

# Instability and Patterning of Thin Polymer Films

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## Lecture No. # 32

### Spontaneous instability and Dewetting of Thin Polymer Film - II

Welcome back, in the previous class we just talked about what dewetting is, we talked about bulk dewetting on a partially wettable surface, we talked about two types of way you can trigger dewetting, one is, can be you just forcibly spread the liquid and then, the other one we talked about is in a scenario, where you can have a evaporation and that can also lead to dewetting.

Now here, **talk** we now talk about a liquid thin film (Refer Slide Time: 00:42). And see, how dewetting though the essential physics remains the same, it is the imbalance that govern imbalance in the horizontal component of surface tension, but how the dewetting can additionally get engendered or triggered in an ultra-thin film. And why this is now related to what we have already studied is these dewetting in an ultra-thin film often gets triggered by or gets triggered due to the interaction forces that we talked about.

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Handwritten notes on a blue background discussing thin film stability and dewetting. The notes include diagrams of a thin film on a substrate, a perfectly horizontal substrate with a liquid layer, and a lubricant layer. Key points include:

- Active Interfacial Interaction.
- \* Condition that is prevailing at the film-air interface.
- Perfectly Horizontal Substrate, its a layer of liquid.
- No pressure applied from outside.
- Perfectly Horizontal.
- If a Film Ruptures and dewets  $\rightarrow$  It forms some patterns/structures (micro scale dimensions).
- \* One Popular Recent Approach is to use instability as a viable patterning technique. (SELF ORGANIZATION)
- Coating Application: - Want the instability NOT to get set in.

Small diagram showing a lubricant layer between two surfaces, labeled "Lubricant" and "1 2".

$\Delta G_{12}$   
From the Stand point of Lubrication  $\rightarrow$   
③ Remain Intact-

So, let us build our concepts slowly we talk about a thin film and all I would request you to remember that, since it is a thin film you have an active interfacial interaction forget about everything else. So, this interaction there can be Van der Waals force, so it is attractive you have already seen, there can be situation, where Van der Waals force can also can engendered negative repulsion, so forget it, but we have an active interfacial interaction that is all.

Now in order to understand, what is the origin of this spontaneous instability? We need to understand the situation that is prevailing or the condition that is prevailing (No audio from 02:19 to 02:31) at the liquid or the film-air interface that is extremely important to understand. So here, we have a film let us say, it is in a liquid form, here we have a solid substrate and here it is air or vacuum. So, this is the perfect example of a coating and we need to understand two things.

So, if we are talking in terms of a coating application you would like your film to remain stable. For example, yesterday we were or in the previous couple of lectures back we were talking to a situation, where you have two components two objects and you have a liquid 3 in **in** between them and they were coming in contact dislodging the liquid 1 and 2. So, this is fine if you are sort of looking from the stand point of coagulation you definitely want to have a situation, where 1 and 2 come in contact by dislodging 3.

And as we argued that, there **there** has to be an interfacial attraction between 1 and 2 that results to a situation like this, we all understand, what is the corresponding change in the delta G 1 3 2 whether it is negative or positive whatever. But, think from the other point, if you are now talking in **in** the stand from the point of lubrication let us say, let us say this 3 is the lubricant. So, in that case, you will never want this 1 and 2, the liquid layer of 3 drains out and 1 and 2 come in contact. So, from the stand point of lubrication (No audio from 04:28 to 04:39) you would expect film 3 to remain intact.

Same is valid here, if you are talking about a very thin film we will see that, if a film sort of ruptures and dewets this we will comes soon (No audio from 04:58 to 05:07), it forms some patterns, structures, often they have meso scale dimensions. So, one of the approaches what we will see that, is to use instability as a viable patterning technique. So, (No audio from 05:41 to 06:10) in one of our very early classes, where we talked

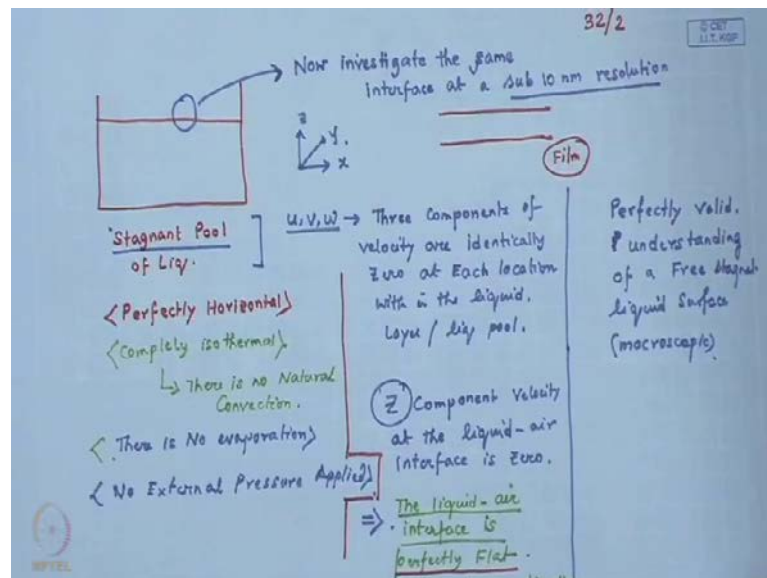
about the different approaches for meso scale patterning we did talk about the bottom up, top down and also this, which is known as which we referred to as the self-organization.

However, if you are now talking in terms of a coating application, which is the most widely used industrial application of thin films incidentally, you definitely want instability not to set in, so this type of an area, it is important to understand the physics, what exactly happens? So that, depending on your choice of application you can trigger instability or you can suppress the instability, both are equally important.

So, if you are talking in terms of patterning of course, this course talks about patterning, so probably we are in favor of having the instability, so that we can create structures of our choice. But reality is that, if you are interested to use your coating as as a as a or your thin film as a coating, you would try to sort of prevent the instability at any cost, because if the film becomes unstable it ruptures, the functionality of the coating is completely destroyed.

So, let us examine the condition that is prevailing at the film-air interface. So, this is simply put let us say, it is on a horizontal perfectly horizontal substrate, it is a layer of liquid you can compare this with also a tank full of water Now, this again the bottom surface of the tank is perfectly horizontal perfectly horizontal. Now, if the bottom surface this can be a thin layer of liquid or it can be a pool of liquid or whatever it is, if it is horizontal and there is no pressure applied from outside applied from outside, then then it is a it is a perfectly static layer of liquid where, so let let me draw it once again.

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So, you have a stagnant pool of liquid, the surface is perfectly horizontal, it is completely isothermal. So, this sort of this statement reduces that, there is no natural convection, (( )) there is no evaporation, no external pressure applied (No audio from 10:25 to 10:34). So, if all these conditions are met, then this indeed is a stagnant pool of liquid. So, what it means that  $u$ ,  $v$ ,  $w$  that is the three components of velocity are identically 0 at each location within the liquid, layer or liquid pool.

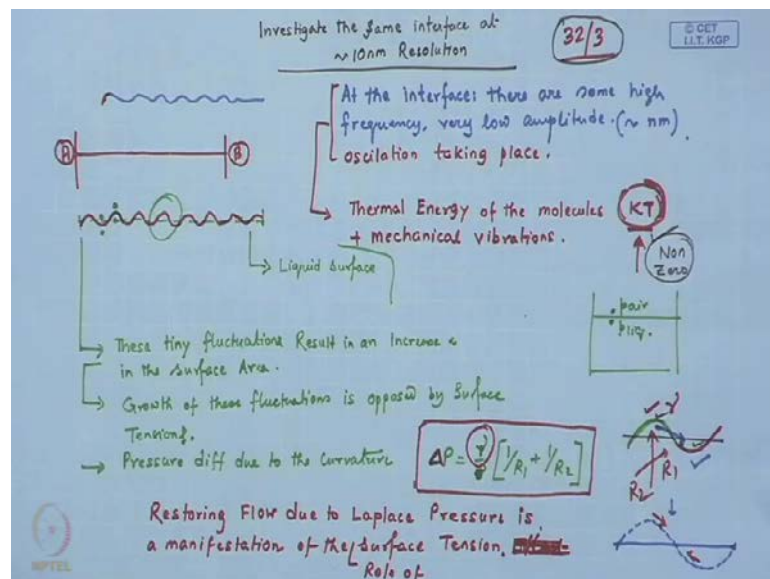
So,  $u$ ,  $v$  and  $w$  let **let** that be the  $x$ ,  $y$  and  $z$  components of velocities. So, what it means is that and this is valid, this should be ideally valid for irrespective of the thickness of the liquid layer. So, whether you are **talking to a** talking about a 1 meter deep tank of water or a 100 nanometer thick stagnant liquid film. It is a situation, where you have the liquid completely wetting the surface. So, this is, if you follow classical fluid dynamics, this is what you should be getting.

The three components of velocity zero at every location means that, the  $z$  component velocity we just identify this thing, because this is important. The  $z$  component velocity at the liquid,  $z$  component velocity as well as the other components of velocity of course, at the liquid-air interface is zero, which implies and this is a perfectly valid picture that the liquid-air interface is perfectly flat and there is no flow any direction.

Now, this is a perfectly valid picture **of a** of a free surface of a liquid stagnant liquid, if you take a macroscopic view. So, this is this picture that the liquid-air interface is

perfectly flat and there is no flow in any direction is a perfectly valid picture or a understanding of a perfectly valid understanding of a free liquid surface free stagnant surface. However, if you now investigate the same interface (No audio from 14:22 to 14:35) at let us say, a sub 10 nanometer resolution. It is a little bit of thought experiment, but if you think of **you are** you are sort of magnified the interface to a large extent and one to see, what is happening.

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What you will find that, **the interface** at the interface, there are some high frequency (No audio from 15:03 to 15:21), very low amplitude couple of nanometers. Oscillation that is taking place continuously, this oscillation are attributed to the thermal energy or thermal motion of the molecules, which is related to  $K T$  component of energy, where  $K$  is the Boltzmann constant, as well as, some mechanical vibrations under real settings.

Now, when you are talking about any practical setting, these oscillations will always be present, because in most cases you are doing your experiment at room temperature or at some finite temperature. For most polymers you do the dewetting experiments at a temperature of let say, a 100 or 120 degree centigrade, which is above the glass transition temperature. So,  $T$  is the order of 370, 350 or 400 Kelvin. So, therefore, this number is always going to be finite. At any temperature, if you are not at absolute zero and therefore, this thermal fluctuation will always be present with in the molecules.

Important thing to realize is, this thermal fluctuation this very high frequency, low amplitude thermal fluctuations are present, irrespective of whether you take a tank full of liquid or an ultra thin film. Now, two things happen, so we talk about a oscillation amplitude of 1 nanometer or couple of nanometers. So, let us say, you have taken a tank which is 1 meter deep. So, you just calculate the scales 1 nanometer or couple of nanometer by 1 meter, so it is 10 to the power 9 orders, small errors compared to the characteristic length scale of **of** a macroscopic flow reservoir for example, a reservoir.

So, nobody even cares about these things but, so that is why in classical fluid dynamics you do not even talk about anything like these, you assume a very nicely with perfect valid results that, your free surface is perfectly flat etcetera **etcetera**. But, we already realize based on what we have discussed that, the free surface is not exactly flat, but you have some very tiny oscillations, which decorate the free surface.

Now, let us see, what is the consequence of this free of this vibrations, do they grow or what happens? Now, you need to understand that, when you are talking about a flat surface let us say between 2 points the now the minimum surface energy configuration is the perfectly flat surface. So, if you have 2 points let us say, point A and point B you know very very well that, the minimum distance is, if you join them through a straight line.

So, the moment because of this fluctuations (Refer Slide Time: 18:45), the moment you have these fluctuations on the interface on **on the liquid interface on** the liquid surface, the actual surface area goes up as compared to a flat surface. So, these fluctuations however, tiny they are (No audio from 19:17 to 19:38). Therefore, the growth of these fluctuations is opposed by surface tension, because we know that surface tension always tries to minimize the area.

So, if you have a flat surface whatever will be the total surface energy, if you have an undulating surface, because of this fluctuation the surface energy goes up. Therefore, the surface tension will try to oppose immediately oppose these fluctuations. The other important thing now again we referred back to our understanding in one of the previous modules is that, we now talk about a liquid surface, which is no longer flat, but it is in mechanical equilibrium; but, since the surface is not flat therefore, the pressure just outside and the liquid side is not the same anymore.

And you have a pressure difference due to the curvature (No audio from 20:58 to 21:09), which is given by the Young's Laplace equation; and this is related to the local radius of curvature of any fluctuations let us say, we pick up, so whatever is the specific local radius of the curvature here (Refer Slide Time: 21:33), and the surface tension.

So now, you have a in plane pressure difference along the surface. So, at every location the Laplace pressure is different depending on the curvature whether it is concave or convex, the pressure the Laplace pressure is going to be different at every location. So, if we just look at one set of oscillations carefully, the Laplace pressure over here is going to be higher than the Laplace pressure over here (Refer Slide Time: 22:00).

And this will result in a flow of liquid from this zone to this zone (Refer Slide Time: 22:09), trying to eventually flatten the film surface. So, this was the initial fluctuation, which sort of flew which sort of resulted in a flow of liquid from the high pressure zones to low pressure zones; and this high pressure or low pressure zones are created **because of the** because of a difference in the Laplace pressure.

So, you have **three things** two things essentially of course, Laplace pressure is or in other words, the restoring effect the restoring flow due to Laplace pressure is a manifestation of the surface tension effect, because Laplace pressure at the manifestation of the role of surface tension I would say so, because Laplace pressure is related to surface tension.

So, what is the new understanding we have developed based on the last few minutes of discussion? Last few minutes of discussion the understanding we have developed, let me just quickly do a quick recap we argued that, if you have a layer of liquid on a perfectly horizontal surface with no external pressure from outside, it can be a tank of liquid or it can be a liquid thin film or whatever; and all these conditions are met that is the, it is perfectly horizontal, so there is no  $G \sin \theta$  component, which can trigger a flow.

It is completely isothermal, so there is no chance of natural convection, there is no evaporation. And there is no external pressure applied to trigger a flow in that case, if you **if you** decide to solve Navier-Stokes equations or even, if do not solve, you understand that it is a you are talking about a stagnant pool of liquid. So,  $u$ ,  $v$  and  $w$  at every location, the three components of velocity within this zone is identically zero.

And since the z component velocity as well as the all other components of velocity at the free liquid air interface are zero, so here I would say, all velocity components are zero. Therefore, this interface is perfectly flat and there is **there is** no flow in any direction and which is a perfectly valid picture or understanding of a free stagnant liquid surface or it is a perfectly valid macroscopic view.

But then, we argue that, if we investigate the same interface at a very high magnification or at let us say 10 nanometer resolution we find that, we investigate the same interface at at a 10 nanometer lateral resolution let us say. So, then we find that, the interface is no longer perfectly flat as we had argued or assumed in a macroscopic picture.

But, you have some very tiny fluctuations, which are decorating the interface. And these fluctuations of their origin in the thermal energy or the thermal vibration of the molecules, which is attributed to the  $K T$  component of internal energy and the important of course, there can be some mechanical vibrations in a real situation which can also augment or lead to these fluctuations.

Important thing to understand that, we are talking about a situation, so we have assumed everything; but we have not assumed anywhere, that we are talking about the liquid pool at an absolute zero temperature. So, the temperature is a practical temperature, it can be room temperature, it can be elevated temperature or whatever. And the moment you are talking about this type of a temperature, what it means that? This component of energy it is non-zero, so this is finite.

So, these fluctuations are going to be always present. Now, the next thing we understood that what happens to this fluctuations. So, if you have some fluctuations and there can be two things happening, these fluctuations can eventually die down or these fluctuations can grow.

Now here, what happens is? We understood that, because of the surface tension opposes **the** these fluctuations or growth of these fluctuations, because of the fact that, these fluctuations actually whatever small be the amount results in an increase in the interfacial area interfacial the or the **the** total area of the liquid interface, which results in increase of the total surface energy. And therefore, surface tension opposes the growth of these fluctuations.



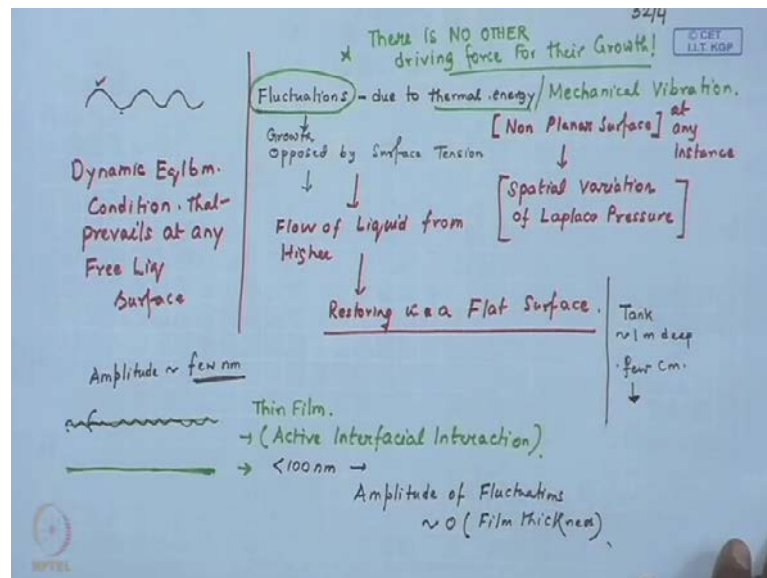
Also now, since you have a corrugated surface of the **the** surface is no longer flat of **of** the liquid therefore, you have a non zero spatial distribution of Laplace pressure, because we have already read or studied in one of our previous lectures that, if you have a non planer surface, there is Laplace pressure. So, a fluctuation like this will engender or result in a Laplace pressure difference in plane radiant in the Laplace pressure.

So, depending on the curvature, there will be locations, where the Laplace pressure is high, depending and locations where Laplace pressure is low. So, the liquid then flows back from the zones, where you have high Laplace pressure to zones, where you have a low Laplace pressure and eventually try to flatten out (Refer Slide Time: 28:31).

So, this dynamic competition between your thermal energy driven fluctuations occurring an Laplace pressure surface tension driven sort of opposition or balancing or restoring is continuously going on. So, this is more of a dynamic equilibrium **that** that is the condition, that prevails at any liquid surface. Important to understand that, this is actually the condition this dynamic equilibrium prevails on any liquid surface, irrespective of your talking about a 10 nanometer thick film or your talking about a few meter deep water tank.

But, for macroscopic things, what is important to realize that, we do not consider these fluctuations at all. Because, if the characteristic dimension forget about meter, **if** even if they are a few centimeter deep layer of liquid you are talking about, these fluctuation the amplitude is of the order of a nano meter and they are very fast very, so the frequency is very very high. So, they have no significant effect on the overall dynamics of the system. So, in Navier-Stokes equation you do not see the manifestation of these interaction forces typically, if you are talking about a macroscopic entity.

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What is just introduce you to one more terminology. So, this occurrence of this fluctuation due to, so this is the sequence fluctuations, thermal oscillation or thermal energy and their growth of the fluctuation is opposed (No audio from 30:26 to 30:39). So, these fluctuations also result in a non-planer surface at any instance, these results in a spatial variation of Laplace pressure.

And surface tension and Laplace pressure both are sort of manifestation of the same effect opposed by surface tension. So, this triggers flow liquid from higher pressure zones are these area to these areas (Refer Slide Time: 31:36), so resulting in restoring in a **in a** flat surface. So, this is what is the dynamic equilibrium I would say, dynamic equilibrium condition.

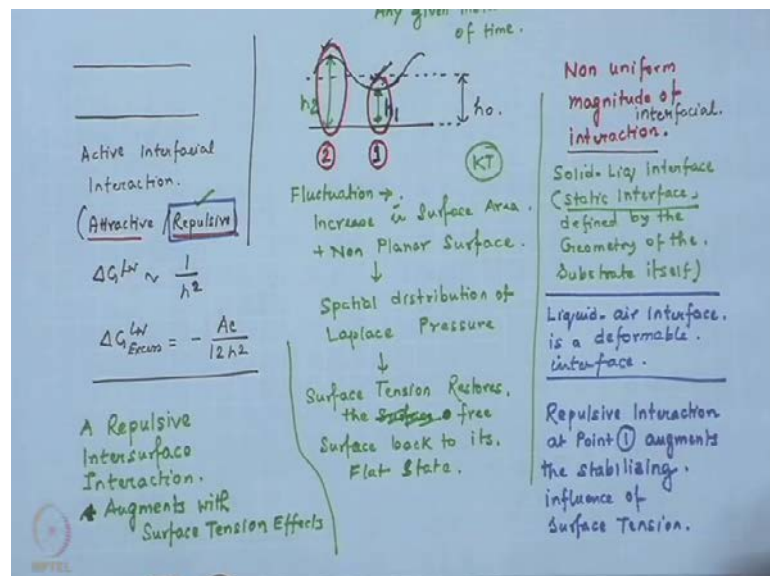
That, prevails at any free liquid surface and for a macroscopic object or a macroscopic body, it is extremely easy to sort of I mean no one even cares about this 1 nano meter fluctuation, whether they remain or not. But now let us, focus our attention to a thin film, where all the interesting thing is. So, the other important thing is that, these fluctuations originate, because of this thermal noise or thermal energy or mechanical vibration.

And there is no other driving force for their growth, particularly in a macroscopic object. But now, let us have our attention focused on a thin film. So, let us say that, this is a thin film (Refer Slide Time: 33:30), so we have of course, defined a thin film based on the fact that, there is active interfacial interaction. And we have also argued that, we have

seen that physically these interfacial interactions remain active as long as you are in the range of less than 100 nano meter or may be even thinner.

So, let us now say that, we are talking about a 40 or a 50 nanometer thick film and you have it is a liquid film and you have these fluctuations, so earlier when we talked about a tank of water let us say, 1 meter deep or even let us say, few centimeter we were talking about a 1 or couple of nanometer fluctuation with these type of dimension. But now here, the amplitude is in the few nanometers. So, what it implies? That, the amplitude fluctuations is now of the same order of film thickness. So, first thing to understand is that, unlike in a macroscopic case, you probably should not straight away neglect these fluctuations you have to address their existence.

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The other important thing is that we now understand, there is an active interfacial interaction, which can be attractive or repulsive. What are the conditions under which it becomes attractive or repulsive, we will come later. But, all we understand that, there is some active interfacial interaction; and this interaction scales as the film thickness or we have, if we consider only the Van der Waals interaction.

So, at any instance of time, if you now investigate the surface let us say, it is like this, one fluctuation has result we are tracking one single fluctuation. And let us say, this was your (( )) film thickness you have this instantaneous fluctuation let us say here (Refer

Slide Time: 36:46), the thickness is now  $h_1$  and here it is  $h_2$ , this is at any given instance of time.

Earlier, what was happening, what we have argued that? The moment, there was a fluctuation, surface tension tries to oppose it and flattens it down, so there is a spatial distribution of Laplace pressure. So, a fluctuation results in a increase in surface area plus a non planar surface, which results in a spatial distribution of Laplace pressure, which results in a flow of liquid from the high pressure zones to the low pressures zones are essentially surface tension restores **the surface or** the free surface back to its flat state.

However, so these were the only four fields that were active. So, the origin of the fluctuation was attributed to the thermal energy or the  $kT$  component of energy. And once the fluctuation results the only opposing force, there was nothing that was favoring the fluctuation any more, the only opposing field was the surface tension induced flow and it used to flatten out.

But now, **you** if you are talking about a thin film, because of the thinness of the system or because of the active interfacial interaction, now there is an additional interaction. And what happens is? The magnitude of the inter surface attraction at these two locations is now different. So, let us say, this is location 1, this is location 2, so there is now an additional difference or additional field that arises, because of the non-uniform magnitude **of interaction** of interfacial interaction I would write non uniform magnitude of interfacial interaction.

So, what happens is that? The interfacial interaction, the magnitude of interfacial interaction over here and the magnitude of interfacial interaction over here is different. Now, we need to understand that, the interfacial interaction can be of two types, so it can be either repulsive or attractive.

So, let us first talk about the situation, where the interfacial interaction is repulsive. So, if the interfacial interaction is now repulsive. What happens is? That the repulsion is stronger over here as compared to this area (Refer Slide Time: 40:39). So, as if this solid liquid interface which one needs to understand, it is a static interface defined by the geometry of the substrate itself, because the substrate is rigid, it a static interface. In contrast, the liquid-air interface one needs to understand that, the liquid-air interface is a deformable interface.

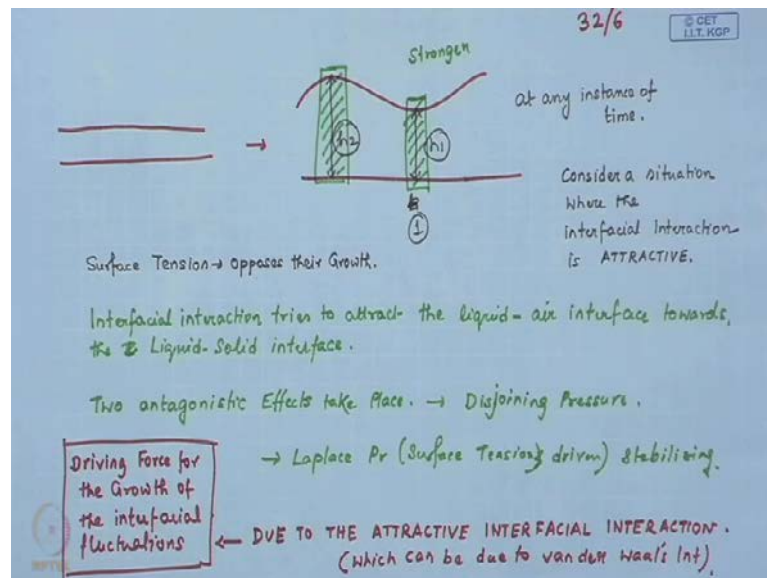
So, if you now have a we are talking about the situation, where you have a repulsive interaction between the two interfaces. Then, since this is closer to the or at point 1 the two interfaces are closer, it will experience a greater repulsion as compared to this zone. So, this repulsive interaction now augments the stabilizing role of surface tension. So, repulsive interaction at point 1, so what happens that this undulation subside, but unlike in macroscopic setting, where the undulation subsided only because of the stabilizing effect of surface tension.

Here, in addition to the stabilizing effect of surface tension you also have a repulsive inter surface interaction, which sort of augments with surface tension effects. And therefore, the film remains perfectly stable. Consequently, because so, now the stability is imparted by two effects a repulsive inter surface interaction and also the stabilizing effect of surface tension.

So, when we talked about this lubricating film yesterday (Refer Slide Time: 44:10), here also the condition was that this film should would remain stable, if there is a repulsive inter surface interaction between the 1 3 and the 2 3 interfaces. Then in that case, the film will remain stable. And we argued when we talked about spreading coefficient that, a repulsive interaction between the two interfaces will ensure that, the film remains stable.

And it is exactly qualitatively quantitatively we will come probably in the next class we understand that, if you have a repulsive interaction between the two interfaces, even if you consider the existence of the surface fluctuations, which are often referred to as the capillary wave spectrum also, **if you** if you consider the existence of the surface fluctuations, even then because of this repulsive interaction repulsive interfacial interaction and the stabilizing role of surface tension, the film remains completely stable.

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But now, let us have a look at the other situation that, you have this thin film. So, I draw an amplified picture now, you have this undulations, here the it is at location 1 the thickness let us say, the local thickness intrinsic thickness is  $h_1$  and  $h_2$  respectively at **at** any instance of time. And now, for the first time we consider a situation, where the interfacial interaction is attractive.

So, in that case, what happens? You have this fluctuation at any given instance of time, so surface tension as usual opposes their growth. However, you need to understand that, the magnitude of the interaction is stronger at this location as compared to this (Refer Slide Time: 46:43), which was also the case in the previous case, where we had a repulsive interaction here (Refer Slide Time: 46:51), the interaction was stronger, but the nature of the interaction was repulsive.

So here, the liquid the deformed liquid-air interface was strongly repelled by the interfacial interaction. However, here we have a stronger interaction, but **the it is** it is attractive. So, if it is attractive what would it mean that, this interfacial interaction now tries to sort of attract (No audio from 47:22 to 47:33) **attract** the liquid-air interface towards the liquid-solid interface.

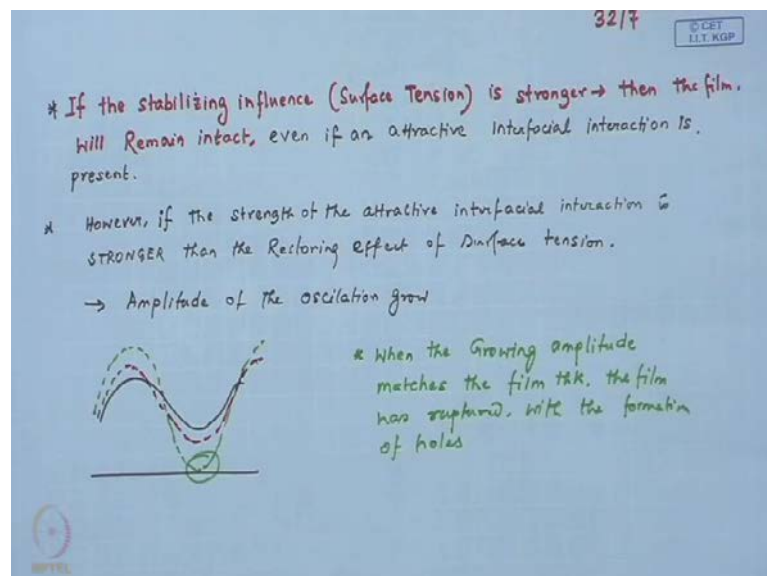
So now, for the first time you have a situation that, where **where** there is a competition are two antagonistic effects take place, one is a attractive interfacial interaction, which

results in the disjoining pressure and one is the Laplace pressure driven of the surface tension driven stabilizing effect.

So now, unlike a macroscopic situation, where you have the **thermally** thermal fluctuations, but there is no mechanism **for or** for their growth. Here, for the first time in a thin film, where there is active interfacial interaction between the two interfaces and the nature of the interaction is attractive. Then for the first we see that, there is a situation where you have a driving force for growth of the interfacial fluctuations and which is provided by due to the attractive interfacial interaction, which can be due to Van der Waals interaction.

So now, you have a again a competition between the stabilizing influence of Laplace pressure or surface tension and the attractive or the destabilizing influence of the attractive interfacial interaction and in **in** an event now, so if you are stabilizing influence is stronger, even in presence of this attractive interfacial interaction, the film will remain flat.

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So, if stabilizing influence due to surface tension is stronger than the film, will remain intact, even if you have an attractive interfacial interaction is present. However, if the magnitude of the strength of the attractive interfacial interaction, so this interaction (Refer Slide Time: 52:15) now is stronger **stronger** than the restoring effect of surface tension, then the amplitude for the first time we talk about a situation, where the

amplitude of the oscillation would grow. And instead of sort of flattening out the amplitude of the oscillation would grow and eventually, when the growing amplitude matches the film thickness, the film has then ruptured, with the formation of holes.

So, this is a situation, where just based on the interfacial interaction you take an initially flat film, which spontaneously ruptures and forms holes. So, we will pick up the subsequent discussion from this point and discuss, how probably I will just emphasis once more and give you show you some actual examples or actual microscopic view, where you can see a film dewetting or (( )) appearing.

And then, we will try to quantify mathematically the the scenario under which a film can become unstable and then, talk about some critical aspects of thin dewetting thin film thin polymer film dewetting experiments, thank you.