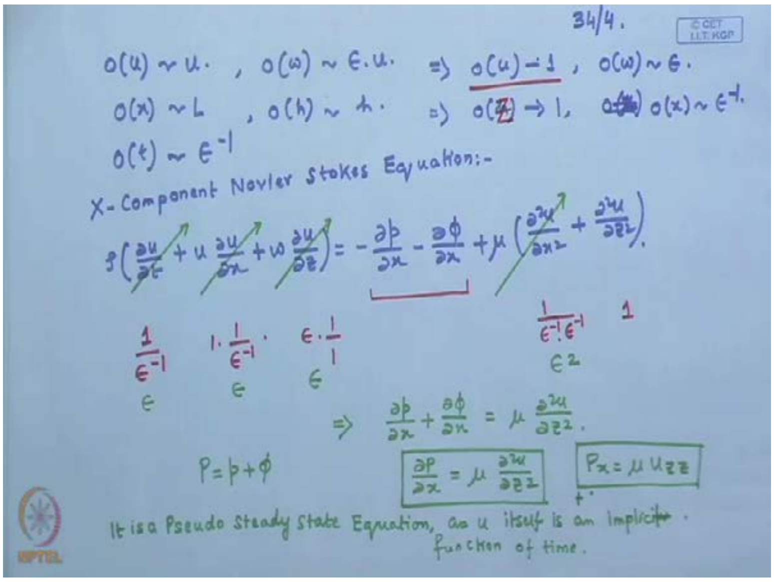
So, this is the kinematic boundary condition we have, so the equation is (No audio from 12:37 to 12:45), so we plug in the respective orders, order of h is now known h or z or whatever (Refer Slide Time: 12:33). So, this is h by order of t, second one is order of u s is of the order of 1, first term is this, second term is 1, this is h, and x is L, and w is also of the order of epsilon order h by L, so this is the order of the first term (No audio from 13:27 to 13:47) (Refer Slide Time: 12:33).

Third term, so you can see that the orders of the second and third term sorry this is u, this is u, and this is also u, but u is of the order of 1, so this is this is perfectly fine (Refer Slide Time: 13:58). So, you can see, there is second and third term, both have the order of h by L and the first term is h by order of t. So, these two now matches, so what comes out the order of time is of the order of L.

And now, we know that h is a a L is large, therefore the time scale, the magnitude, the order of the time is large or in other words, the dynamics of the systems is slow, but it implies physically is the dynamics (No audio from 15:11 to 15:19) is slow.

So, this is the other implication of the, is that this is the implication of performing the order of magnitude analysis on the kinematic boundary condition. Now, if we look at the, so it is large means that, we take that order of time is epsilon inverse, epsilon is small. So, the order of time is epsilon inverse and what it gives is, so these are the orders we have.

(Refer Slide Time: 16:29)



So, here are the orders we have, order of u is u, order of w is epsilon times u, we normalize the order of u to be equal to 1, therefore order of w is equal to epsilon, order of x is L, order of h is h, we normalize the order of h to be equal to 1, therefore order of L is, order of x is epsilon inverse and we also have order of time is epsilon inverse.

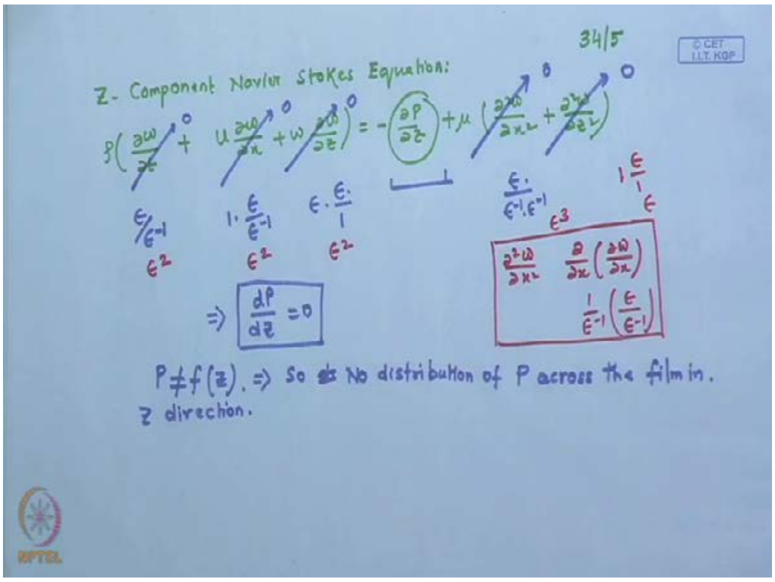
So, having these orders now ready at our disposal, we now try start investigating the Navier-Stokes equation, the x component (No audio from 17:30 to 17:44) Navier-Stokes equation, so this is the equation we have (No audio from 17:47 to 18:14) (Refer Slide Time: 17:47).

Now, if we plug in the respective orders, we will find the first term, we will have an order of 1 corresponding to u and epsilon inverse, the second term will have an order of the u is 1, again 1 and x is epsilon inverse, third one is w is a epsilon u is 1, z is 1, this term remains, we do not do anything, we because we have no idea about their order and out of these two (()) terms, the first term you see is u is 1 divided by x del u del x. So, x is epsilon inverse and again a differentiation with respect to x where epsilon to the power minus 2, and the second term is u is 1and z or h, this is z or h is also 1, so this order is 1

So, if you simplify this is epsilon this is epsilon, this is epsilon, and this is epsilon square (Refer Slide Time: 19:23). So, based on an order of magnitude analysis for a thin film, we see that from the x component Navier-Stokes equation, all these terms sort of are insignificant. And therefore, the final equation, governing equation takes the form of (No audio from 19:48 to 19:58) (Refer Slide Time: 19:48), we define a capital P as a non gravitational pressure as p plus phi. Therefore, the equation takes this shape of del P, del capital P del x is equal to mu del 2 u del z square or in a compact form one can write P x is equal to mu u z z.

So, this is what we get from an order of magnitude analysis of the x component Navier-Stokes equation. Now, this is going to be the final governing equation and it is going to be very important also, now it is apparently a steady state equation. However, the reality is it is a pseudo steady state equation as a (No audio from 20:50 to 21:07) as u itself is an implicit function of time (Refer Slide Time: 20:50).

(Refer Slide Time: 21:39)



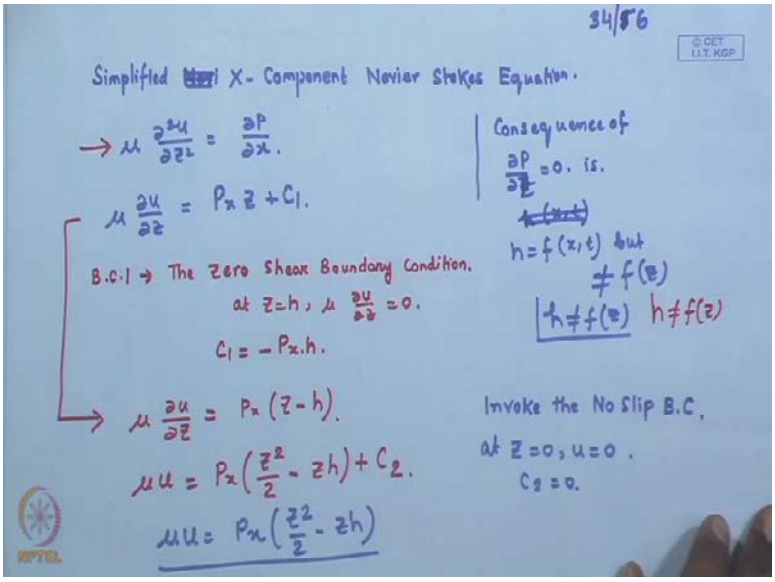
Now, let us investigate the z component Navier-Stokes equation (No audio from 21:35 to 21:54), and the equation is del t u del w del x plus del w (No audio from 22:14 to 22:32), we have used the expression of the non gravitational pressure combining p and phi straight away (Refer Slide Time: 22:14).

Now, if you plug in the respective orders, what you will find here is that this first term w, the order of w is any where let us have these orders here. So, order of w is epsilon divided by epsilon inverse, order of u is 1 epsilon, and order of x is epsilon inverse. So, this is w is epsilon, omega is epsilon, this is 1, this we leave untouched and this one turns out to be omega is epsilon divided by epsilon inverse epsilon inverse, remember that this type of a term del 2 w del x square, one looks at the order like del del x of del w del x (Refer Slide time: 23:00).

So, first we will look at the order of del w del x, it is epsilon by epsilon inverse and then again look at it as del del x. So, it is epsilon divided by epsilon inverse and the final term is w is. So essentially we are looking at del del z of del w del z, w is of the order epsilon z is of the order of 1, so 1 into 1. So, overall what we find that, this has an order of epsilon square, epsilon square, epsilon cube, and this is epsilon (Refer Slide Time: 24:13).

So, all the terms sort of are insignificant, and what emerges out that d p d z is equal to 0, which means that P is not a function of z, now this is significant that is there is no distribution of pressure across the film in z direction (No audio from 24:58 to 25:17), this will be another very significant finding as a we will see.

(Refer Slide Time: 25:39)



So, now, that sort of brings us back to the governing equation which is this we will go back to this equation which is the simplified (No audio from 24:39 to 25:50) X component Navier-Stokes equation which is mu into del 2 u del P del x.

So, we will write down the appropriate boundary conditions as the time comes. So, the other thing that is that I have just liked to highlight is that the consequence of, before I move further sorry I forgot to mention it, consequence of del P del t is equal to 0 is h sorry not del P, del P del z is equal to 0 is that h is a function of x t, but not a function of z. So, h is not a function of z, this is important.

Now, this is the simplifier Navier-Stokes equation. So, you integrate it to once or with respect to z, you get mu del u del z is equal to P x z plus c 1. Now, first we invoke the first boundary condition, we invoke is the 0 shear boundary condition (No audio from 27:39 to 27:51) which gives that at that the free surface, the shear stress is 0. So, at z equal to h mu del u del z is equal to 0, therefore you substitute the the what you get is the value of the constant of integration c 1 as minus P x into h, and the if you substitute that you get mu del u del z is equal to P x z minus h.

You integrate it further, we get mu into u is equal to P x into z square by 2 minus z h plus c 2, at this point we invoke the no slip boundary condition that is at z is equal to 0, u is equal to 0 if you substitute that z is equal to 0 is equal to 0 what you get is c 2 equal to 0 therefore, you get mu u is equal to P x into z square by 2 minus z h.

So, I will just quickly repeat as to what we have been trying to do before proceeding further so that you do not get confused. So, what we started to look at after we got to all the relevant equations is that, these are the set of equations, set of the governing equations we have, we will continue our discussion once we do a quick recap at this stage.

So, we are looking at the hydro dynamics of a free surface of a liquid film. So, what we are looking at (No audio from 30:07 to 30:16), interface this is what we are trying to investigate of a thin film and based on refer to the previous class, so you will understand, what are the equations we need to talk about. So, we have the equation of continuity, we have the x component Navier-Stokes equation, the z component Navier-Stokes equation the only additional terms you find are the effective interface potential or the phi which arises out of the interfacial interaction between the two interfaces, because we are talking about a thin film.

So, this interaction that originates the, which can be Van der Waals or which can be other forces that will be taken care of through the expression of phi. So, please understand that this form, in this particular form, the present form the Navier-Stokes equation is not limited to Van der Waals interaction alone. It it is the Navier-Stokes equation which incorporates the effective interface potential that is it is valid for any system where there is an additional interfacial interaction. Now, the expression of phi you have you can have terms which can represent only the Van der Waals interaction, or you can have additional terms also that can take care of a additional interactions, let us say acid base, polar or (()) interactions.

Now, you can use this form of Navier-Stokes equations for all your fluid dynamic derivations you have done so far, because do not forget that phi will definitely be a function of h which is the film thickness. And if your film thickness is higher, in most cases what is going to happen that h will have some exponential power and it will be in the denominator. So, in most cases what we, what is very likely to happen is that for higher values of h, phi will tend to 0. Therefore, this term has no significance in in the macroscopic derivations or deductions and therefore, we often tend to neglect it, but there is a absolutely no problem if you have this term (()) in your macroscopic derivations as well.

Subsequently, we talked about the fact that the interface we are talking about is not a flat interface and therefore, we have the surface fluctuations or the undulations which results in a liquid interface which is non planar. Therefore, you have these resulting into local Laplace pressure distribution and since we have a Laplace pressure, so we invoke the equation, the young Laplace equation for an axisymmetric undulation, we we assumed the undulations we are talking about where the surface are axisymmetric.

Then, all we did was to invoke the condition for what is known as the log wave instability that as essentially implies that del h del x is very very less or it is close to 0. So, once you plug that in into your expression of the young Laplace equation for an axisymmetric surface, this is the form of young Laplace equation that you are left with.

Then we talked about the about the fact that, now that you have undulating top surface, therefore the surface components of velocity u and w are not 0 and therefore, they are finite. So, we needed an expression which will sort of combine the function or provide functionality between u s and w s and that is precisely what is given in the form of this kinematic boundary condition, the derivation we have done in the previous class. So, if you are still confused and like to like to request you to repeat that video once more, tell your instructor to repeat the video once more so that you get an insight of what the kinematic boundary condition is.

So, these are the five governing equations what we have based on which we would like to investigate mathematically, the necessary condition or the criteria for the or or how the a a free surface of a thin film, thin liquid film behaves.

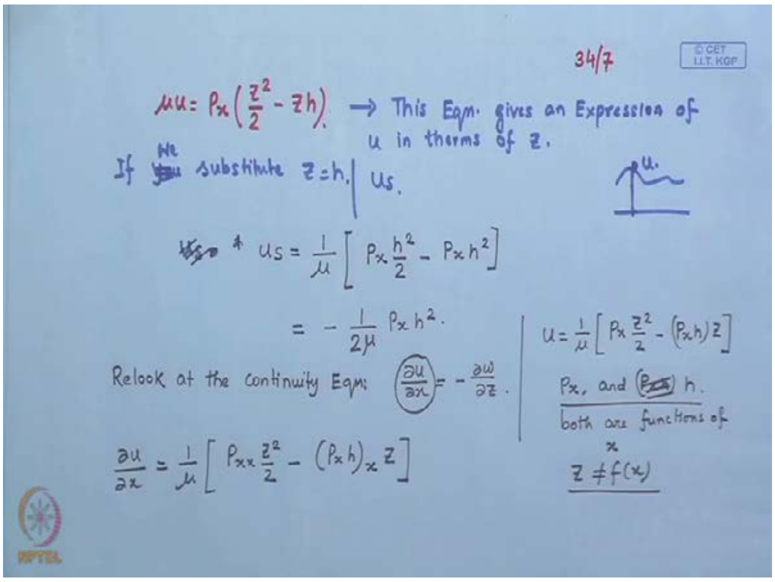
So, this is what we how we started off, then I introduced you to the concept, I guess it is known to most of you the concept of the so called order of magnitude analysis, which essentially gives you some sort of an idea about the expanse or the relative magnitude of the individual terms. So, we just briefly talked about how to perform an order of magnitude analysis and I told you to refer to some derivation related to boundary layers in any standard text book like (()) or even (( )) may be, but (( )) for sure and Adore Began of course, so are the key figures of order of magnitude a, popularizing the order of magnitude analysis easy transfer, book or convection heat transfer, that is the book which where he talks about the boundary layer, the the order of magnitude analysis in very detail and use it for various, deriving various mathematical functionalities.

So, once we started to look at the order of magnitude analysis, we individually did the order of magnitude analysis of all the equations that we are considering, the first we used the order of magnitude analysis in the continuity equation which gave us the fact that, the order of w that is the z component velocity is much much smaller as compared to order of u.

And then, we looked into the order of magnitude analysis of the kinematic boundary condition which told us that the order of time is epsilon inverse that is time is slow, then we looked at the order of magnitude analysis of the x component Navier-Stokes equation which gave us this simplified form that all other terms are much much smaller as compared to these terms. So, this is our final governing equation, and we also looked at the order of magnitude analysis of the z component Navier-Stokes equation which gave us del p del z is equal to 0, which eventually tells us that h is not a function of z.

So, with that we started to look at the simplified x component Navier-Stokes equation, and we have integrated it twice, already with respect to z and invoked appropriate boundary condition, the first boundary condition we invoked is that of a zero shear boundary condition which tells that at a free interface the shear stress is 0. So, we plug that into get the first value of the first constant of integration and the second boundary condition, we have invoked is the no slip boundary condition at the film substrate interface which gives us c 2 is equal to 0.

(Refer Slide Time: 37:52)



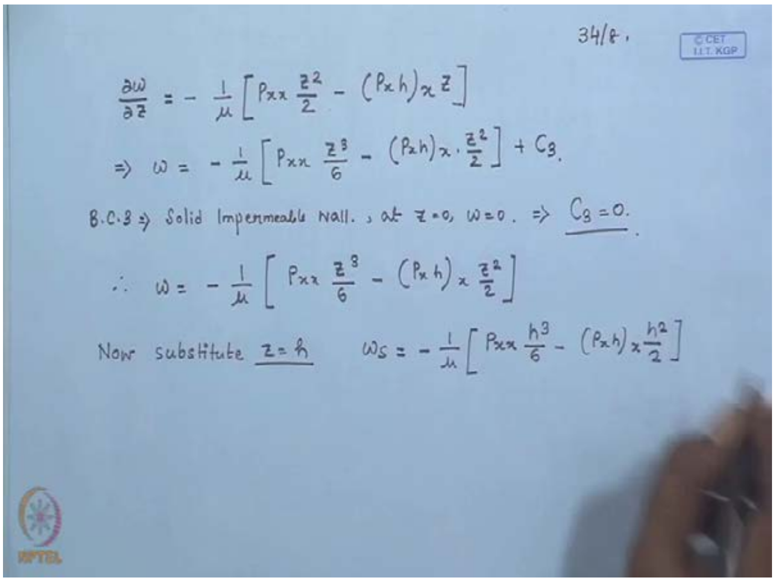
So, at this point before we started this quick recap, we have reached up to this stage where we have got an expression that mu u (No audio from 37:45 to 38:00) (Refer Slide Time: 37:50), now what we can do is that we understand, so this equation gives an expression of u in terms of h (No audio from 38:16 to 38:38) z.

Now, if you plug in (No audio from 38:42 to 38:51) z equal to h, what we actually get is the value of u at the free interface. So, for z is equal to h from this equation, we will get the value of u s and which turns out to be, u s is equal to 1 by mu into P x h square by 2 minus P x h square, or it turns out to be minus 1 by 2 mu P x h square.

Now, we relook at the continuity equation (No audio from 39:47 to 39:58) which gives del u del x is equal to minus del w del z. Now, we have an expression of u is equal to 1 by mu into P x z square by 2 minus P x h into z. Now, if you look carefully in this expression on the right hand side, P x and P x into h or or P x and h, both are functions of x, z is not a function of x.

So, what we do, we take this expression of u and find out the partial derivative del u del x. So, from here we get, del u del x is equal to 1 by mu into P x x z square by 2 minus P x into h del del x of P x into h into z, which now we have the del u del x is equal to minus del w del z.

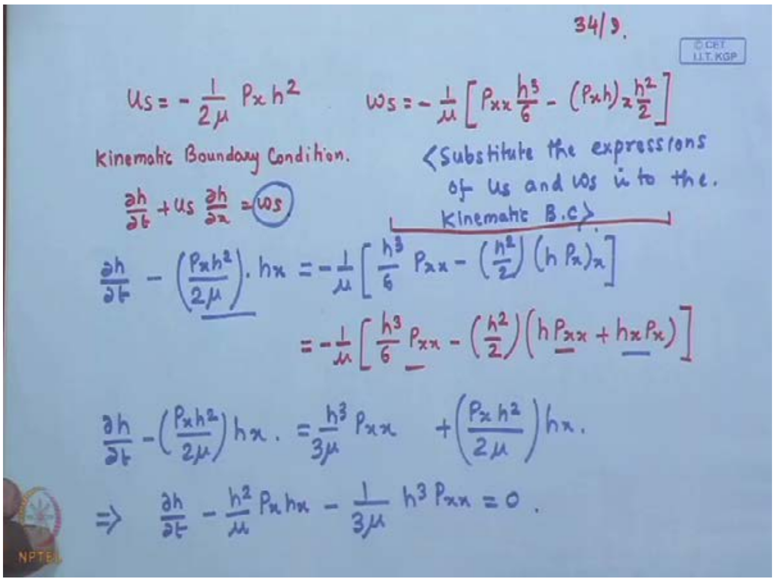
(Refer Slide Time: 41:59)



So, we do that substitution and we get del w del z is equal to minus 1 by mu P x x z square by 2 minus P x h x z. If we now do, again do an integration what we are left with now is w is equal to minus 1 by mu P x x z cube by 6 minus P x h x into z square by 2 plus c 3, at this point we invoke the third boundary condition which is that of a solid impermeable wall that is at z is equal to 0, w is equal to also 0, which gives c 3 is equal to 0, therefore we are now left with another expression of w in terms of z.

So, if you now substitute the expression, if you now substitute z is equal to h in the above equation, what you will get, you will get an expression of w s which turns out to be minus 1 by mu into P x x h cube by 6 minus h square by 2.

(Refer Slide Time: 45:04)



So, what we have now is in the, from the previous expression we got. we have an expression now of u s in terms of h (Refer Slide Time: 44:35), which is we have an expression for u s from here which is, and we also have an expression for w s now (No audio from 45:16 to 45:35) (Refer Slide Time: 45:16). So, once we have these two expressions in hand, we can now invoke the kinematic boundary condition and which is, which has this form which is here and which is (Refer Slide Time:45:55), which gives del h del t plus u s del h del x is equal to w s.

Now, if we substitute the expression, so what the strategy now is to substitute the expressions of u s and w s into the kinematic B.C and once you do that, what you get is del h del t del h. So, you substitute the expression for this P x h square by 2 mu into h x is equal to minus 1 by mu h cube by 6 P x x minus h square by 2 h P x x, you just substitute this expression over here on the right hand side which contains the w s and on the left hand side you have u s into del h del x.

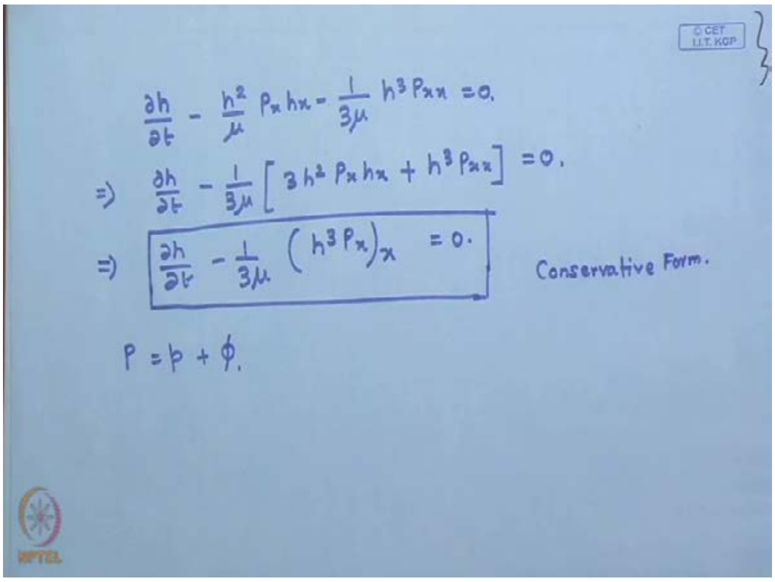
So, once you do that, all you do is you need to do a little bit of algebraic manipulation, particularly on the right hand side. So, it is minus 1 by mu h cube by 6 into P x x minus h square by 2 into, so this this differential we now one to break up, h P x x plus h x P x, because both h and P are functions of x.

So, if you do that, you find that these two terms actually combine, this and this, and it results in, and this term on the other hand has a h x P x multiplied by h square which also this term has h x, P x h x into P x multiplied by x square (Refer Slide Time: 48:26).

So, this is a also has the same pre factor of minus half, but this minus gets added with a plus. So, this term results in, this second term results in a plus P x h square by 2 mu into h x and the first term actually is now half minus 1 6th. So, it is essentially 1 3rd mu h cube into P x x, so this is what you get del h del t minus P x h square by 2 mu into h x as this.

So, you do a transposition and you get del h del t minus h square by mu into P x h x minus 1 3rd mu h cube P x x is equal to 0.

(Refer Slide Time: 50:18)



And this one, so I will just write down, rewrite the expression for taking it into a more compact form h square by mu P x h x minus 1 3rd mu h cube P x x is equal to 0, we will just write del h del t minus 1 3rd mu to 3 h square P x h x plus h cube P x x is is equal to 0.

What are you really request you, and this is what I tell also to my classroom students when I teach this here at Kharagpur is that, please go through this derivation, you do it yourself once, other than just listening to it.

So, note down the best approach to go about it would be to, note down the whole sequence of derivation, take a pen and a paper and do the whole sequence once clearly. I am sure it will it will make things very very clear to you, there is nothing great thing is there, only a couple of manipulation from this form to that form, you use continuity some some place, you some other equation some place. So, apparently if you are just sitting back, relaxing and listening to this lecture, I am sure it will hardly make any sense. But the moment you take a pen and a paper and try to do this derivation yourself derivations yourself, I am sure it will be very very clear to you, there is nothing really great that that is going on over here.

And so, if if you combine this now, you find that this can be very compactly written as, this can be very compact nicely and compactly written as minus 1 3rd 3 mu into h cube P x x is equal to 0. So, this is the final characteristic, this is the final equation in a, in the conservative form.

Now, we need to worry about what is P, it is the non gravitational pressure which is essentially p plus phi. Now, there are two things when we had been talking about the instability of a surface, we had been talking about the two types of pressure, or two types of factor, one is the Laplace pressure due to the curvature. So, P will come from the Laplace pressure, so this will be provided from the Laplace pressure and phi essentially takes care of the interfacial interaction.

So, we will get the expression of phi from the interfacial interaction, now we are running out of time in today's class. So, I would request all of you to please go through the derivations up to this point in great detail so that you are you are conversant with what is happening, you understand what, how exactly this whole thing comes, and we will pick up our subsequent discussion from this point, thank you.