Instability & Patterning of Thin Polymer Films

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Lecture No. # 35

Spontaneous Instability & Dewetting of Thin Polymer Film-V

Welcome back, we will continue our discussion on the linear stability analysis, which we were performing for trying to understand the Spontaneous Instability of an ultra thin liquid film.

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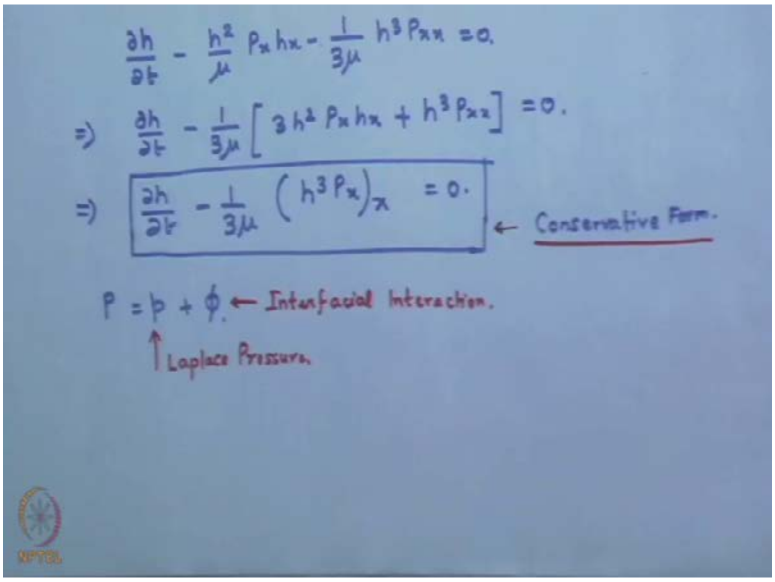

$$\frac{\partial h}{\partial t} - \frac{h^2}{\mu} P_x h_x - \frac{1}{3\mu} h^3 P_{xx} = 0.$$

$$\Rightarrow \frac{\partial h}{\partial t} - \frac{1}{3\mu}\left[3h^2 P_x h_x + h^3 P_{xx}\right] = 0.$$

$$\Rightarrow \boxed{\frac{\partial h}{\partial t} - \frac{1}{3\mu}\left(h^3 P_x\right)_x = 0.} \leftarrow \text{Conservative Form.}$$

$$P = \underset{\uparrow \text{ Laplace Pressure.}}{p} + \phi. \leftarrow \text{Interfacial Interaction.}$$

You, may recall that in the previous class, we reached up to we were doing the derivations. So, we were looking at the order of magnitude analysis of the governing equation and incorporating the appropriate conditions, which include the kinematic boundary condition and other conditions that we have been looking in, so we have reached up to this stage; so this is a quick recap I would like to do.

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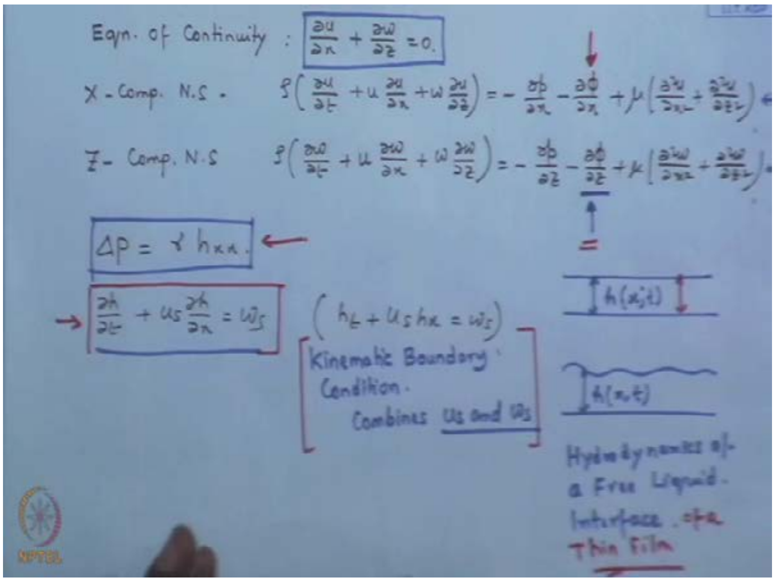

Eqn. of Continuity : $\boxed{\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} = 0.}$

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

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

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

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

$(h_t + u_s h_x = w_s)$

Kinematic Boundary Condition.
Combines u_s and w_s

Hydrodynamics of a Free Liquid Interface of a Thin Film

So, we started of with the continuity equation and the x and y component, x and z component navies stoke equation understanding or plugging in our concept of a fluctuating interface instead of a completely flat interface. And we also derive two classes before the condition of the kinematic boundary condition, which which takes care of the surface fluctuations are non zero interfacial velocities.

And once we started looking into, so these are the set of equations that we have looked into, continuity the x and z component navies stokes equation along with the the young Laplace equation for an axis symmetric surface. Simplified for the long way of approximation and this is the kinematic boundary condition, we started to do an order of magnitude analysis; we just discussed briefly what an order of magnitude analysis is.

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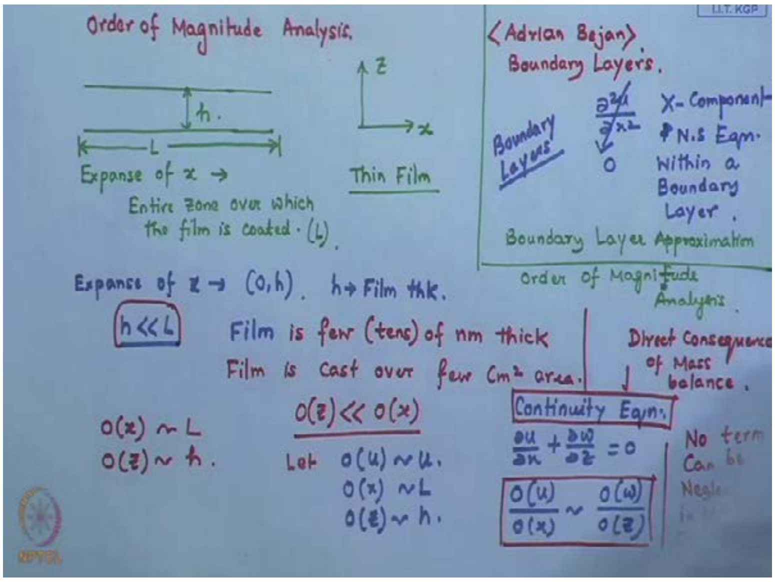

Order of Magnitude Analysis.

Expanse of $x \rightarrow$
Entire zone over which the film is coated. (L).

Thin Film

Expanse of $z \rightarrow (0,h)$. $h \rightarrow$ Film thk.

$\boxed{h \ll L}$ Film is few (tens) of nm thick
Film is cast over few Cm^2 area.

$O(x) \sim L$
$O(z) \sim h$.

$O(z) \ll O(x)$

Let $O(u) \sim U$.
$O(x) \sim L$
$O(z) \sim h$.

⟨Adrian Bejan⟩.
Boundary Layers.

Boundary Layers
$\cancel{\frac{\partial^2 u}{\partial x^2}} \rightarrow 0$
X-Component N.S Eqn. Within a Boundary Layer.

Boundary Layer Approximation

Order of Magnitude Analysis.

Direct Consequence of Mass balance.

Continuity Eqn.

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

$\boxed{\frac{O(u)}{O(x)} \sim \frac{O(w)}{O(z)}}$

No term Can be Negl

And that eventually showed us which are the relevant and which are the non relevant terms.

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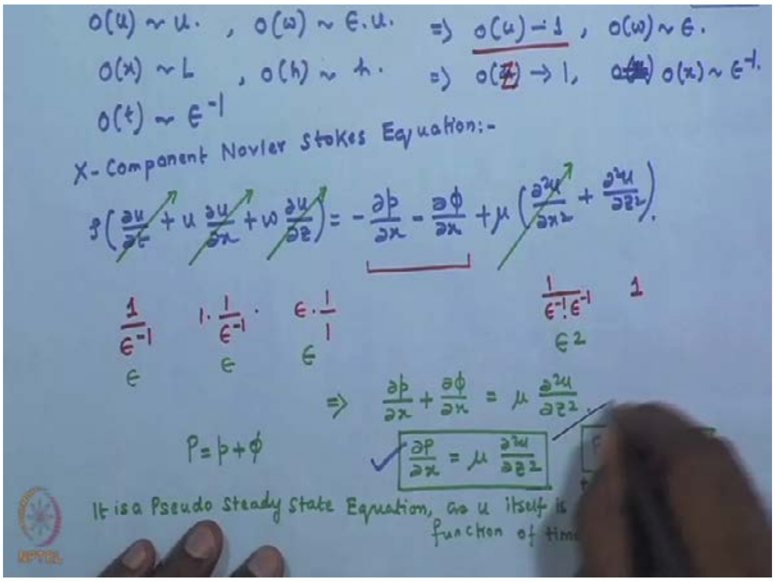

$O(u) \sim U$. , $O(w) \sim \epsilon.U$. $\Rightarrow$ $O(u) \sim 1$, $O(w) \sim \epsilon$.
$O(x) \sim L$, $O(h) \sim h$. $\Rightarrow$ $O(z) \rightarrow 1$, $O(x) \sim \epsilon^{-1}$.
$O(t) \sim \epsilon^{-1}$

X-Component Navier Stokes Equation:-

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

$\frac{1}{\epsilon^{-1}}$ $\quad 1.\frac{1}{\epsilon^{-1}}$. $\quad \epsilon.\frac{1}{1}$ $\quad \frac{1}{\epsilon^{-1}.\epsilon^{-1}}$ $\quad 1$

ϵ $\quad \epsilon$ $\quad \epsilon$ $\quad \epsilon^2$

$$\Rightarrow \frac{\partial p}{\partial x} + \frac{\partial \phi}{\partial x} = \mu \frac{\partial^2 u}{\partial z^2}.$$

$P = p + \phi$

$$✓ \boxed{\frac{\partial P}{\partial x} = \mu \frac{\partial^2 u}{\partial z^2}}$$

It is a Pseudo Steady State Equation, as u itself is function of tim

And finally, this is the form of the final governing equation, which we obtained from the x component navier stokes equation.

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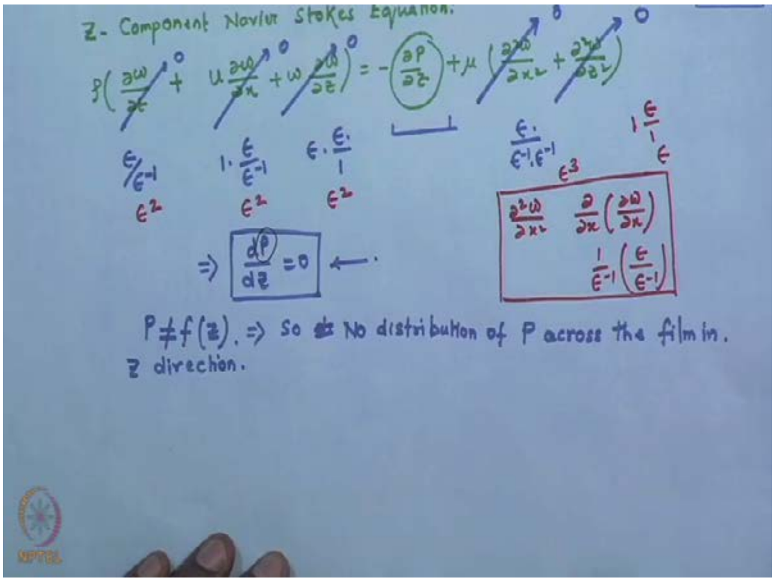

Z- Component Navier Stokes Equation.

$$\rho\left(\cancel{\frac{\partial w}{\partial t}}^{0} + u\cancel{\frac{\partial w}{\partial x}}^{0} + w\cancel{\frac{\partial w}{\partial z}}^{0}\right) = -\frac{\partial P}{\partial z} + \mu\left(\cancel{\frac{\partial^2 w}{\partial x^2}}^{0} + \cancel{\frac{\partial^2 w}{\partial z^2}}^{0}\right)$$

ϵ/ϵ^{-1} $\quad 1\cdot\frac{\epsilon}{\epsilon^{-1}}$ $\quad \epsilon\cdot\frac{\epsilon}{1}$ $\quad \frac{\epsilon}{\epsilon^{-1}\cdot\epsilon^{-1}}$ $\quad 1\frac{\epsilon}{1}$

ϵ^2 $\quad \epsilon^2$ $\quad \epsilon^2$ $\quad \epsilon^3$ $\quad \epsilon$

$\frac{\partial^2 w}{\partial x^2}$ $\quad \frac{\partial}{\partial x}\left(\frac{\partial w}{\partial x}\right)$ $\quad \frac{1}{\epsilon^{-1}}\left(\frac{\epsilon}{\epsilon^{-1}}\right)$

$$\Rightarrow \boxed{\frac{dP}{dz} = 0} \leftarrow$$

$P \neq f(z)$. ⇒ So No distribution of P across the film in. z direction.

We also obtained d p, p is the non gravitational pressure d p d z is equal to 0 from the z component of navier stokes equation.

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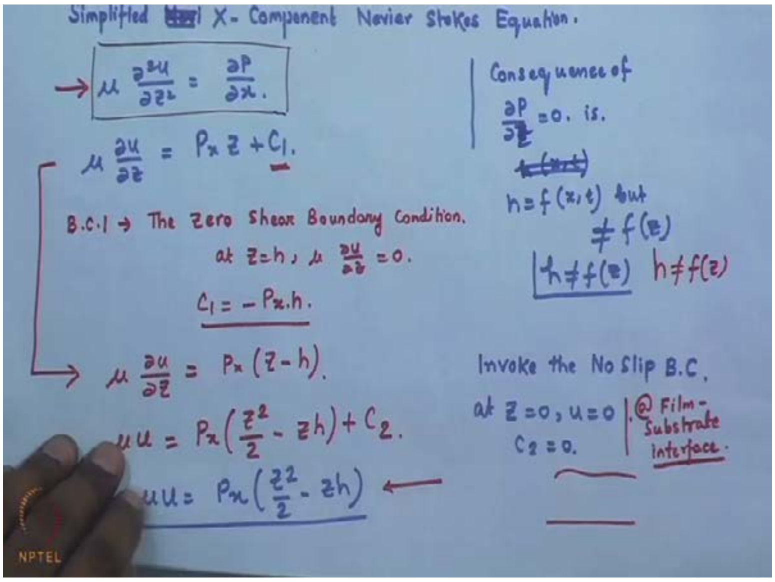

Simplified X- Component Navier Stokes Equation.

$$\rightarrow \boxed{\mu\frac{\partial^2 u}{\partial z^2} = \frac{\partial P}{\partial x}.}$$

$$\mu\frac{\partial u}{\partial z} = P_x z + C_1.$$

B.C.1 → The Zero Shear Boundary Condition.

at $z = h$, $\mu\frac{\partial u}{\partial z} = 0$.

$C_1 = -P_x . h.$

$$\mu\frac{\partial u}{\partial z} = P_x(z-h).$$

$$\mu u = P_x\left(\frac{z^2}{2} - zh\right) + C_2.$$

$$\mu u = P_x\left(\frac{z^2}{2} - zh\right) \leftarrow$$

Consequence of $\frac{\partial P}{\partial z} = 0$. is.

~~$h = f(x,t)$~~

$h = f(x,t)$ but $\neq f(z)$

$h \neq f(z)$ $\quad h \neq f(z)$

Invoke the No Slip B.C.

at $z = 0$, $u = 0$ | @ Film-Substrate interface.

$C_2 = 0.$

And then we started to work with the governing equation for the system started to integrate it with appropriate boundary conditions.

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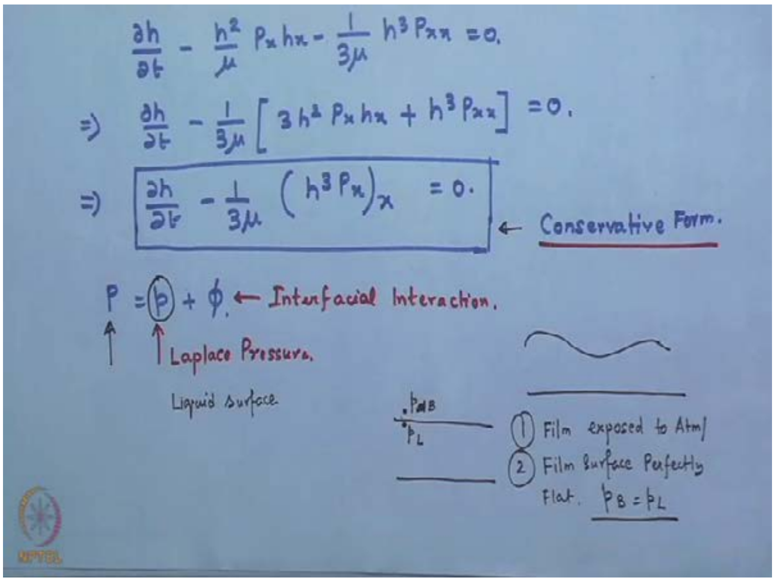

$$\frac{\partial h}{\partial t} - \frac{h^2}{\mu} p_x h_x - \frac{1}{3\mu} h^3 p_{xx} = 0.$$

$$\Rightarrow \frac{\partial h}{\partial t} - \frac{1}{3\mu}\left[3h^2 p_x h_x + h^3 p_{xx}\right] = 0.$$

$$\Rightarrow \boxed{\frac{\partial h}{\partial t} - \frac{1}{3\mu}\left(h^3 p_x\right)_x = 0.} \leftarrow \text{Conservative Form.}$$

$$P = \textcircled{p} + \phi. \leftarrow \text{Interfacial Interaction.}$$

$\uparrow$ Liquid surface

$\uparrow$ Laplace Pressure.

① Film exposed to Atm/

② Film Surface Perfectly Flat. $p_B = p_L$

And which has finally, laid us to this particular point, which gives us del h del t is equal to 1 by 3 mu h 3 p x x in the in a conservative form.

We also understand the p is a function of pressure plus pi. Now, this pressure if we are considering the liquid surface had the film in perfectly flat, the pressure right at the surface on the liquid side p l or p s or whatever you want to write and let us say this is the p outside or p b. So, had this film been (No audio from 3:29 to 3:38) and (No audio from 3:40 to 3:48) perfectly flat, then we know that the surface been mechanical equilibrium, then p B would have been equal to p L.

But now that we understand that we have surface fluctuations (No audio from 04:02 to 04:12), which means that the surface is no longer flat therefore, p B is not equal to p L anymore. In fact p B, let us draw it separately.

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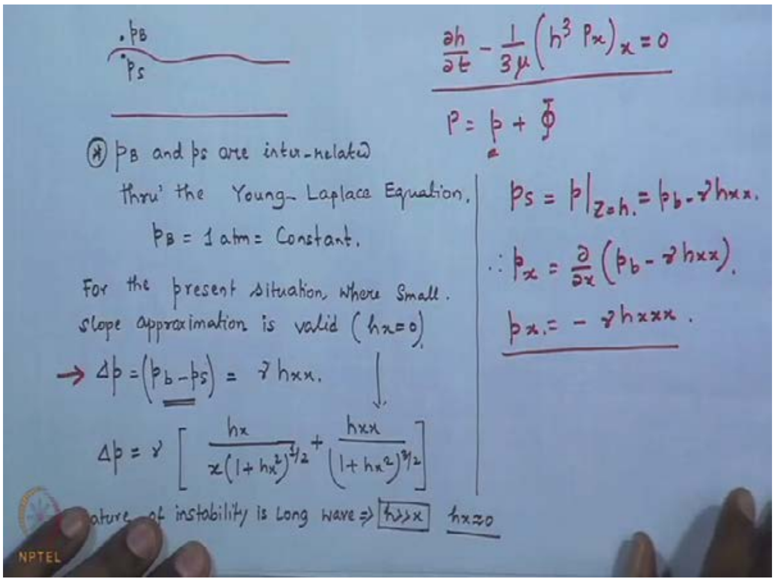

$$\frac{\partial h}{\partial t} - \frac{1}{3\mu}\left(h^3 P_x\right)_x = 0$$

$$P = p + \Phi$$

(*) p_B and p_s are inter-related thru' the Young-Laplace Equation.

$p_B = 1$ atm $=$ Constant.

For the present situation where Small slope approximation is valid ($h_x = 0$)

$$\rightarrow \Delta p = (\underline{p_b} - p_s) = \gamma h_{xx}.$$

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

ature of instability is Long wave $\Rightarrow \boxed{h \gg x}$ $\underline{h_x \approx 0}$

$$p_s = p|_{z=h} = p_b - \gamma h_{xx}.$$

$$\therefore p_x = \frac{\partial}{\partial x}\left(p_b - \gamma h_{xx}\right).$$

$$\underline{p_x = -\gamma h_{xxx}.}$$

So, this is the situation we have, this is the equation which we have derived up to this point, anyone who has a confusion about the origin of this equation or joining late please refer to the previous couple of lectures, which gives you a very clear idea about how this equation comes.

Now, we are do that P is equal to or we understand P is equal to p plus pi, we are now looking at this p at the interface, so over here. So, let us say that, this is p S and this is p B. Since the liquid is not flat, the film surface is not flat therefore, p B is not equal to p S and p B and p S are interrelated through the young Laplace equation.

If the film is exposed to atmosphere, then of course, p b is equal to 1 atmosphere and is equal to constant. So, what we have for the situation (No audio from 06:12 to 06:22), where a small slope approximation is valid that is h x is equal to 0, we have delta p which is p b minus p s in this is equal to gamma into h x x, this is the convention, so p b minus p s, so do not confuse the signs.

So, it remains like this therefore, it it gives us p b equal to gamma into h x x, let me just quickly remind that for an axis symmetric surface, this is the complete expression for the young Laplace equation. And if we assume that the nature of instability is long wave (No audio from 07:04 to 07:42), that is h is much larger than x, then of course, one gets each x is close to 0 and therefore, once you substitute that you get to this form of the young Laplace equation.

Now, what we get is p s is equal to essentially p evaluated at z is equal to h and which is p b minus gamma h x x therefore, p s p x if we differentiate it, so this is essentially you are looking at del l x of p b minus gamma h x x, p b is constant, so what you are left with is minus gamma h x x x.

Similarly, so this is one important parameter, now why we are looking into it is essentially we need to find out an expression for p x in this expression (Refer Slide Time: 08:53) and we know p is equal to small p that is the pressure the plus pi. So, we need to essentially, find out independently p x and pi and that precisely, what we are doing and in doing, so you see that, we now have an expression for p x.

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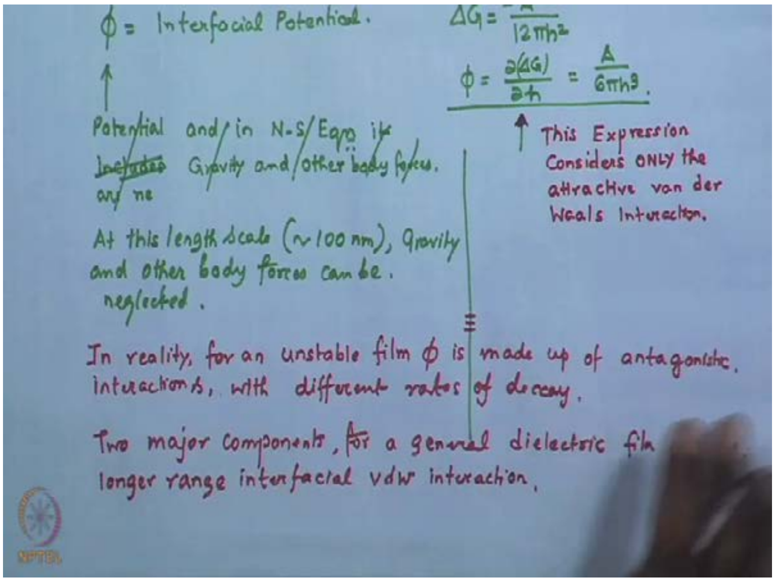

ϕ = Interfacial Potential.

$\Delta G = \frac{-A}{12\pi h^2}$

$\phi = \frac{\partial(\Delta G)}{\partial h} = \frac{A}{6\pi h^3}$.

Potential and / in N-S/ Eqn if ~~Includes~~ any ne Gravity and/other body forces.

↑ This Expression Considers ONLY the attractive van der Waals Interaction.

At this length scale (~100 nm), Gravity and other body forces can be. neglected.

In reality, for an unstable film ϕ is made up of antagonistic. interactions, with different rates of decay.

Two major components, for a general dielectric fil longer range interfacial vdw interaction.

Now, what is pi? Pi is the essentially it is the interfacial potential and which we have seen that considering the x based on the excess interfacial potential and from an expression of dill del G is equal to a minus A divide by 12 pi h square, which comes from the when considering the interfacial Van der Waals interaction, we have already have obtained an expression of pi, which is 6 pi h cube.

But these expression, please remember it comes from the only from the attractive Van der Waals interaction, so typically this pi is the potential and in navier stokes equation it includes gravity or let us gravity and other body forces are neglected or I will say that at this length scale. So, let it let me put it like this for simplicity, that at this length scale, which is of the order of roughly 100 nanometer, we have already argued that gravity other body forces can be neglected.

Of course, your talking of a situation, where you do not apply any external imposed electric or magnetic field and that is the reason, that they do not show up as the body forces. But, in cases where you you can you can apply essentially or in principle an electric field or a magnetic field to a thin film to restabilize it, I think we will take it up in one of the last lectures.

So, that is what is the situation, where the instability is triggered by the application of an external field rather than the spontaneous instability, that we are talking here, the only laviting thing about this particular expression though we will continue our discussion with this expression is that, this considers this expression considers only the attractive Van der Waals interaction.

A morph a rather, but in in reality for a for an unstable film pi is made up of antagonistic interactions with different rates of decay, two major components as we have already talked for a general dielectric film are the longer range interfacial Van der Waals interaction (No audio from 14:02 to 14:15). And rather short range satiric repulsion which any way we have talked about the hot c r model and the contact repulsion, because of the overlap of electron charge clouds, etcetera.

So, this is in essentially a satiric, so essentially the molecules are coming in contact with each other and therefore, manifests in the repulsion. So, these are the two general terms, which are most popular in a in a general dielectric film.

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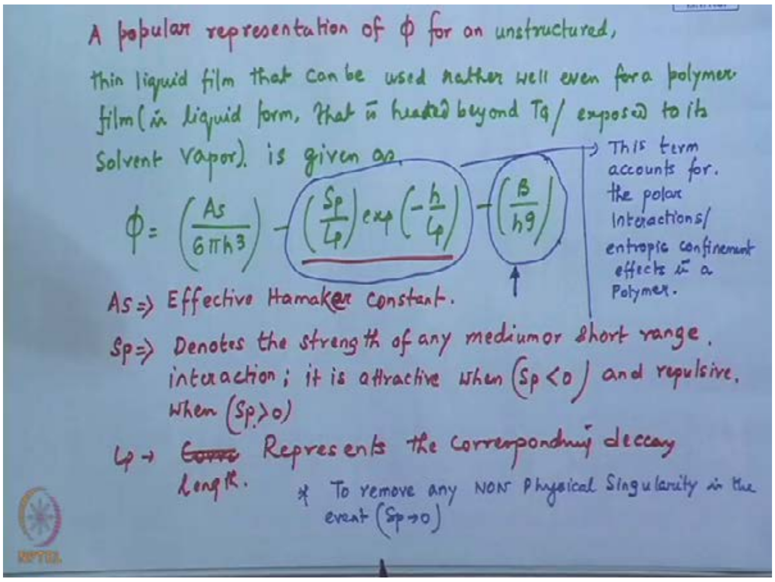


A popular representation of ϕ for an unstructured, thin liquid film that can be used rather well even for a polymer film (in liquid form, that is heated beyond T_g / exposed to its Solvent vapor). is given as

$$\phi = \left(\frac{A_s}{6\pi h^3}\right) - \boxed{\underline{\left(\frac{S_p}{l_p}\right)\exp\left(-\frac{h}{l_p}\right)}} - \boxed{\left(\frac{B}{h^9}\right)}$$

This term accounts for. the polar Interactions/ entropic confinement effects in a Polymer.

A_s ⇒ Effective Hamaker constant.

S_p ⇒ Denotes the strength of any medium or short range. interaction; it is attractive when $(S_p < 0)$ and repulsive. when $(S_p > 0)$

l_p → ~~Corre~~ Represents the corresponding decay length.

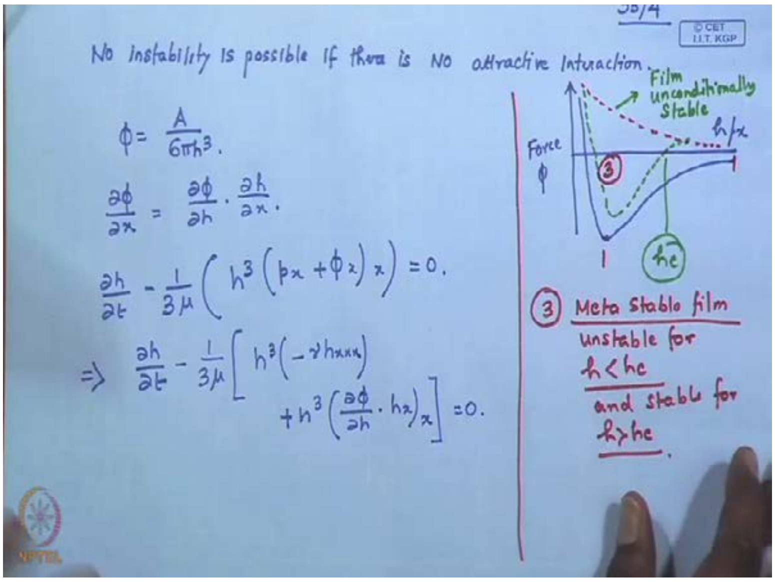
* To remove any NON Physical Singularity in the event $(S_p \to 0)$

A popular representation of pi (No audio from 15:03 to 15:18) for an unstructured thin liquid film that, can be used rather well even for a polymer film in liquid form that is heated beyond T G or exposed to its solvent vapor is given as pi is equal to A S. So, we just write A S for the effective haymaker constant for the system which we already know (No audio from 16:44 to 16:54).

Now, this term you can immediately see that, this term is the corresponds to the interfacial Van der Waals term. So, A S is the effective haymaker constant (No audio from 17:12 to 17:24), S P denotes the strength of medium or short range interaction with and it is it it denotes any medium or short range interaction it is attractive, when S P is less than 0. Because S p is less than 0 because; so and repulsive, when S P is greater than 0 and L P represents the corresponding decay length.

This terms sort of accounts for the A b type interaction or the polar interaction, so it is this term for the polar interaction as well as the any entropic confinement effects (No audio from 19:38 to 19:48) in in a polymer. So, this third term is rather interesting this is more of an artificial term and particularly included for simulation, which is present to remove any non physical singularity in the event S P tents to 0 that is, there is no repulsive term present in the system.

(Refer Slide Time: 21:34)



No instability is possible if there is No attractive Interaction.

$$\phi = \frac{A}{6\pi h^3}.$$

$$\frac{\partial \phi}{\partial x} = \frac{\partial \phi}{\partial h} \cdot \frac{\partial h}{\partial x}.$$

$$\frac{\partial h}{\partial t} - \frac{1}{3\mu}\left(h^3 \left(p_x + \phi_x \right)_x \right) = 0.$$

$$\Rightarrow \frac{\partial h}{\partial t} - \frac{1}{3\mu}\left[h^3 \left(-\gamma h_{xxx} \right) + h^3 \left(\frac{\partial \phi}{\partial h} \cdot h_x \right)_x \right] = 0.$$

③ Meta Stable film

unstable for $h < h_c$

and stable for $h > h_c$.

Because as we have already talked about that under the hydrodynamic frame work, no study of wetting or rewetting is possible until and unless there is a short range repulsion or repulsive terms are present. So, in the event there are no repulsive terms present in your system physically, you cannot run your simulations based on the hydrodynamic frame work or based on the way, we are performing the analysis that is considering the nervier stokes equation to be the governing equation.

So, you need to have sort of something is a non physical singularity a very local which sort of is (( )) to a local contact repulsion or something like that, that term has to be present. Of course, one has to understand, that no study of instability is possible if there is no attractive interaction or in other words no not only study, but no instability (No audio from 21:40 to 21:57). So, this is the you may want to recall that if if plot delta g verses the force potential verses h of the separation distance or x whatever, this is the type of a film which is going to be unstable.

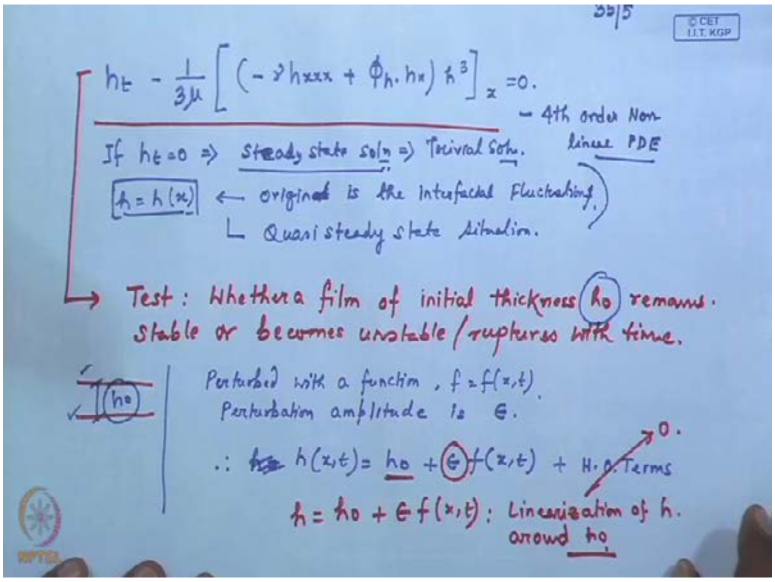
So, this this part of the system is rep is due to the attractive interaction, in case there is no attraction there is repulsion all the way, you will get a curve like this which will represent the film to be unconditionally stable at all conditions (No audio from 22:35 to 22:45). And this is a typical curve for a meta stable film, where one can say that, this is a critical thickness corresponding to that meta stable film, where the film is. So, the third curve represents the curve of a meta stable film, which is unstable for and stable for h greater than h c.

(Refer Slide Time: 23:34) So, yeah this is some bit of understanding that we need to have about the expression of the potential, the interface potential, but for all the analysis, we are looking at the possible origin of instability which is attributed as we have already talked; which is attributed to the interfacial attraction long range Van der Waals attraction that is the only reason of instability we are assuming (Refer Slide Time: 24:06). So, far or in other words the long range attractive or the attractive long range of Van der Waals interaction between these two interfaces is the only force that is responsible for instability that is what we are assuming.

So, we will limit or we will consider this expression of or may be you can write it a a expression of pi for our analysis (Refer Slide Time: 24:35), so coming back to pi we started to pick it up. So, we are essentially looking at this particular expression we have looking at p and we we would like to find out p x and in order to do that we need p x and pi x, p x we have already done. And we already have an expression for p x which means to be plugged in into our system and we also now have an expression for pi, so which we are going to use for our subsequent analysis.

So, what we have is at this point of time is pi is we need to find out del pi del x which turns out to be del pi del h as pi is a function of h and del h and del x. So, which if we now look back at our governing equation which is del h del t equation, where we started our discussion which now if you substitute the values of pi x and p x you will get.

(Refer Slide Time: 27:11)



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$$h_t - \frac{1}{3\mu}\left[\left(-\gamma h_{xxx} + \phi_h . h_x\right) h^3\right]_x = 0.$$

– 4th order Non linear PDE

If $h_t = 0 \Rightarrow$ Steady state soln $\Rightarrow$ Trivial Soln.

$\boxed{h = h(x)}$ ← originated is the Interfacial Fluctuating.

└ Quasi steady state situation.

Test : Whether a film of initial thickness (h_0) remains. Stable or becomes unstable / ruptures with time.

Perturbed with a function, $f = f(x,t)$.

Perturbation amplitude is ϵ.

$$\therefore h(x,t) = \underline{h_0} + \epsilon f(x,t) + \cancelto{0.}{\text{H.O. Terms}}$$

$h = h_0 + \epsilon f(x,t)$: Linearization of h. around $\underline{h_0}$

(Refer Slide Time: 26:31) So, that expression of p x we already have which we will simply plug this one in and of course, the expression of pi x is here (No audio from 26:30 to 26:47) and finally, what we have is it is if we write this equation in a little compact form what we will get is h t, where as I have mentioned previously also a suffix refers to differentiation, so del h del t is essentially h t (No audio from 27:23 to 27:37).

So, if h t is equal to 0, then one gets a steady state solution; however, we know that h is a function of h x right and which is essentially a non uniform steady state and as it is not flat which is originates from the origin is the interfacial fluctuations. So, this is essentially a fourth order non-linear P D E and it might have infinite number of it it actually has infinite number of steady state solutions, so any h is essentially a solution for this if the if h t is equal to 0.

So, essentially since h is equal to h x which is the surface is not flat, so it is essentially a quasi a steady state solution is a trivial solution (( )) here, it is a quasi steady state situation. Now, one of the major utilities of this particular equation is to test numerically whether a film of initial thickness h 0 remains stable or becomes unstable and ruptures with time.

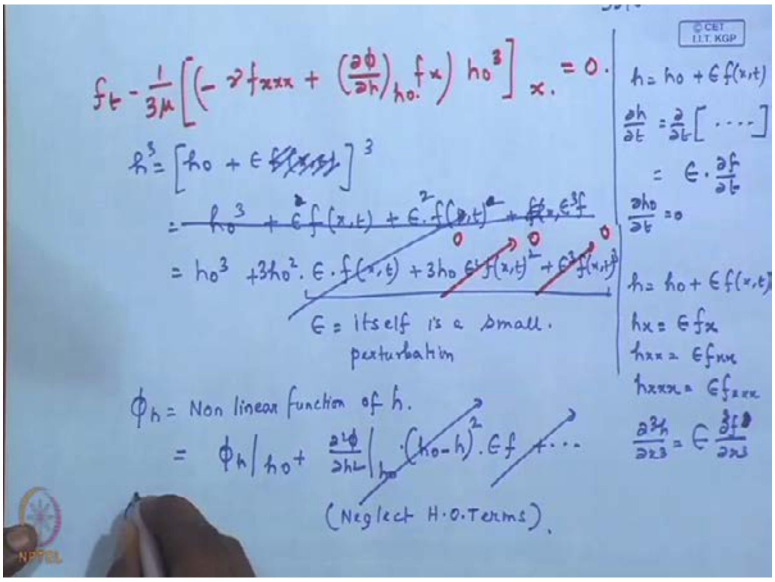
(Refer Slide Time: 30:08) So, in the previous class or couple of classes before we had shown a video of a spontaneous rupture of a film, so I just try to replay it, so this is what you are talking about, so what we have done or what we would like to test that by means of spin coating. So, we we you have created a film which has a thickness of h 0 and qualitatively, we already know several factors that if a film is a thinner than the chances of the possibility of instability is higher, because the interfacial there are two interfaces will be closer to each other therefore, the magnitude of the interfacial attraction will be stronger, etcetera, etcetera.

But, here this equation gives us the opportunity to quantify that and in terms, so essentially one can use this equation to test whether a film of initial thickness h 0 remains stable with time or not. So, essentially what is done to do that is the tick is the film the the initial height h 0 is sort of perturbed with a function; if the function of f x and t and let us say the perturbation amplitude is epsilon. So, therefore, h becomes h at any given instance of or rather let me put it, h x t becomes h 0 plus epsilon into f x t and we neglect any possible (( )) terms.

So, essentially we try to find the stability of the solution by try to check the stability of the thickness of the film by giving a small fluctuation, around h is equal to h 0 and this perturbation amplitude is sort of a ma gives gives us the extent of how the film, how to what extent the film thickness deviates from its equilibrium thickness h 0. So, what we can do is h becomes h 0 plus epsilon f x t which is linearised of h around h 0 using the simple Taylor series expansion and therefore, if we now plug in this value of h into the equation here.

So, now h zero is essentially a constant and what you have is epsilon and f is a epsilon is also a constant, so f is a function of x and t.

(Refer Slide Time: 33:17)



$$f_t - \frac{1}{3\mu}\left[\left(-\gamma f_{xxx} + \left(\frac{\partial\phi}{\partial h}\right)_{h_0} f_x\right) h_0^3\right]_x = 0.$$

$$h^3 = \left[h_0 + \epsilon \cancel{f(x,t)}\right]^3$$

$$= \cancel{h_0^3 + \epsilon^3 f(x,t) + \epsilon^2 f(x,t)^2 + f(x), \epsilon^3 f}$$

$$= h_0^3 + 3h_0^2 \cdot \epsilon \cdot f(x,t) + 3h_0 \cancel{\epsilon^2 f(x,t)^2} + \cancel{\epsilon^3 f(x,t)^3}$$

0 0 0

ϵ = itself is a small. perturbation

ϕ_h = Non linear function of h.

$$= \phi_h \big|_{h_0} + \frac{\partial^2\phi}{\partial h^2}\bigg|_{h_0} \cdot \cancel{(h_0 - h)^2 \cdot \epsilon f + \ldots}$$

(Neglect H.O.Terms).

$h = h_0 + \epsilon f(x,t)$

$\frac{\partial h}{\partial t} = \frac{\partial}{\partial t}[\ldots]$

$= \epsilon \cdot \frac{\partial f}{\partial t}$

$\frac{\partial h_0}{\partial t} = 0$

$h = h_0 + \epsilon f(x,t)$

$h_x = \epsilon f_x$

$h_{xx} = \epsilon f_{xx}$

$h_{xxx} = \epsilon f_{xxx}$

$\frac{\partial^3 h}{\partial x^3} = \epsilon \frac{\partial^3 f}{\partial x^3}$

So, this equation now in the linearised domain transforms to (No audio from 33:20 to 33:42), so you can see that a mechanically all the terms containing h have, now been substituted with f for it it is very simple essential if you if you just want me to go into little deeper a little step by step just to clear your doubts. What we have is h is equal to h 0 plus epsilon f x t, so del h del t del del t of this whole thing and what you was since h 0 is constant, so del h 0 del t is equal to 0, so you are left with epsilon del f del t.

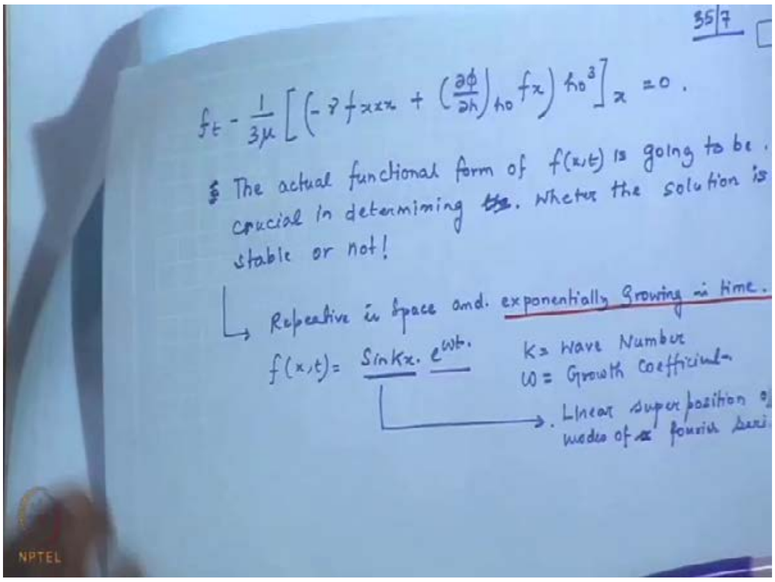
Similarly, if you perform let us say a tom like you take a tom like h x x x, so you have h is equal to h 0 plus epsilon f x t you take h x; so what you get is epsilon f x, because del h 0 del x again is equal to 0, h x x you get epsilon f x x h x x x you get epsilon f x x x or in other words del three h del x cube here, which is written in a compact form as h x x x is epsilon del f 3 del x t, so the, that is essentially del 3 f del x t.

So, that is how you convert this equation into this equation, in terms of f h into an equation in terms of f, one might argue what about h cube, well you can write h is equal to h 0 plus epsilon f x t, then h cube becomes this whole thing cube and. So, its essentially h 0 cube plus epsilon f x t epsilon square plus epsilon f x t square plus f x t plus, so it is epsilon into epsilon square, then epsilon cube I am sorry I am sorry for this expression.

So, it is h 0 cube plus h 0 square 3 (( )) factor is there epsilon f x t plus 3 h 0 epsilon square f x t square plus epsilon cube f x t cube

Now, epsilon itself is a small perturbation therefore, all these terms tent to 0, so that is how you essentially get this h cube over here gets replaced with h 0 cube the only other thing is pi h is a non-linear function of h. We which if we expand, which you can write as a pi h h 0 plus del 2 pi del h square even (( )) as h 0 into h 0 minus h square into epsilon f and so on.

(Refer Slide Time: 37:58)



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$$f_t - \frac{1}{3\mu}\left[\left(-\gamma f_{xxx} + \left(\frac{\partial\phi}{\partial h}\right)_{h_0} f_x\right) h_0^3\right]_x = 0 .$$

\$ The actual functional form of $f(x,t)$ is going to be crucial in determining ~~the~~. Wheter the solution is stable or not!

↳ Repeative in space and. exponentially growing in time.

$f(x,t) = \underline{\sin kx} . \underline{e^{\omega t}}.$

k = Wave Number

ω = Growth Coefficient

→ . Linear superposition o
modes of fourier seri

So, if you neglect all the high higher order terms, then you can get pi h is equal to pi h 0 as well and therefore, you get to the final equation which is, let us write it again which is f t minus 1 3 rd mu gamma (No audio from 38:04 to 38:17).

Now, one can understand that the function f x t, the actual functional form (No audio from 38:24 to 38:40) is going to be crucial in determining, the whether the solution is stable or not. And therefore, we need to choose an appropriate perturbation function which can sort of test the stability of a film the logic here, very simply put is that you take a pick up a or choose a function, which sort of can have the maximum destabilizing influence on the on the on the stability of a film.

So, idea is that if any film is stable against the worst type of a perturbation function worst in the in the sense that it has the maximum potential to damage or or destabilize the film, then for any other type of perturbation or fluctuation the film will definitely be stable or let me put it again.

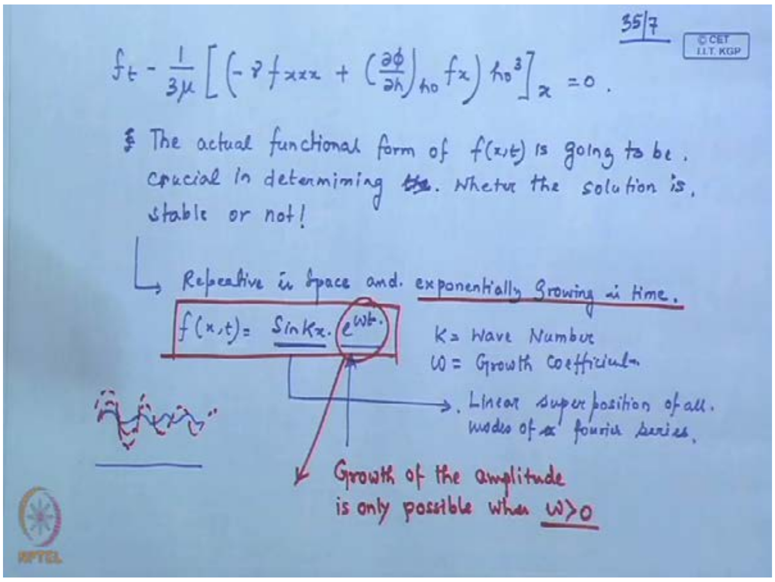
So, you pick up a perturbation function f, which is a function of x and t we (( )) in such a fashion that it it is going to be most difficult in terms of the stability of a film, so if it destabilizes the film it is perfectly fine. So, in real setting the film is likely to destabilize there are possibilities that it might not destabilize, because the function we are going to choose the functional form (( )) again qualitatively discussed is such.

But if a film is found to be stable again this perturbation function, we are speaking up then the logic is that this is the worst type of worse possible destabilization that is that is possible at the interface, but since it can sustain or withstand this this type of a perturbation and it is going to be stable against in any other form of perturbation because which is going to be mild.

So, this is what you known as the concept of linear stability analysis and is routinely used in various branches of science and engineering, it is a very standard mathematical procedure, which, why, what linear stability analysis, because what you are doing is that you are taking a non-linear differential equation. And your linearizing it with a perturbation function around a mean film thickness h 0 or or any mean solution for that matter to to be general to put it in general terms and then checking it is stability.

So, what we do we pick up a perturbation function which is repetitive in space and exponential in time this is the type of a perturbation function, we pick up; let us say the functional form we take is f x t is sin K x into e to the power of omega d. So, essentially this sin K x is repetitive in space and K corresponds to different way of number, e to the power omega t takes care of the exponentially growing with time part of the perturbation function. So, K is the wave number, omega is the growth coefficient and K can have all (( )) from 0 to infinity, so essentially it is a linear super position of all modes of a furious series (No audio from 42:47 to 43:06).

(Refer Slide Time: 43:17)



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$$f_t - \frac{1}{3\mu}\left[\left(-\gamma f_{xxx} + \left(\frac{\partial\phi}{\partial h}\right)_{h_0} f_x\right) h_0^3\right]_x = 0.$$

§ The actual functional form of $f(x,t)$ is going to be. crucial in determining ~~the~~. Whetur the solution is. stable or not!

↳ Repeative in space and. exponentially growing in time.

$$\boxed{f(x,t) = \underline{\sin Kx}.\, e^{\omega t}.}$$

K = Wave Number

ω = Growth coefficient

→ Linear super position of all. modes of ~~a~~ fourier series.

Growth of the amplitude is only possible when $\omega > 0$

So, considering this functional form or corresponding to this functional form of (No audio from 43:17 to 43:45) this is the equation like to have it in place, so based on this, what we can find out is our f t is equal to (No audio from 43:57 to 44:05) and (No audio from 44:07 to 44:32) now this is simple mathematics you can just find out up to the del 4 f del x four because you will be (( )) you already have a x x x and another (( )), so we reached up to this particular term.

So, this now also what you can do is that now that everything has been sort of linearised you can x sort of subsequently work on this expression, so this now becomes gamma f x x x x. And so, del phi or phi h 0 f x x into h 0 cube is equal to 0, because this is now a constant now, it is no longer a function of x because you have evaluated that at h is equal to a h 0.

So, once you have these expression so, out of these expression you will essentially be needing these three terms this one, this one and this one (Refer Slide Time: 45:50), which eventually will substitute here here and here (Refer Slide Time: 45:55). So, once you do that what you get is omega sin K x e to the power omega t minus 1 by 3 mu minus gamma into K to the power 4 sin K x e to the power omega t plus pi h 0 into minus sorry minus will come here, it is there minus k square sin K x e to the power omega t h 0 cube is equal to 0.

So, from this step to this step it looks a little biggish, but really does not matter all what we have done we have substituted f t, we have substituted f x x x x and we have substituted f x x. So, if you do that, what comes out is sin K x e to the power omega t sort of you can cancel out from both the sides and what you are left with is (No audio from 47:19 to 47:39).

Therefore, now if we use the expression of pi is equal to A divide by 6 pi h cube considering attractive Van der Waals interaction, we can calculate the pi h 0 is equal to minus A divided by 2 pi h 0 to the power 4. So, if we plug in that expression, what we are left with is omega is equal to h 0 cube by 3 mu into A divided by 2 pi h 0 to the power 4 K square minus gamma K to the power 4.

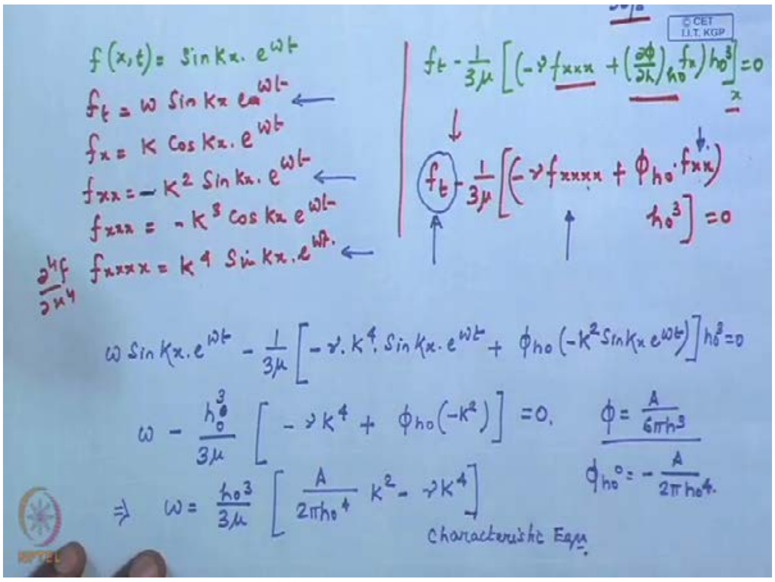
Now, this is what is known as the characteristic equation and this is also very interesting see, we have taken the form the functional form of the perturbation equation to be (Refer Slide Time: 48:43) sin K x into e to the power omega t now this; so what is this? This is the surface fluctuation of the perturbation you have taken.

Now, in order for the film to become unstable as we have discussed in some of our previous classes that the what has to happen is that this interfacial fluctuations should grow and then the amplitude of the qualitatively this we have discussed. So, it becomes possible only when this interfacial fluctuations grow and sort of the amplitude of the growing fluctuations match that of the film thickness, then only one can argue that the film has ruptured.

(Refer Slide Time: 49:33) So, from this perturbation function a growth of this amplitude is only possible. So, the amplitude, the growth of the amplitude (No audio from 49:38 to 49:52), when omega is greater than 0, if omega is less than 0, then what is going to happen that with time, this term is going to tent towards 0 and the perturbation is going to die down.

In physical terms what; that means, is that we know that these fluctuations are always opposed by surface tension, so in that case physically a negative omega would mean that the strength of your attractive Van der Waals interaction or the destabilizing force to be more general was not strong enough to overcome the stabilizing influence of surface tension.

(Refer Slide Time: 50:35)



$f(x,t) = \sin kx \cdot e^{\omega t}$

$f_t = \omega \sin kx\, e^{\omega t}$

$f_x = k \cos kx \cdot e^{\omega t}$

$f_{xx} = -k^2 \sin kx \cdot e^{\omega t}$

$f_{xxx} = -k^3 \cos kx\, e^{\omega t}$

$\frac{\partial^4 f}{\partial x^4}$ $f_{xxxx} = k^4 \sin kx \cdot e^{\omega t}$

$f_t - \frac{1}{3\mu}\left[\left(-\gamma f_{xxx} + \left(\frac{\partial \phi}{\partial h}\right)_{h_0} f_x\right) h_0^3\right]_x = 0$

$\boxed{f_t} - \frac{1}{3\mu}\left[\left(-\gamma f_{xxxx} + \phi_{h_0} \cdot f_{xx}\right) h_0^3\right] = 0$

$\omega \sin kx \cdot e^{\omega t} - \frac{1}{3\mu}\left[-\gamma \cdot k^4 \cdot \sin kx \cdot e^{\omega t} + \phi_{h_0}\left(-k^2 \sin kx\, e^{\omega t}\right)\right] h_0^3 = 0$

$\omega - \frac{h_0^3}{3\mu}\left[-\gamma k^4 + \phi_{h_0}(-k^2)\right] = 0.$

$\phi = \frac{A}{6\pi h^3}$

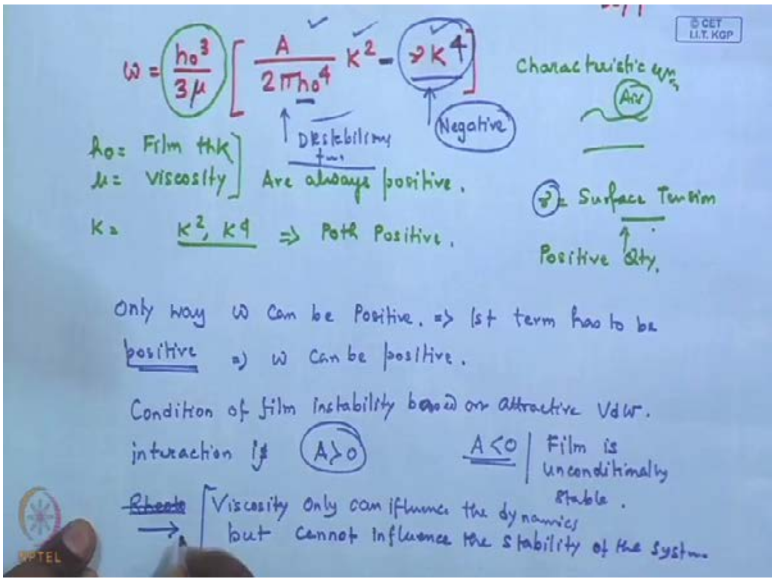
$\phi_{h_0} = -\frac{A}{2\pi h_0^4}.$

$\Rightarrow \omega = \frac{h_0^3}{3\mu}\left[\frac{A}{2\pi h_0^4} k^2 - \gamma k^4\right]$

Characteristic Eqn.

Therefore, from this using this perturbation function the film can only become unstable the condition of instability of a film, now turns out to be or let us use a fresh sheet (No audio from 50:45 to 51:04), now based on the concept, we discussed here film can only become unstable (Refer Slide Time: 51:12), (No audio from 51:12 to 51:23), when omega is greater than 0 right.

(Refer Slide Time: 50:50)



$\omega = \boxed{\frac{h_0^3}{3\mu}}\left[\frac{A}{2\pi h_0^4} k^2 - \boxed{\gamma k^4}\right]$ Characteristic eqn.

Destabilizing term

Negative

h_0 = Film thk

μ = viscosity

Are always positive.

γ = Surface Tension

Positive Qty.

k = k^2, k^4 ⇒ Both Positive.

Only way ω can be Positive. ⇒ 1st term has to be positive ⇒ ω can be positive.

Condition of film instability based on attractive VdW. interaction if $\boxed{A > 0}$

$A < 0$ | Film is unconditionally stable.

~~Rheolo~~ → [Viscosity only can influence the dynamics but cannot influence the stability of the system

Therefore here also let us now examine the expression of omega carefully you see, h 0 is a film thickness mu is the viscosity, so these two are always positive; so therefore, this prefecture h 0 cube by 3 mu is always positive.

Now, there is also another interesting thing that is hidden here, which we will discuss later K we know is any real number or K is any any integer, so irrespective of whether K is positive or negative both the terms are positive. Gamma is surface tension it is again a positive quantity, we are talking about a film that is exposed to air, we are not talking about any interfacial tension and we have always argued that the surface tension is always positive.

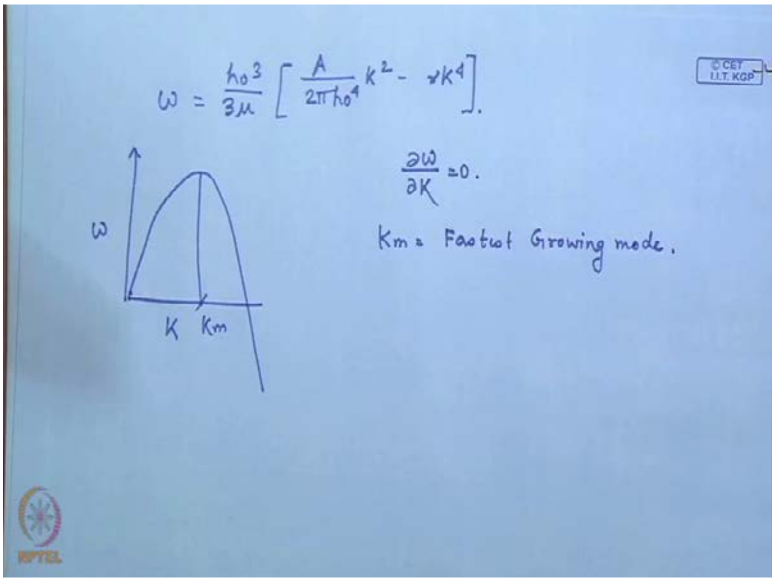
Therefore this term, since it has a negative sign is always going to be negative, this multiplied by a positive number, so this is always going to be negative K square is positive h 0 to the power 4 s also positive. So, the only way omega can be positive is this first term has to be positive only then this term is positive and this term is negative. So, if the magnitude of this particular term is now higher than the magnitude of this particular this the second term, then only omega can be positive

Therefore now we clearly understand the condition of film instability based on attractive Van der Waals interaction is A greater than 0, so A has to be higher than 0, this is number 1.

So, for any system where effective haymaker constant is negative, then this term is negative this term is also negative (Refer Slide Time: 54:29) therefore, the film is unconditionally stable, further you see; so in this expression this is the potential destabilizing term, which arises from van der Waals interaction this is the stabilizing term and we have always argued that whenever you have the surface fluctuation surface tension opposes the growth.

So, here it is you can see that the term to which the surface tension is associated it is the stabilizing term, other thing is you see that the in the prefecture, viscosity is at the denominator, which means that higher is the magnitude of mu, lower will be the value of omega. But, mu can not cannot influence the sin of omega that is the rhealogy of the system or the viscosity of the system only can influence the dynamics but, cannot influence the stability of the system, these are important findings that comes out from linear stability analysis.

(Refer Slide Time: 56:05)



The other, the only other remaining important thing is that if you now look at the expression for the characteristic equation again, you can find out the mode at which the growth is fastest by setting del omega del K is equal to 0 and which gives you the fastest growing mode (No audio from 56:33 to 56:42).

So, in this class we will stop here and we will pick up from the fastest growing mode in the next class and get an expression for the instability wave length as well as the number density of the features that comes from the linear stability analysis. And then move on to some real experimental evil sequence of thin film dewetting, polymer thin film dewetting thank you.