Instability & Patterning of Thin Polymer Films

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

Lecture No. # 33

Spontaneous Instability & Dewetting of Thin Polymer Film- III

Welcome back, in the previous class we started to talk about the condition under which an ultra thin film can spontaneously become unstable with the formation of holes due to the attractive interfacial interaction between its two interfaces.

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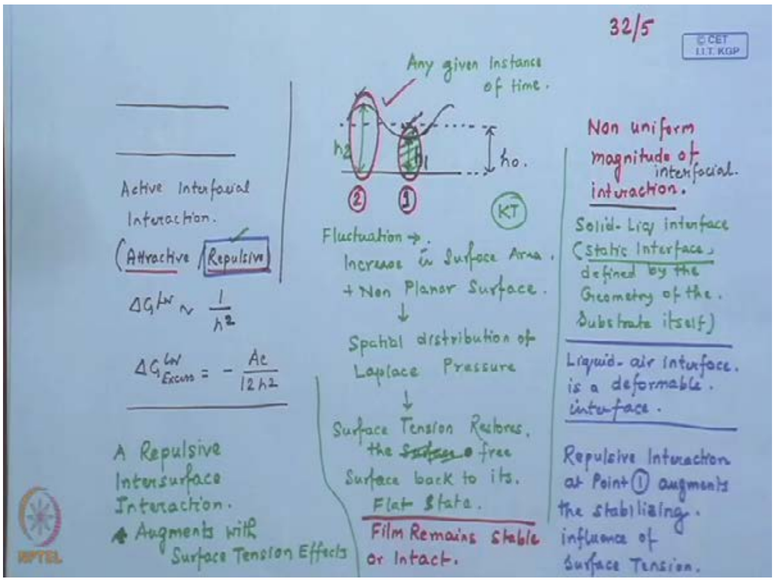

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Active Interfacial Interaction.
(Attractive / Repulsive)

$\Delta G^{LW} \sim \frac{1}{h^2}$

$\Delta G^{LW}_{Excess} = -\frac{A_c}{12h^2}$

A Repulsive Intersurface Interaction.
Augments with Surface Tension Effects

Any given Instance of time.

Fluctuation →
Increase in Surface Area + Non Planar Surface.
↓
Spatial distribution of Laplace Pressure
↓
Surface Tension Restores the ~~Surface~~ free Surface back to its Flat State.

Film Remains Stable or Intact.

Non uniform magnitude of interfacial interaction.

Solid- Liq interface (Static Interface, defined by the Geometry of the Substrate itself)

Liquid- air interface is a deformable interface.

Repulsive Interaction at Point ① augments the stabilizing influence of Surface Tension.

So, the essential concepts that we discussed that, a liquid film surface irrespective of its thickness.

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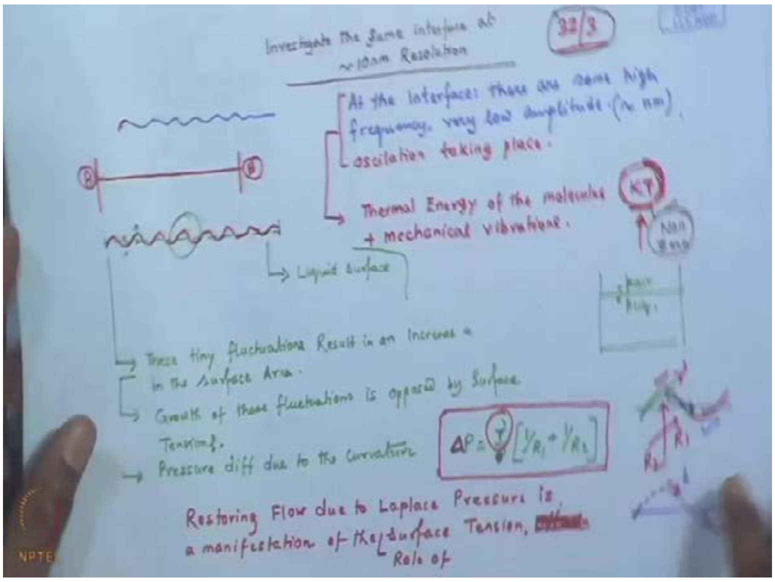

Have some very tiny fluctuations, even if it is completely stagnant and it is isothermal.

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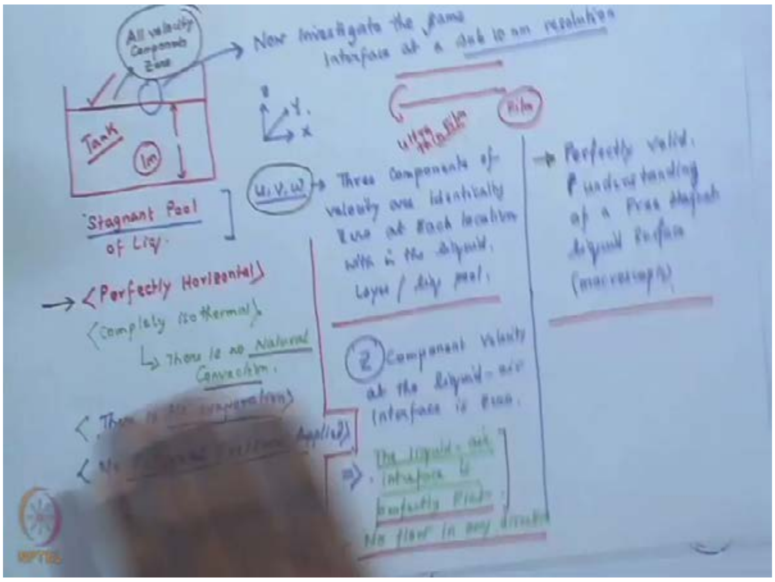

So, there is no temperature gradient, there is no evaporation, there is no external pressure from outside.

So, in a situation like this, irrespective of whether you are talking about a film or you are talking about a pool of a liquid or a tank or a bucket of water or a liquid any liquid, it really does not matter, macroscopically such a system will offer a completely flat interface, the top surface and when we (()), so this we all know. So, what it implies that, the velocity components of velocity u, v and w at every location within the flow field will be uniformly 0, which implies that the top surface of such a liquid layer will be completely flat.

So, this is a perfectly valid, we are would, this is the perfectly valid picture of the interface if you are talking about macroscopic length scale. But when we investigate the same interface at a sub 10 nanometer resolution which say, we find that there are some very tiny fluctuations which are present on the surface of the liquid, the origin of which is attributed to the thermal energy of the molecules which is omnipresent, always present, because they scale as K T and it for your performing your experiments or you were operating at temperature which is not at absolute 0, then this component of energy you can never sort of eliminate, and you can also have some mechanical vibrations.

So, consequently there are, this very tiny little high frequency low amplitude of oscillations which are always present on the surface of the interface. And typically, the movement, these fluctuations sets in; surface tension opposes these growths of these fluctuations.

So, you have a dynamic equilibrium prevailing on the surface of the film. So, essential features are, this is triggered by the thermal fluctuation and which is opposed by the restoring effect of surface tension and these fluctuations also give rise to a non planar liquids surface. So, there are localized or special variation of Laplace pressure along the surface of the film and which results in flow of liquid from these zones, the zones with were the sort of the peaks of the fluctuating surface to the (( )) of the fluctuating surface, restoring the film back to its original flat morphology. So, this we understood to its flat morphology (No audio from 3:50 to 3:56).

Now, in a macroscopic situation, these tiny fluctuations have no significant implication, because of the fact that these have typical amplitude of the order of couple of nanometer. So, in the macroscopic length scale, even if a layer of liquid is couple of centimeter thick, these are very insignificant.

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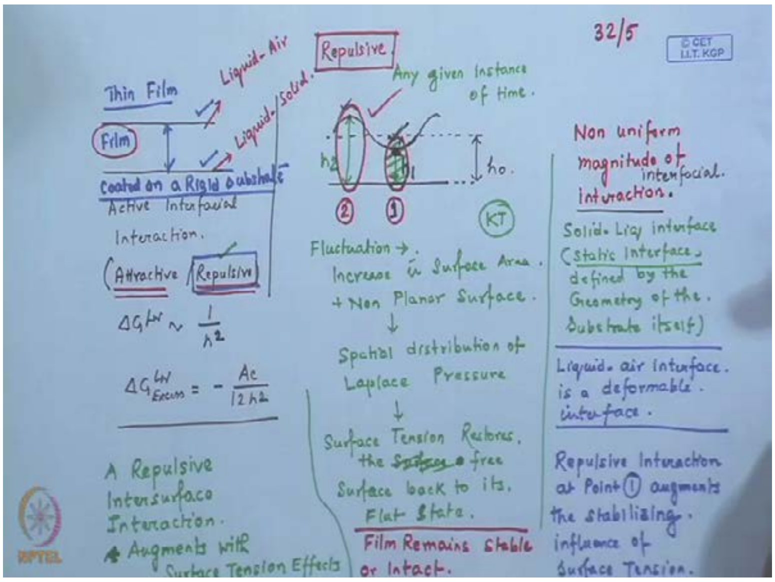

Thin Film

Coated on a Rigid Substrate

Active Interfacial Interaction.

(Attractive / Repulsive)

$\Delta G^{LW} \sim \frac{1}{h^2}$

$\Delta G^{LW}_{Excess} = -\frac{A_c}{12h^2}$

A Repulsive Intersurface Interaction.

Augments with Surface Tension Effects

Repulsive

Any given instance of time.

Fluctuation →.

Increase in Surface Area.

+ Non Planar Surface.

↓

Spatial distribution of Laplace Pressure

↓

Surface Tension Restores, the ~~Surface~~ free Surface back to its. Flat State.

Film Remains Stable or Intact.

Non uniform magnitude of interfacial. Interaction.

Solid. Liq interface (Static Interface, defined by the Geometry of the. Substrate itself)

Liquid. air interface. is a deformable. interface.

Repulsive Interaction at Point ① augments the stabilizing. influence of Surface Tension.

And there is also, these fluctuations are provided by this thermal energy of the molecules where there is no additional scenario or additional driving force, but amplification of these oscillations. The situations sort of changes, when we now start talking about a thin film, and we identify thin film as a system, this we have already talked several times where there is active interfacial interaction between the two interfaces. So, here you have a film, which let us say is coated on a rigid substrate and so, this is the substrate, this is the thin film (Refer Slide Time: 4:59).

Since, we use the word thin film, so it implies that there is active interfacial interaction between the two interfaces, that is the film air or the in case it is a liquid film, it is the liquid air interface and the liquid-solid interface. So, there is an active interaction between these two interfaces, and these interactions can be either attractive or repulsive, then we argued that if there is, we considered individually the two cases where you have individual attractive and repulsive interaction. So, we saw in a situation where you have a repulsive interaction, what happens is this area or the valley of any instantaneous surface fluctuation which is actually closer to the, or this is a location where the two interfaces are closer to each other.

Now, since there is an active interaction between the two over here, the repulsion now is stronger as compared to the repulsion in this particular zone. Therefore, the repulsive interaction augments with the stabilizing influence of surface tension. So, the repulsive interaction sort of augments with the stabilizing influence of surface tension and the film remains unconditionally stable or intact, I just add the word unconditionally stable.

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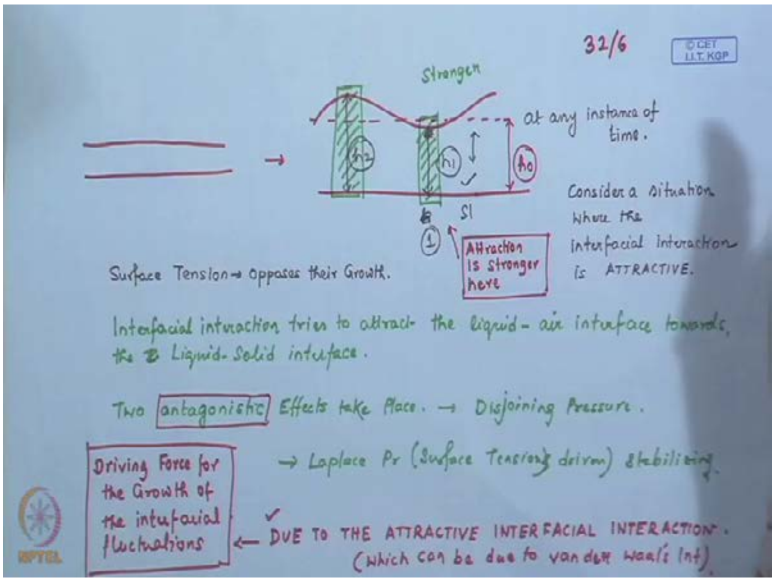

at any instance of time.

Consider a situation where the interfacial interaction is ATTRACTIVE.

Attraction is stronger here

Surface Tension → opposes their Growth.

Interfacial interaction tries to attract the liquid-air interface towards, the Liquid-Solid interface.

Two antagonistic Effects take Place. → Disjoining Pressure.

→ Laplace Pr (Surface Tension driven) stabilizing.

Driving Force for the Growth of the interfacial fluctuations ← DUE TO THE ATTRACTIVE INTERFACIAL INTERACTION. (which can be due to van der waal's Int)

So, this is what happens if you have a very thin film with a interaction, interfacial interaction which is repulsive in nature. In contrast, if you have a scenario where the interaction is now attractive, then what happens is that over this zone, the a zone which is a which corresponds to a valley of an instantaneous fluctuation, the two interfaces are now closer, then closer over here as compared to a valley, a peak of the surface fluctuation. Let us say this is the h 0, this is my mean film thickness.

So, therefore, what happens now, the the interaction now which is attractive, the interaction or the attraction is stronger here (No audio from 7:35 to 7:44) as compared to the other zones. So, now, the two forces or two force fields that is the interfacial interaction and surface tension have antagonistic or opposite roles.

So, these are the two antagonistic influences now, while surface tension, even now tries to stabilize the film that attractive interfacial interaction now tries to destabilize the film in way of trying to amplify the surface fluctuation or trying to enhance the amplitude (No audio from 8:20 to 8:34) surface fluctuations.

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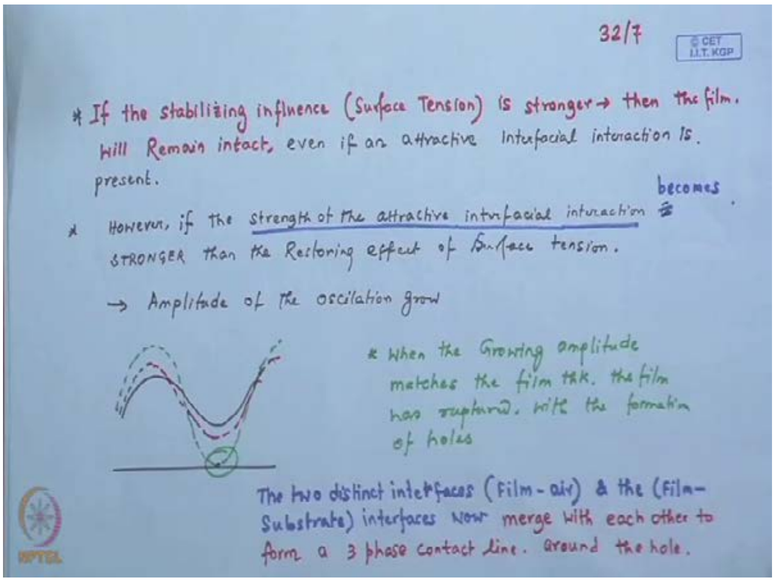

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- If the stabilizing influence (Surface Tension) is stronger → then the film will Remain intact, even if an attractive Interfacial interaction is present.
- However, if the strength of the attractive interfacial interaction becomes STRONGER than the Restoring effect of Surface tension.

→ Amplitude of the oscillation grow

- When the Growing amplitude matches the film thk. the film has ruptured. with the formation of holes

The two distinct interfaces (Film - air) & the (Film-Substrate) interfaces Now merge with each other to form a 3 phase contact line. around the hole.

And in the event that this attractive interaction, sort of becomes stronger than the strength of the attractive interfacial interaction becomes stronger, stronger than the restoring effect of surface tension, then what happens is that, eventually these tiny surface fluctuations grow in amplitude, progressively their amplitude grows. And when the amplitude of the film matches the growing amplitude of the film, matches the film thickness, the film has ruptured. What it means that the amplitude of the film matches the film thickness, essentially the two distinct interfaces that is the film-air and the film-substrate interfaces, now merge with each other to form a 3 phase contact line around the whole.

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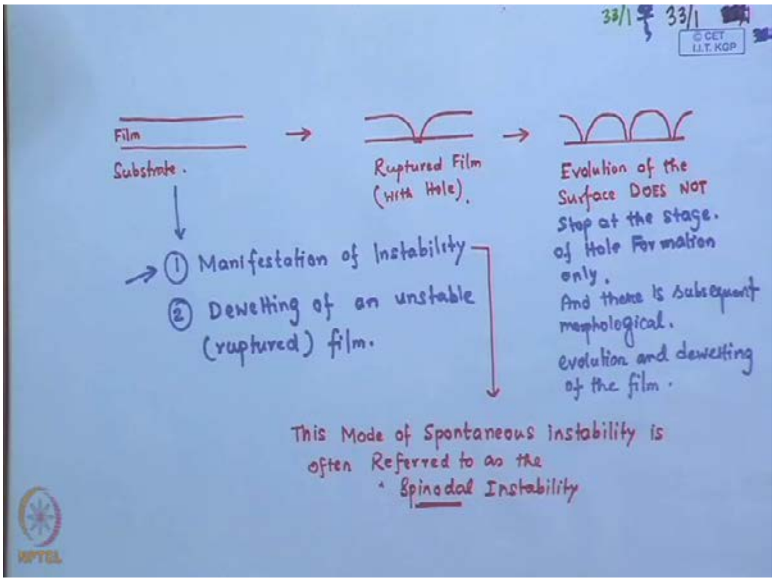


Evolution of the Surface DOES NOT Stop at the stage. of Hole Formation only.
And there is subsequent morphological. evolution and dewetting of the film.

① Manifestation of Instability
② Dewetting of an unstable (ruptured) film.

This Mode of Spontaneous instability is often Referred to as the Spinodal Instability

Now, there is some additional subsequent dynamic. So, what happens is that the scenario is like this now; all you have done is that you have taken a film on a substrate and simply based on the interfacial interaction, the strength of the attractive interfacial interaction, now this film has ruptured forming a hole (Refer Slide Time 10:40).

Now (No audio from 11:03 to 11:13), there is no specific reason if the surface is defect free, there is no preferential spot where a hole should nucleate, there is no reason to assume that only hole will form. And what eventually happens is there are the formation the several holes, sort of form like this and the dynamics of the evolution of the surface does not stop at the stage of hole formation only, and there is subsequent morphological evolution and dewetting of the film (Refer Slide Time: 11: 28).

So, there are essentially two aspects to thin film instability, or the spontaneous instability of a thin film, the first thing is that you initially start of or take a continuous thin film with spontaneous ruptures. And the second aspect is this ruptured film subsequently evolves, so there is some additional reorganization within this ruptured film which eventually results in the final (()) morphology.

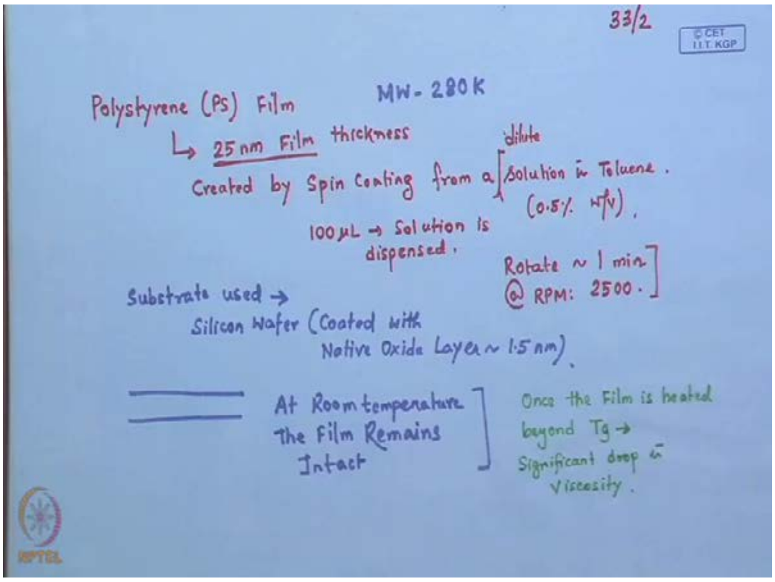
So, there are essentially two specific or different parts of the whole process of instability and dewetting of a polymer thin film. So, if you look at the title of the module, I have deliberately kept it as instability and dewetting of the polymer thin film.

So, essentially if we look into this film. So, first part is the manifestation of instability, and second part is the dewetting of an unstable, one can also say ruptured fill. What we have discussed so far, qualitatively is the manifestation of the spontaneous instability which you may just want to note down that this mode of spontaneous instability (No audio from 14:18 to 14:30) is often referred to as the spinodal instability which has it is a sort of similarity or the origin in fluid mixtures, where the spinodal decomposition in fluid mixtures where there is a fluctuation in in the composition. You can just do a internet search to find out what exactly spinodal decomposition means, but this is since its, these fluctuations you have at the interface which eventually results in this spontaneous form of instability, these are often referred to as the spinodal instability.

What we do now in the remaining part of this particular class is, we do a quick mathematical treatment of this manifestation of instability and try to figure out what exactly or how exactly the system becomes unstable, and more importantly, mathematically, how you can distinguish between a stable, unstable and meta stable film.

But before we do that, I would like to give you or show you a real time movie in which you can actually see, so this is a movie that has been taken in my lab by my research students where you can see, so this is what you are seeing is under an optical microscope, a real time picture and you all you see that you have taken this grey color is actually an intact thin film, and you see that there are some holes which have just started to appear (Refer Slide Time :15:47). So, these holes you now understand has appeared due to spinodal instability. So, this was a this was a spinodally unstable film, these holes are just started to appear (Refer Slide Time: 16:17).

(Refer Slide Time: 16:30)



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Polystyrene (PS) Film MW - 280 K

↳ 25 nm Film thickness

Created by Spin Coating from a [dilute Solution in Toluene. (0.5% w/v).

100 μL → Solution is dispensed.

Rotate ~ 1 min @ RPM: 2500.]

Substrate used →

Silicon Wafer (Coated with Native Oxide Layer ~ 1.5 nm).

At Room temperature The Film Remains Intact]

Once the Film is heated beyond T_g → Significant drop in Viscosity.

So, we have a taken a polystyrene film, it is a very common model system, we will talk in greater detail about dewetting experiments. So, this film, the thickness was grossly of the order of 25 nanometer (No audio from 16:43 to 16:49) which was created by spin coating, from a solution, a very dilute solution in toluene, concentration lies between 0.5 percent width by volume, typically 100 micro liter solution is dispensed, we have talked about spin coating in greater detail.

So, each one of this parameters should make sense to you in a micro desolation is dispensed. And then, typically you rotate at an RPM rotate for one minute at an RPM of 2500 to get these type of 25 nanometer thick film, just would like to highlight the substrate used was a silicon wafer (No audio from 17:58 to 18:13) coated with relative oxide layer, thickness of which is 1.5 nanometer. So, once this film has been coated, then the solvent evaporates, these are long chain polystyrene molecules, the molecular weight is around 280 K. So, they are highly long chain molecule in an entangled state.

So, at room temperature they behave more like a amorphous solid, amorphous solid film. So, you do not, irrespective of whether the film id thermodynamically stable or not, which we have not distinguished or talked in greater detail as of now. But what you can understand that, whether the film, it has been sprayed of a (( )) surface or not irrespective of that, this film remains intact at room temperature.

So, so at room temperature (No audio from 19:13 to 19:32) at room temperature, the film remains intact. Now, in order to manifest the dewetting in order to manifest the dewetting or in order to trigger the dewetting, what is typically done is that the film is heated on its glass transition temperature. So, once the film (No audio from 19:54 to 20:04) (Refer Slide Time: 19:54), then there is a significant drop in the viscosity (No audio from 20:09 to 20:17) (Refer Slide Time: 20:09). And then, depending on the attractive introduction forces, let us say this fluctuation can amplify at at a temperature lower than the glass transition temperature, the material is too stiff so that these fluctuations do not manifest, it behaves more like a solid. So, irrespective of its thermodynamically thermo dynamic stability, the film is the the system is kinetically stabilized, so nothing happens.

One can look into the Deborah's number, essentially which talks about the time scales and the, at room temperature the the system might become, eventually become unstable, because it is a thermodynamically unstable, it remains a thermodynamically unstable system, but it is going to take infinite time.

However, once the film is now heated beyond glass transition temperature, and the viscosity has dropped. So, what happens is that, the the film is now a more in a liquid form. So, this fluctuations now manifest at the surface, and now depending on the interfacial interaction, nature of the interfacial interaction, the liquid-air interface or the film-air interface that is, this interface is now in a position to deform or the the attractions. So, so or the, this interface is can now deform to these interface, the the magnitude of the interfacial forces, because which talking about the AFM, we also picked up cantilevers, which were soft enough so that the deformed due to the interfacial forces.

So, essentially here also, the same thing happens in a once that film is in a liquid form. So, they start deforming to the interfacial forces and then the the fluctuations can amplify (()). So, what you are seeing now on the computer screen is a scenario, where the film has just ruptured and the holes have just started to appear. So, once you heat it further, you are now, in that you see the holes are growing and the there is some additional dynamics that is occurring over here (Refer Slide Time: 22:28). So, these holes grow and eventually it results in some isolated droplets, one can see.

So, this is the video you just saw where it is in a little smaller size now, you have these wholes which are appearing, then the holes grow. And eventually at the late stage, they form some isolated drops, you can see here a higher magnification what happens at the late stage, so you see some polymer ribbon like structures, and then these ribbons eventually break down, this ribbons becomes unstable and they break down forming a random isolated polymer drops.

So, this lets (()) break the, breaking down of the ribbons are attributed to a form of instability which is very well known and which we have already covered, I will show you this video again, which we have already covered as a part of this course and it is nothing other than the Rayleigh instability.

So, essentially we have some very thin threads of polymer which now disintegrate due to Rayleigh instability, resulting in final divided droplets. So, now, what you have seen, you have actually had a firsthand look under a real time microscope, may be the dynamics can be a little (()) depending on the molecular (()) but which can, which might have been a little bit exaggerated.

So, let us have a quick look at both the movies again. So, here is it, you have some isolated holes appearing due to the mechanism we have talked here, I will repeat. So, here you see the holes, the holes at the appearance of the holes is due to (No audio from 24:07 to 24:16) amplification of thermally excited capillary waves due to attractive interfacial interaction.

And so, you have seen that the holes have just appeared, and then the subsequent section is the growth of the holes and dewetting of the film on the substrate, which we have not yet talked so far and which we will take have been a subsequent (()), but you can just have a look at what happens so the holes grow, and then there can be different morphologies depending on a very a host of parameters. So, on the right hand side of the stream, you have the whole sequence of a film dewetting the different stages which are written.

So, the first two should make sense to you as of now, because the first one is the formation of these undulations, which is the capillary wave we are talking about and that the thermally excited capillary waves and in the event that they they are amplified, because of attractive interfacial interaction, it results in the formation of holes. The subsequent four stages are also very common, but I think we will discuss it at a subsequent class when we talk in greater detail about dewett, the different stages associated with dewetting.

And here is again a, a quick look at the, what happens at the late stage. So, this is interesting, you have at a stage, at an intermediate stage and these are all part of this second stage which we which we have not yet discussed, the dewetting sequence.

So, dewetting sequence is yet to be discussed is a part of dewetting sequence towards the latter stages, this polymer feds sort of a break into isolated droplets due to Rayleigh instability, so this part we will take up later.

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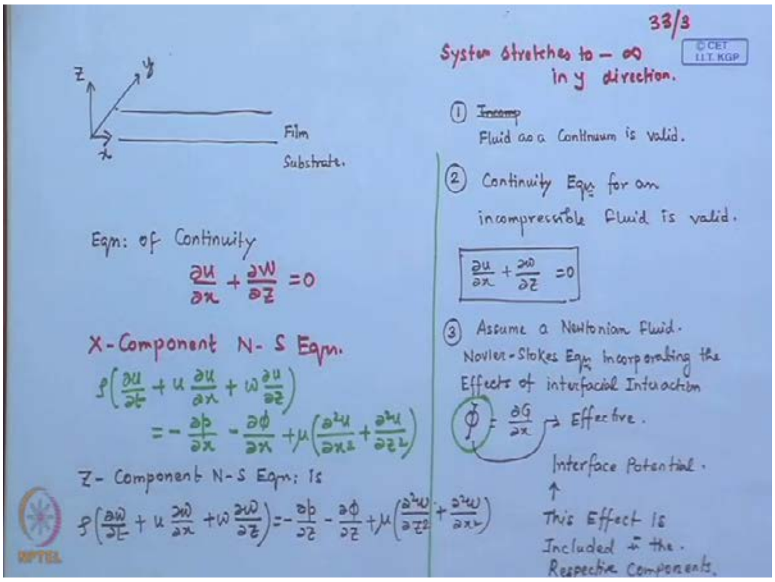

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Eqn: of Continuity

$$\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} = 0$$

X-Component N-S Eqn.

$$\rho\left(\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + w\frac{\partial u}{\partial z}\right) = -\frac{\partial p}{\partial x} - \frac{\partial \phi}{\partial x} + \mu\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial z^2}\right)$$

Z- Component N-S Eqn: Is

$$\rho\left(\frac{\partial w}{\partial t} + u\frac{\partial w}{\partial x} + w\frac{\partial w}{\partial z}\right) = -\frac{\partial p}{\partial z} - \frac{\partial \phi}{\partial z} + \mu\left(\frac{\partial^2 w}{\partial z^2} + \frac{\partial^2 w}{\partial x^2}\right)$$

System stretches to − ∞ in y direction.

① ~~Incomp~~ Fluid as a Continuum is valid.

② Continuity Eqn for an incompressible fluid is valid.

$$\boxed{\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} = 0}$$

③ Assume a Newtonian Fluid. Navier-Stokes Eqn Incorporating the Effects of interfacial Interaction

$$\phi = \frac{\partial G}{\partial x} \rightarrow \text{Effective.}$$

Interface Potential.

↑

This Effect is Included in the Respective Components.

But let us now try to quantify mathematically how a film becomes unstable, and what are the conditions under which a film becomes a unstable, and a thin film becomes spontaneously unstable, and based on that we try to distinguish a stable, unstable and a meta stable film.

So, the background information or the background equations that we may want to have is that, we have a incompressible. So, in other words, let us started with fluid as a continuum is still valid though we are talking about a very thin film, the second thing is the continuity equation for a incompressible (No audio from 27:56 to 28:02) fluid is valid which takes the form (Refer Slide Time: 28:06), we assume that the flow is extremely wide. So, these are, this is my coordinate system, this is our coordinate system this is x and this is z, we assume that the system stretches to infinity in the y direction. And therefore, all the derivatives with there is no (No audio from 28:29 to 28:42) variation of the flow properties in y direction (Refer Slide Time: 28:29). So, essentially we are talking about a two dimensional flow.

We further assume which can be sort of a little bit of a counter intuitive, assuming the fact that we are talking about a polymer, we assume an Newtonian fluid and it turns out that the assumption works rather well, Newtonian fluid and the governing equations are the Navier-Stokes equation (No audio from 29:14 to 29:20) incorporating the effect of interfacial interaction. So, we essentially incorporate phi which is del G del x and is phi is known as the effective interface potential or the, these effect is is included in the respective components (No audio from 30:14 to 30:26) of the Navier-Stokes equation.

So, the equations essentially take the fault of, so this is my equation, this is our equation of continuity which is (No audio from 30:49 to 30:58) then we have a scenario, like the x component Navier-Stokes is (No audio from 31:12 to 31:28) extended Navier-Stokes equation for a 2 D system this is the only additional term where we incorporate the influence of the interfacial interaction in the form of considering the phi (Refer Slide Time: 31:00).

We will come to the expression of phi, but for the time being you just understand that phi bears the signature of the interfacial interaction, something which is absent in a macroscopic flow and therefore, we never consider it. And the z component (No audio from 32:04 to 32:45) (Refer Slide Time: 32:04). So, these are the essentially the three equations which we will be using one can sorry, one can write it as (( )), the cyclic form nothing was wrong in the way I wrote it, but may be you just wanted to have it in this form (Refer Slide Time: 32:57).

In addition, so this is my equation of continuity, this is my x component of Navier Stokes equation, this is my z component of Navier Stokes equation (Refer Slide Time: 33:09). In addition to these there are certain additional equations which are active in the background, the first thing is that though we assume a film, a flat film, we understand that the top surface is not flat, this is important. So, the movement the top surface is not flat, there is the pressure is not uniformed at the outside and inside of the film.

So, if this is exposed to atmosphere, you cannot say that the entire film surface, the first layer inside the liquid layer is at p atmosphere, instead you have a special variation of Laplace pressure, because of the curvature effect of the non flatness of the film surface.

So, consequently what we have is that, the young Laplace equation is valid on the on the surface and the other thing, we assume that we regard these undulations to be axisymmetric.

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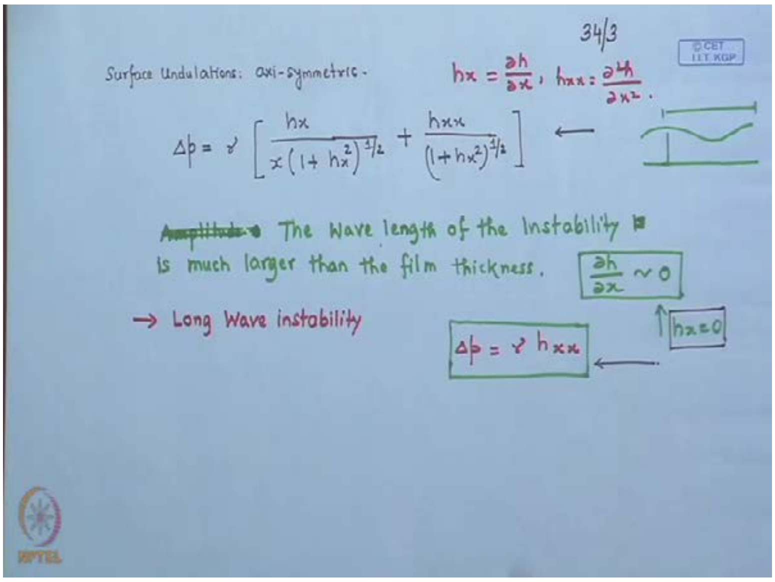

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Surface Undulations: axi-symmetric.

$h_x = \frac{\partial h}{\partial x}$, $h_{xx} = \frac{\partial^2 h}{\partial x^2}$.

$$\Delta p = \gamma \left[\frac{h_x}{x(1+h_x^2)^{1/2}} + \frac{h_{xx}}{(1+h_x^2)^{3/2}} \right] \longleftarrow$$

~~Amplitude~~ The wave length of the Instability is much larger than the film thickness.

$$\boxed{\frac{\partial h}{\partial x} \sim 0}$$

$$\uparrow \boxed{h_x = 0}$$

→ Long Wave instability

$$\boxed{\Delta p = \gamma h_{xx}} \longleftarrow$$

So, the surface undulations (No audio from 34:41 to 34:52) and consequently, the form of young Laplace equation that is, that can be used is this one, we have already done this derivation (Refer Slide Time: 34:58). So, refer to your previous class notes, or refer to some of the previous lectures for detail derivation of this in within the, I think the first seven or eight lectures its self we did this detail derivation, considering the helm holes free energy which leads to, our essential motivation was to find out the geometry of the surface which corresponds to a minimum thermodynamic energy criteria.

And the same thing is held also here, yesterday or the previous few lectures, we have talked about the sin of delta g and we have argued that two surfaces or or a film will rupture, depending on the scenario where delta g becomes negative or sort of a ruptured film results or leads to further reduction of the energy.

So, the basic motivation based on which we did this derivation, and based on which a spontaneous, a a intact thin film becomes spontaneously unstable, they are same, both are both have the same motivation of energy minimization.

Now, what we all, so what this equations gives you or if you look at how we derived it, it gives you that h or which is the film thickness is h. So, what it implies that h is not uniform and h is a junction of x.

Now, what we can do here, we can we can regard that the amplitude or the the wave length of the instability is much larger than the film thickness, which implies that del h del x is nearly equal to 0. So, it is a it is like this, it is much larger as compared to the film thickness. So, del h del x is equal to 0, this is what is known as the long wave instability (No audio from 38:02 to 38:12).

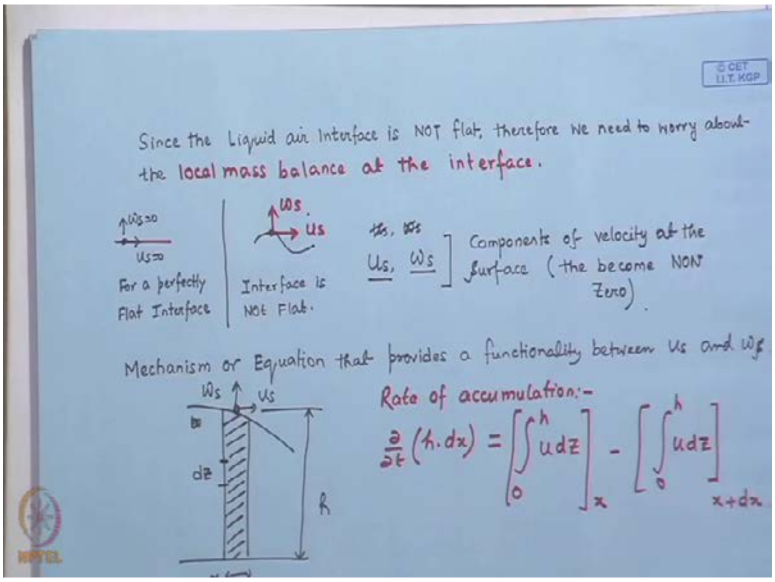
So, if you now plug in the condition of long wave long wave instability, let me just remind this h x in this equation, implies del h del x, h x x refers to del 2 h del x square and so on. So, if we now plug in the condition of long wave instability into the young Laplace equation, or the expression for young Laplace equation for a axisymmetric surface, we get a very neat expression for young Laplace equation which is delta p into gamma terms h x x.

Now, please do not confuse yourself with the fact that if h x is equal to 0. So, this implies that h x is equal to 0, please do not confuse yourself with the fact that if h x is equal to 0, h x x also has to be 0, you just refer to a basic fundaments about optimization or maximum minimum, what you do, you take a you have a function y equal to f x, the necessary condition for finding the minima, the optima is you set the f dash x is equal to 0. And then evaluate that x, and then you find out what you typically do is, you find out the sin of a double dash x. So, check out whether it is positive or negative, and based on that, you tell whether it is a minima or maxima.

So, there is a set of a huge set of problems where you have already encountered that at a specific x, f dash x is equal to 0, but f double dash x is not equal to 0. While teaching in the class, I have often encountered this question from students that well, sir h x h x is equal to 0, then one should also set h double dash is equal to 0, and immediately one gets the delta p should be equal to 0 which essentially implies that you are now looking at a perfectly flat interface which is not the case.

So, please do not confuse the condition of long wave instability, which in other wise in simple words means that the wave length of the instability is much much higher as compared to the film thickness, results in sort of a very very sort of an, sort of relax slopes or curvature of the film surface which means that del h del x is equal to 0 and you plug it in to get this form of the young Laplace equation. So, along with the three governing equations, which I we have listed in this, these are the three governing equations, we have a forth equation which we will be leading to use.

(Refer Slide Time: 40:54)



Since the Liquid air Interface is NOT flat, therefore we need to worry about the **local mass balance at the interface.**

For a perfectly Flat Interface

Interface is NOt Flat.

~~us, ws~~ $\underline{u_s}$, $\underline{w_s}$] Components of velocity at the surface (the become NON Zero).

Mechanism or Equation that provides a functionality between u_s and w_s

Rate of accumulation:-

$$\frac{\partial}{\partial t}(h.dx) = \left[\int_0^h u\,dz\right]_x - \left[\int_0^h u\,dz\right]_{x+dx}$$

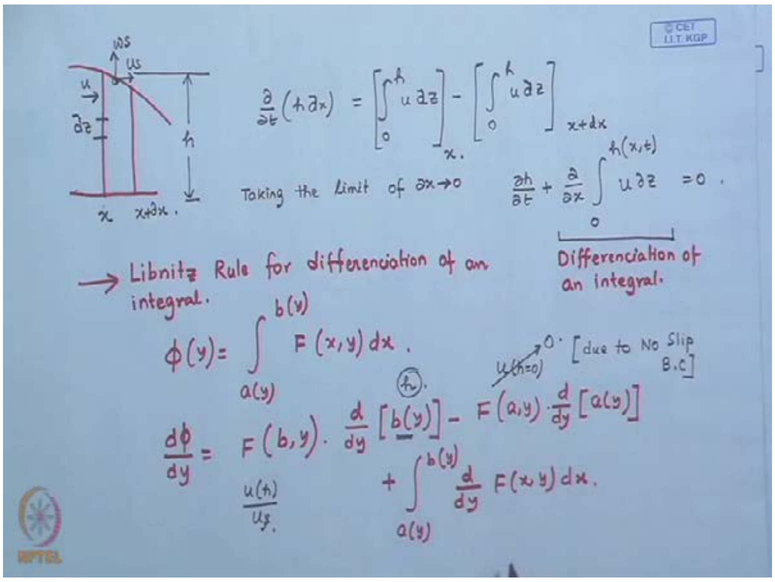
Now, the other condition we need to look at is that, since the liquid-air interface is no longer flat (No audio from 40:54 to 41:12), we need to care about the local mass balance at the interface (No audio from 41:17 to 41:42) or in other words, what it means that this is a flat interface.

So, we argued that for a flat interface, the surface, the velocities, the components of the surface velocities will be 0 (No audio from 42:00 to 42:12) (Refer Slide time: 41:50). However, what happens here is that, you have an an interface which is no longer flat (No audio from 42:22 to 42:30), this means that there are u s and w s, these are the components of surface velocity, are components of, they become non zero or they exist (Refer Slide time: 42:33).

So, we have to worry about some sort of a local mass balance at the interface or in other words, we need to worry about a mechanism to (No audio from 43:31 to 43:40) that provides functionality between u s and w s. So, for that we consider a mass balance about the shaded area (No audio from 44:09 to 44:24), let us say this is the local height of the film which is h, this is w s (Refer Slide Time: 44:09). So, if we just calculate the rate of accumulation (No audio from 44:40 to 44:49), what we can find out del del t into h d x, of course the density remains constant is integral 0 to h u d z x minus integral 0 to h u d z at x plus d x.

So, this integral refers to the amount of liquid that centering from this phase for for the entire height 0 to h, and this refers to the amount of liquid that is leaving or entering, do not be worried about whether it is leaving or entering, because the appropriate sign of u will be there to take care of it.

(Refer Slide Time: 45:47)



$$\frac{\partial}{\partial t}(h\,\partial x) = \left[\int_0^h u\,\partial z\right]_{x.} - \left[\int_0^h u\,\partial z\right]_{x+dx}$$

Taking the limit of $\partial x \to 0$

$$\frac{\partial h}{\partial t} + \underbrace{\frac{\partial}{\partial x}\int_0^{h(x,t)} u\,\partial z}_{\text{Differenciation of an integral.}} = 0.$$

→ Libnitz Rule for differenciation of an integral.

$$\phi(y) = \int_{a(y)}^{b(y)} F(x,y)\,dx.$$

$$\frac{d\phi}{dy} = \underset{\frac{u(h)}{u_s.}}{F(b,y)}\cdot\frac{d}{dy}\left[\underline{b(y)}\right] - \overset{\cancel{u(h=0)}\nearrow 0.\ [\text{due to No Slip B.C}]}{F(a,y)}\cdot\frac{d}{dy}\left[a(y)\right] + \int_{a(y)}^{b(y)}\frac{d}{dy}F(x,y)\,dx.$$

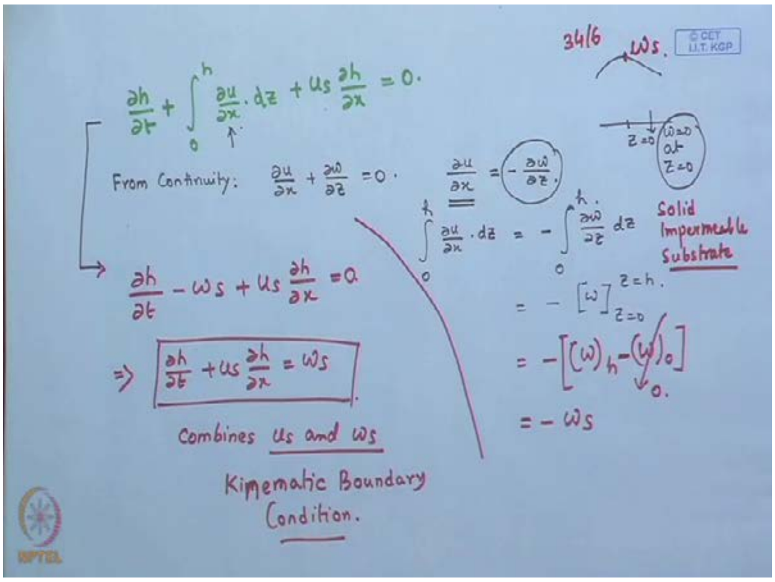
ⓗ.

So, I will just quickly re draw this figure (No audio from 45:49 to 46:12), so the rate of accumulation is del del t into h d x, of course we assumed that it stretches the infinity in the y direction (No audio from 46:22 to 46:35) (Refer Slide Time: 45:46). So, taking the limit (No audio from 46:40 to 46:48) of d extending to 0, we essentially get to the equation h itself is a function of x and t (Refer Slide time: 47:05).

So, this is essentially we need to apply to evaluate this integral, this is your first year mathematics, we need to this is essentially the differentiation of an integral as you can see as you can see and you need to apply the Leibniz rule for differentiation of an integral, and what we have that phi y is equal to (No audio from 48:15 to 48:27) del phi del y is given as F b y into d d y of b y minus F a y into d d y of a y plus, you can look at any standard mathematics text book like crazy or whatever to find out this, so this is the Leibniz rule, if you apply this, what you get and this is our equation (Refer Slide Time: 48:12). So, if you apply this we will get F b y here is u at h, which we are terming as u s, F a y here is u at h is equal to 0 that is at the bottom surface which is 0 due to no slip boundary condition (No audio from 49:42 to 49:51) (Refer Slide time: 49:12).

And b y is nothing but, the film thickness actually in our case. So, this term remains, this term vanishes and this term essentially takes the shape integral of a is 0, p is h, f is essentially u here del u del x into del z in our setting, so if you do that carefully into this equation (Refer Slide Time: 49:57).

(Refer Slide Time: 50:32)



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$$\frac{\partial h}{\partial t} + \int_0^h \frac{\partial u}{\partial x} . dz + u_s \frac{\partial h}{\partial x} = 0.$$

From Continuity: $\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} = 0.$

$$\frac{\partial u}{\partial x} = -\frac{\partial w}{\partial z}.$$

$$\int_0^h \frac{\partial u}{\partial x} . dz = -\int_0^h \frac{\partial w}{\partial z} dz$$

$$= -[w]_{z=0}^{z=h.}$$

$$= -[(w)_h - \cancel{(w)_0}]$$

0.

$$= -w_s$$

w_s.

$z=0$

$w=0$ at $Z=0$

Solid Impermeable Substrate

$$\frac{\partial h}{\partial t} - w_s + u_s \frac{\partial h}{\partial x} = 0$$

$$\Rightarrow \boxed{\frac{\partial h}{\partial t} + u_s \frac{\partial h}{\partial x} = w_s}$$

Combines u_s and w_s

Kinematic Boundary Condition.

Then, what you get in the final form is that, del h del t plus integral 0 to h del u del x into del z plus u s del h del x is equal to 0.

So, this is a simple, you just have to plug in, do this integral assuming, understanding that, here your a is u and x is z. So, you just do the integration, plug it in into the Leibniz rule and I have also written the individual terms which will come in. So, just check it out if you can do it yourself and finally, we will get to this expression.

Now, from continuity (No audio from 51:22 to 51:29), we have del u del x plus del w del z is equal to 0, considering that there is no variation in the y direction. Therefore, what comes out is del u del x is equal to minus del w del z, you substitute this expression of del u del x over here to get from this equation, you get or you can write it, therefore integral of del u del x into del z evaluated between 0 and h, turns out to be minus integral of del w del z, del z evaluated between 0 and h, and this turns out to be minis w evaluated at z is equal to 0 and z is equal to h, so this is the film.

So, this is z is equal to 0 and you are talking about w, w is equal to 0 at z is equal to 0, because of the fact this is not because of no slip, but this is because of the fact that you have a solid substrate, solid impermeable substrate. And therefore (No audio from 52:53 to 53:02) this term tends to 0 and w at h, it is over here is nothing but w s, so the second term leads to minus w s. So, if you substitute that you eventually have the expression of the equation as del h del t minus w s plus u s del h del x is equal to 0, or if you reorganize del h del t plus u s del h del x is equal to w s. So, here is an equation that sort of now you can see bridges or combines the u s and w s. So, this is the fifth equation, we will be needing to evaluate our system or understand the dynamics of our system.

So, I will just do a quick recap before proceeding further. So, we are now looking at the mathematical formulation of the condition under which a thin film can become unstable. So, we have taken a thin film like this, and we have argued that there is no variation in the y direction. So, the film is quoted on top of a solid surface and what we have is the fluid as a continuum is valid, a continuity equation for 2 D flow neglecting the variation in y direction and for an incompressible fluid is this. It is a Newtonian fluid and in the Navier-Stokes equation remains the governing equation, we have a incorporated the effect of the effective interface potential which gives us the equation of continuity and the x and y x and z components Navier-Stokes equation like this.

Then since, we have a surface which is no longer perfectly flat, therefore we assume there is a surface is undulated, therefore there is variation of a Laplace pressure which we have therefore, we have considered the young Laplace equation, only thing we have to consider that the undulations are axisymmetric. Therefore, this form of young Laplace equation we can use, into that we have now assumed that the nature of the instability is long wave which makes del h del x is equal to 0.

So, we have plugged in the long wave, instead the condition for the long wave instability, instability has been plugged in here and which give to this form of the young

Laplace equation. And finally, since we understand that the flat off surface is not flat, we are looking for an equation that sort of combines the influence of the surface components, the components of velocity at the surface that is u s and w s which we have done by based on sort of a local mass balance. And for that in order to in order to get to that equation, we have to invoke the Leibniz rule for differentiation of an integral.

And eventually that has given us with appropriate manipulation, little bit of very simple algebraic manipulation which am sure if you look carefully and try it couple of times, you will be able to do it yourself, gets to this equation which is known as the kinematic boundary condition (No audio from 56:30 to 56:37).

Our next lecture, we will start our discussion from these set of governing equations and see based on the linear stability analysis, how we can identify or distinguish a film which is stable, unstable and meta stable, thank you.