

# Instability and Patterning of Thin Polymer Films

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Lecture No. # 36

## Spontaneous Instability & Dewetting of Thin Polymer Film – VI

Welcome back. In the previous lecture, we just derived the expression or the condition under which a film becomes spontaneously unstable, based on attractive vanderwalls interaction. And we obtain the condition that.

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$f(x,t) = \sin kx \cdot e^{\omega t}$   
 $f_t = \omega \sin kx \cdot e^{\omega t}$   
 $f_x = k \cos kx \cdot e^{\omega t}$   
 $f_{xx} = -k^2 \sin kx \cdot e^{\omega t}$   
 $f_{xxx} = -k^3 \cos kx \cdot e^{\omega t}$   
 $f_{xxxx} = k^4 \sin kx \cdot e^{\omega t}$

$$f_t - \frac{1}{3\mu} \left[ -\nu f_{xxxx} + \left( \frac{\partial \phi}{\partial x} \right)_{ho} f_x \right] h_0^3 = 0$$

$$\omega - \frac{1}{3\mu} \left[ -\nu k^4 + \phi_{ho} (-k^2) \right] h_0^3 = 0$$

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

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

Characteristic Eqn  
 $\phi_{ho} = \frac{A}{6\pi h_0^3}$   
 $\phi_{ho}^* = -\frac{A}{2\pi h_0^4}$

So, this is the characteristic equation which we obtained, and from that if we consider the interface - effective interface potential to be made up of only the vanderwalls interaction, which is the major part that so causing the destabilization.

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

$h_0 =$  Film thickness  
 $\mu =$  viscosity  
 $A =$  Hamaker constant  
 $\gamma =$  Surface Tension  
 $k =$  Wave No.  $= \frac{2\pi}{\lambda}$

$A$  and  $\mu$  are always positive.  
 $\gamma$  is positive.  
 $\frac{A}{2\pi h_0^4} k^2$  is Destabilizing and Positive.  
 $\gamma k^4$  is Negative.

Only way  $\omega$  can be positive is if 1st term has to be positive  $\Rightarrow \omega$  can be positive.

Condition of film instability based on attractive VdW interaction is  $A > 0$ .  
 $A < 0$  | Film is unconditionally stable.

$\rightarrow$  Viscosity only can influence the dynamics but cannot influence the stability of the system.

We can see that the only condition under which the film can become unstable is only when the effective hamaker constant is positive. The other important features that we observed is that firstly, surface tension we have been arguing qualitatively that it has a stabilizing role, and you can see from the expression very clearly now that this term is always going to be negative trying to make omega negative, and surface tension is associated with this particular term. So, this shows that for an intact film surface tension always as a stabilizing influence. The second term of course, you can see that the only possible destabilization, this destabilizing term is the first term which is to reach the hamaker constant is associated, and depending on the sign of the hamaker constant, whether it is positive or negative, you can potentially have a stability or instability.

So, in the even that hamaker constant is also negative, the effective hamaker constant is also negative, then you have first term is negative, because this multiplies h zero to the power 4 is always going to be positive, h zero is a positive film thickness, it is a physical number; K square, we have already argued that it is going to be always positive irrespective of whether K is positive or negative. So in that case, both the terms are negative, so omega is going to be negative. The other important aspect is that we find that there is a pre factor and which is h zero divide by 3 mu, which contains the viscosity, the effects of the viscosity of the film mu is always positive. So, this pre factor can never influence the sign of omega, but what it can do is? It can influence the magnitude of omega inversely.

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$$f_t - \frac{1}{3\mu} \left[ -\nabla^2 f_{xxx} + \left( \frac{\partial \phi}{\partial h} \right)_0 f_x \right] h_0^3 = 0.$$

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

Repetitive in space and exponentially growing in time.

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

$k =$  Wave Number  
 $\omega =$  Growth coefficient

Linear superposition of all modes of a Fourier series.

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

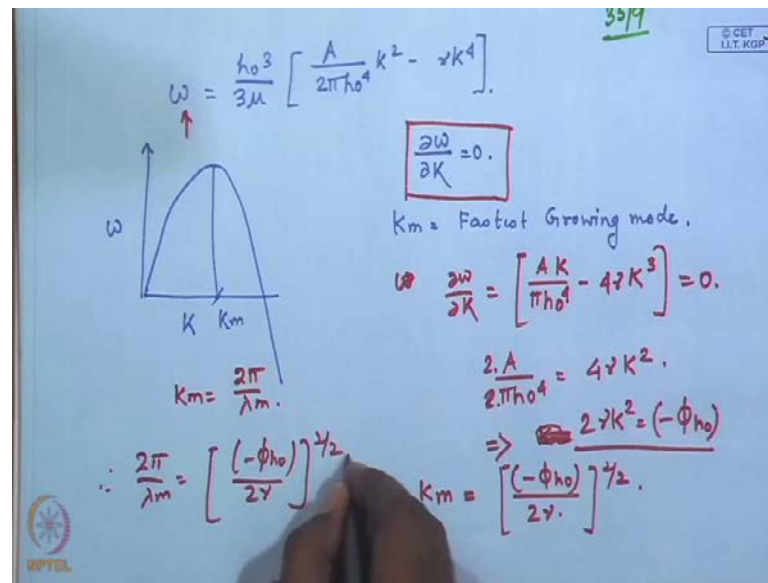
High  $\mu$  → Reduced  $\omega$

Film can only become unstable when  $\omega > 0$

So, higher viscosity lower will be the magnitude of omega, and the after all the growth is going to be determined, the growth of the fluctuation is going to be determine by e to the power omega t. So, what it implies that if higher viscosity will lead to a reduced omega, so the growth of the instability will be sluggish. Therefore, viscosity cannot influence the stabilization or the stability of a system, but it can affect the dynamics, the evolution dynamics of the system. The other interesting thing to notice that even if you have A to be positive, the powers of the exponents of K associated to these two terms are going to be differ or anywhere different. Or in other words, even if A is positive and this term is numerically higher than this term that also is a function of K.

So, for higher case for example; so for higher wave number, what might happen that even if you have A is positive, the second term might be higher than the first term. So, there might be a limit on the magnitude of K up to which the instability can be manifested. So higher wave, in other words, what it physically implies that the higher wave number oscillation are the, we also know that K can be, K is the wave number and it is correlated to the wave length as  $2\pi$  by lambda. So in other words, that higher wave numbers or the lower wave length oscillations, sort of fail to destabilize a film.

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The other important thing that we just started to talk is that you can find out the  $K$ , which sort of exhibits the fastest growing mode by differentiating or setting  $\frac{\partial \omega}{\partial K}$  equal to zero. So, what we have? This is the expression of  $\omega$ , so if you said  $\frac{\partial \omega}{\partial K}$ , the expression of  $\frac{\partial \omega}{\partial K}$ , what you get is  $A$  divided by  $\pi h_0^4$  minus  $4\gamma K^3$  into  $K$ . So once you set this to zero, you get or  $K$  turns out to be and if you look carefully this particular term one can write; and so one can, all we have done is we have multiplied and divided this term by 2; and what you get here, if you remember carefully, this is the expression of  $-\phi h_0$ . So, what you get is you can cancel this 2 with this 2,  $2\gamma K^2$  is equal to  $-\phi h_0$ . Therefore, so this is this correspondence to  $K_m$ , the fastest growing mode; this turns out to be  $-\phi h_0$  by  $2\gamma$  and the root of that. And what we already have,  $K_m$  corresponds to  $\frac{2\pi}{\lambda_m}$ ; therefore,  $\frac{2\pi}{\lambda_m}$  is equal to  $-\phi h_0$  divided by  $2\gamma$  less to the power half.

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Handwritten notes on a blue background showing mathematical derivations for film instability. The notes include:

- $\lambda_m^2 = \frac{8\pi^2\gamma}{(\phi h_0)}$
- $\therefore \lambda_m^2 \sim h_0^4 \Rightarrow \lambda_m \sim h_0^2$  (circled)
- $\phi h_0 \sim h_0^{-4}$
- $N = \lambda^{-2} \therefore N \sim h^{-4}$
- $\tau = 12\mu\gamma [h^3(\phi h_0)^4]^{-1} \ln\left(\frac{h}{\epsilon}\right) \lambda$
- A diagram showing a film of thickness  $h$  with holes of size  $\lambda$ . The scaling  $\lambda \sim h^2$  is indicated.
- A note: "Final morphology does not comprise of holes only  $\Rightarrow$  droplets. ...."

Which gives us lambda m square is equal to 8 pi square gamma divided by phi h zero. You can just do the numerical's yourself and you will be able to get it. Now, phi h zero scales as h zero to the power minus 4; so, if you plug this in, what you will get that lambda m square scales as h zero to the power 4 or lambda m scales as h zero square. Now, this is really important, because in actual experiments you can measure lambda m. And therefore, you can correlate it to the and you know the film thickness. So, you can from experimental condition generate a plot versus h, for h versus lambda. And in cases, where you find that the scaling the on a, if you plot on a log log plot and you find that in your experimental value a lambda is close to h square. Then in a circuit as way sort of you conclude that well my interfacial instability or the film instability has been triggered by attractive vanderwalls interaction.

So this is the standard practice, one can get the expressions for number density of the holes also; so, you have an unit area over which the number density is; let us scales as lambda to the power minus 2 and therefore, number density typically scales with the film thickness as h to the power minus 4. One can also get the shot nine time scale for rupture of the appearance of the instability and the expression of which is given as, there is no need to go in to the detail derivation, but this gives you an idea about when your first holes are the film is going to rupture and your holes are your holes are going to appear.

So, that sort of gives us a very rudimentary type of a theoretical understanding about the physics that governs the thin film instability. So, what  $\lambda$  gives you is that you have taken a flat film, the undulations grow and this is what  $\lambda$  stands for. So, this sort of gives you a 2 D or a sort of line profile of how your unstable structures are going to look at, but it can never give you, the linear stability analysis can never give you the full fledged 3 D morphology of how the things are going to look, which can be achieved by higher order or more complicated three-dimensional numerical simulations. And Professor Ashutosh Sharma has a group at IIT Kanpur is extremely active on this particular area. In fact, they were the first one in 1998 to show or come up with a full fledged three dimensional numerical analysis, to predict the précised morphology. The biggest advantage has been that, once you have 3 D predictions of 3 D simulations, these results of predicted morphologies can be directly compared with experimental findings.

So, the progress in this field has been significant with both experimental findings and results, the simulated results sort of coming parallely, in some cases, they do match; in some cases, they do not match; of course, one has to understand that whatever predefined simulations you do, the interactions of the others forces you have sort of predefined. So, if there are any other force fields of factors that remains sort of unaccounted for in the simulation. And based on inputs from both simulations as well as from experiments, there had been significant development in the whole field.

We will focus, we will not go into that detailed complicated mathematical stuff, but we will focus more into the qualitative aspects of thin film dividing, particularly the morphological evolution. And another important thing we will discuss is the role of visco-elasticity, because do not forget one thing that, the various offending equation has been written the form of the navier stroke's equation we have taken; we have used a simple viscosity  $\mu$ , which implies that it has been model as a Newtonian fluid. But we are telling that, we are repeatedly saying that we are looking at the instability of polymorthian films; so which have long chain molecules and often there is significant visco-elasticity of these molecules.

So, there has been simulations which have considered the effect of visco-elasticity, the appropriate real logical effects have been considered, and there has been significant progress, but those are all research level topics and i really do not want to dump you with all that which is happening. So, these most of these simulation with visco-elasticity of coming in the last two three years. But if you look at the effect of visco-elasticity in the experiments, they are more pronounced and rather easy to detect.

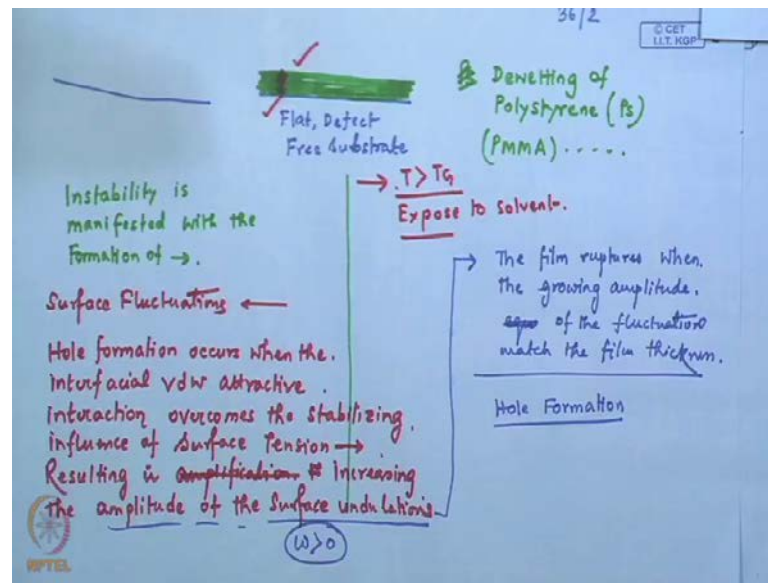
So, subsequent part of this class, we will spend on looking at the evolution sequence and also the roles of critical roles of visco-elasticity and other parameters. Because one thing you have to understand that, if you look into what we have done so far with this apparently complicated, but in reality very simple mathematics. Is we have just looked into the condition at which or under which the film ruptures. But we have already seen in video that even beyond the film rupturing, there is some subsequent morphological evolution. And the final morphology of a deviated film does not really comprise of holes only, but we have seen that in many cases it forms droplets. So, we will see how this subsequent transformation takes place now onwards.

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So, we start of our pickup the thread again by looking at the video we have been seeing for a while now.

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So, let us get back to the real paradigm of experiments; so, what you have done? You have taken a flat substrate, flat defect free substrate on to which you have coated your thin film by any of the standard coating techniques. So, let us say this is polystyrene and polymer like polystyrene, Dewetting of polystyrene is the most well investigated model system; it is very easy to get other polymers which have been very well investigated at PMMA, but there are whole lot of polymers, functional polymers, conducting polymers with which deviating has been studied. So, the theoretical understanding or theoretical foundations as well as the experimental protocol remains roughly the same.

So we will discuss, let us say we just coat a polymer film and all we have to do, if the polymer has a room has a glass transition temperature, which is higher than the room temperature; we typically have to heat it up beyond its glass transition temperature or we can also expose it to its solvent vapor. So, we have discussed briefly what happens, very simply put at room temperature this type of a polymer is in amorphous form. So by increasing the temperature to  $T > T_g$ , all what we do is that we reduce the viscosity. And now, we have these interfacial interactions, so these interfacial interactions are now able to deform the liquefied film with reduced viscosity. And so, what you see here is, in real time that the holes appear, so you now understand the physics which governs the hole to appear.



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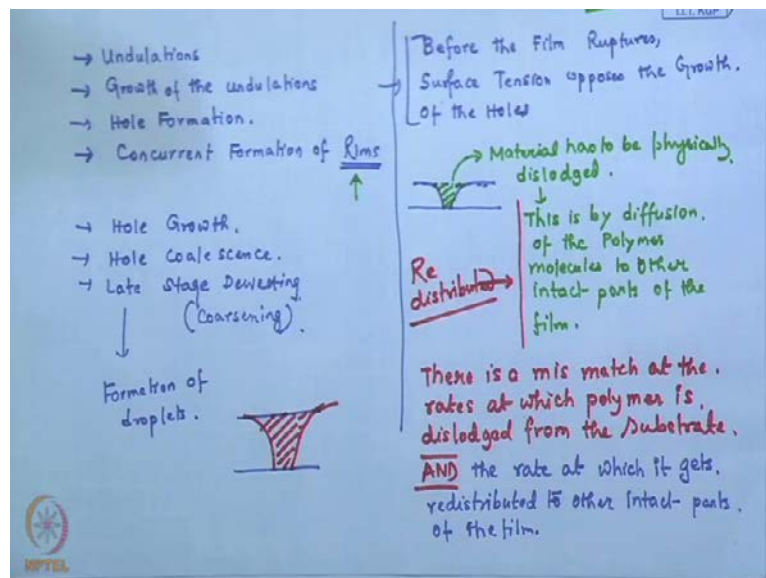


You now understand, so this is the film, all we are doing is under a microscope, we are just heating it up and you see the holes appear. So, you now understand the physics that leads to the appearance of the holes and they grow further. So there is a, and at the late stage, what you can see is that final morphology comprises of formation of holes. So, interestingly though your instability is manifested with the formation of holes **instability is manifested with the formation of holes**, the complete deviating sequence as a few subsequent steps. So let's write down, it is written here; these are the different sequences. So first, even before the formation of the holes, we have these surface undulations or the fluctuations we now understand that; then is the hole formation and we understand briefly what happens, the interfacial attractive van der Waals interaction overcomes the stabilizing influence of surface tension, resulting in the growth of the amplitude of the surface fluctuations.

So, just write down the key word. So first we have surface fluctuations, in the theoretical domain, this fluctuation is to the perturbation function; in the practical domain, this fluctuation is associated to the molecular level fluctuation. So, you have this surface fluctuations, hole formation occurs, when the interfacial van der Waals attractive interaction overcomes the stabilizing influence of surface tension, resulting in amplification, this is important. So, if the interfacial van der Waals interaction overcomes the stabilizing influence of surface tension, what it actually does? It actually amplifies the fluctuation.

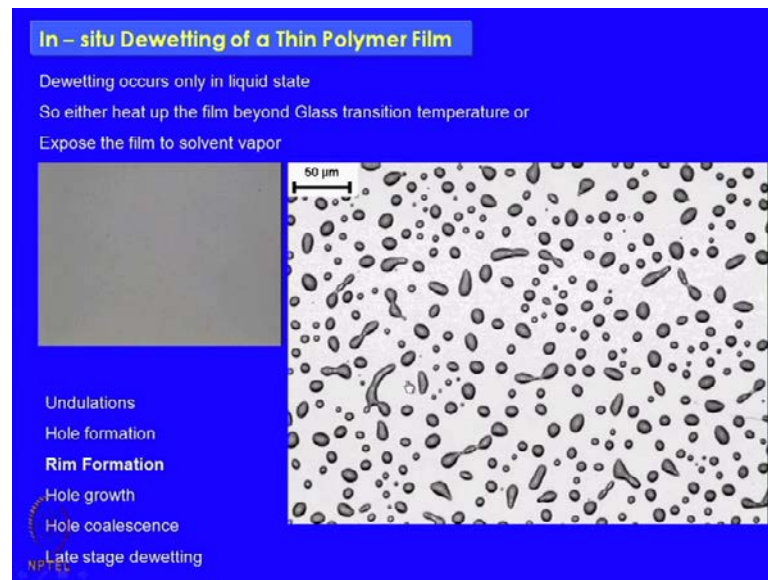
Amplifies the or increases results in increasing the amplitude of the surface undulations. So now, you can compare mathematically also; so, what does this thing mean? Interfacial vanderwalls interaction over comes the stabilizing influence of surface tension. That is in the characteristic equation, now the first term is positive and is higher than the second term. And amplitude of the undulations, so resulting in increased amplitude of the undulations. So, that is in the case when  $\omega$  is greater than zero and the film ruptures, when the growing amplitude matches or equals growing amplitude of the fluctuations match the film thickness. So, this is the step up to which we have understood through our linear stability analysis, the condition under which the film becomes unstable or it ruptures, but then, so this results to hole formation. Beyond this, you have seen in the video that there is growth of holes; so, we will let us write down nicely the different steps.

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So, first you have undulations, growth of the undulations, Hole formation. We will discuss now, that Hole formation is associated with the concurrent formation, of what is known as rims. This is a very important aspect of polymer thin film Dewetting formation of rims. Then hole growth, hole coalescence, and late stage Dewetting, where sometimes one can see some coarsening effects also. So, this is in a not shell, if you now agree to the sequence and look back to this video again, this is it. So, you cannot track the fluctuation stage under an optical micro scope, you are looking from the stage of hole formations; so, now, you are looking at hole growth.

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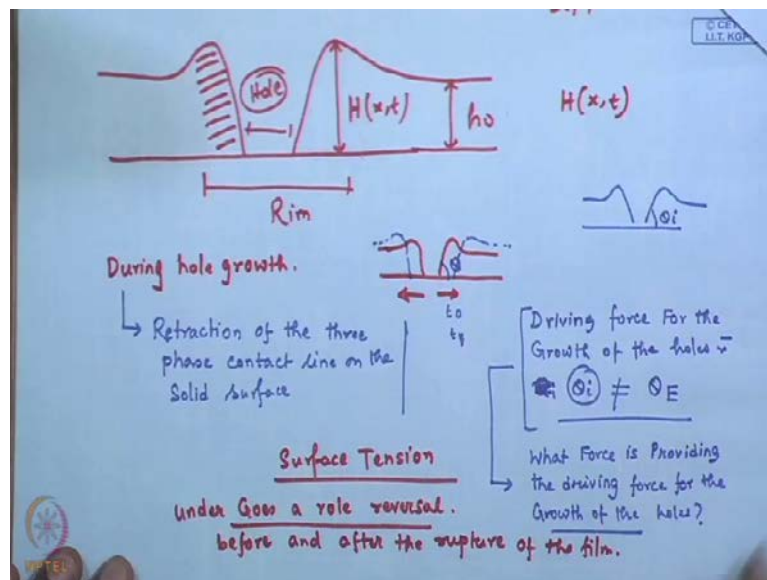


And this tiny black spots, what you see here in the micro graph, these are the rims, we will come to what those rims are; and then beyond hole growth we have the hole coalescence, which is clearer from this particular video at the late stage; so, this is what we call about the late stage Dewetting. Where the coalest holes or the rims sort of break down in to droplets due to Rayleigh instability, so we mark it as, let say formation of drop lets. So, important thing is the formation of rims; so what happens is two things are important. Firstly, we. So, let us note down; before the film ruptures, surface tension opposes the growth of the holes, we all understand that and that is also evident in here characteristic equation, surface tension opposes the growth of the hole.

Now firstly, let us talk about the rim formation; so what happens is, you had intact polymer here and a hole has formed. So, considering the fact that polymer cannot evaporate, because it is it has got very high (( )) pressure. So, if the formation of an hole essentially means that, the material from this particular zone has to be physically dislodged, so this material physically dislodged. And how it is dislodged? This is by diffusion of the polymer molecules to other intact parts of the film. Now, typically what happens is these are long chain molecules, so any way the diffusivity is low. So, what happens is, there is a mismatch at the rates at which polymer is dislodged from the substrate, and the rate at which it gets redistributed to other intact parts of the film.

So, this we will come back a little later, forget about that. So, we understand under what condition a hole forms, but one has to understand that a formation of a hole. So, this was an intact film; so, this a hole forms here. So, the hole can form or associated with the hole formation this material, because we all are chemical engineer, so we understand that mass has to be preserve. So, what happens to the material that was present, where a hole is appearing? So, this material has to sort of gets redistributed to other intact parts of the film; so, it gets redistributed to other intact of the film by diffusion, which is the slower process. So, there is a mismatch at the rates at which the polymer is dislodged from the substrate, and at which it gets redistributed to other intact areas.

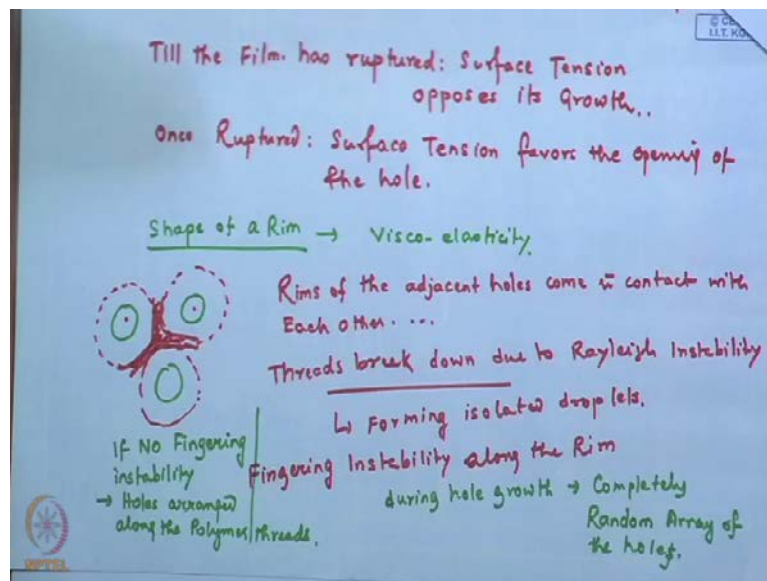
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So, this eventually results in the formation of a zone like this, which is higher than the mean film thickness. So this is what is a, what is known as a rim; this is a hole and with the formation of a rim. So in the stages of Dewetting, we talk that concurrent formation of rims, so here the rims appear. Now, the other important thing is that during hole growth, what happens is? Hole growth is associated with retraction, it is associated with three phase contact line on the solid surface like this. So, if this was the initial configuration at are  $t$  equal to  $t_0$ , this is  $t$  equal to  $t_1$ , the next one. And what is the driving force for this growth? So the driving force for this growth, let us write to once more holes is  $\theta_i$ , the intrinsic contact angle is not equal to the equilibrium contact angle  $\theta_e$ .

So, what is  $\theta_e$ ?  $\theta_e$  is the equilibrium contact angle made by the polymer on the substrate. And as the intrinsic contact angle, still does not match the equilibrium contact angle, therefore there is retraction; and we have already talked that this dynamics continuous up to the stage, when  $\theta_i$  becomes equal to  $\theta_e$ . Therefore, what is providing the driving force or what force is providing growth of the holes? This is a very important question, and the answer is equally exciting the answer is surface tension. So, surface tension essentially under goes a role reversal, before and after the rupture of the film.

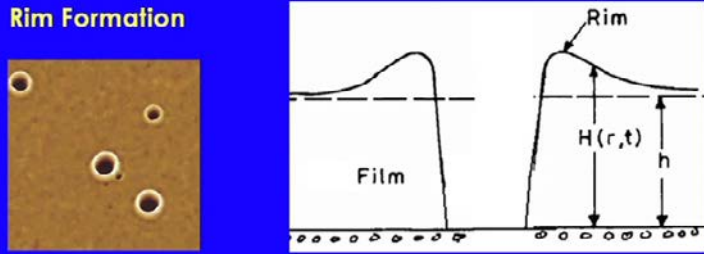
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So, till the film has ruptured, surface tension opposes its growth and once ruptured favors the opening of the hole.

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**Rim Formation**



The image contains two parts. On the left is a micrograph showing a brown surface with several circular holes and raised rims. On the right is a schematic diagram of a polymer film on a substrate. The diagram shows a flat film on the left and a film with a raised rim on the right. The rim is labeled 'Rim' and its height is denoted as  $H(r,t)$ . The original film thickness is denoted as  $h$ . The substrate is represented by a series of small circles at the bottom.

Rims form due to a mismatch in the rates at which polymer is dislodged from the surface and redistributed to the other parts of the film

The Shape of the Rim Contains significant information about the forces that are dominating the dewetting at any given instance

During various stages of dewetting, the shape of the Rim undergoes some morphological changes

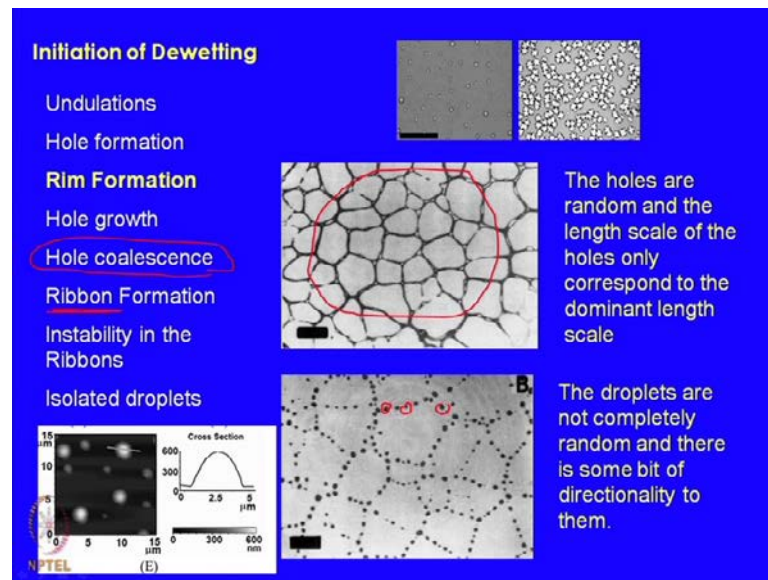
In some specific cases there can be instability of the rim itself.

The geometry of the Rim is strongly influenced by the presence of Slippage at the Substrate - film interface.

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So, this is something that we have already talked about, something we have already talked about; it is essentially, this is my atomic force microscope image which shows the clear formation of this rims of the polymer rich zones. So, as we have already talked at these rims formed due to a mismatch in the rates at which polymer is dislodged from the surface and it is distributed to other intact parts of film. The shape of a rim contains significant information about the forces that are dominating. So, this we will talk in detail, the shape of a rim, it is another very interesting aspect of polymer thin film Dewetting, which we will talk while discussing the effect of visco-elasticity shortly may be in this lecture or may be in the subsequent lecture.

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So, this is how it grows nut shell. So, appearance of holes, growth of holes, then what happens is? As the holes, so there is certainly not going to be the formation of only one hole as you saw in the video, there are many holes that appear together. So, that growing holes what happens is? So, you have holes here, you have holes her, so each of the hole is growing; so, each of the hole has a rim, which is also growing. So beyond this stage, because of the growth of adjacent holes, so the rims of these holes are adjacent holes. The other thing that you may understand, so you have a system, where you see a whole lot of holes. Typically, the  $\lambda$  that you have calculated from you linear stability analysis, roughly or grossly gives an idea about the center to center distance of the holes. So, an experiment in principle, you can take a snapshot, you can measure the center to this center distance for many number of holes and can do an average, and see whether it matches the predicted values from linear stability analysis, anyway.

So, you have these holes, thus the holes grow and eventually the rims of the advancing holes sort of start or oval or sort of merge with each other. Eventually, resulting in this type of a morphology, which is which resembles the polymer ribbons or this what is known as so subsequent to hole coalescence due to hole growth or coalescence of adjacent holes; you have what is known as the ribbon formation. So these are long, but pretty high isolated polymer threads, and as we have also seen, in this particular video, now this will make sense you. So at the late stage, you have this ribbons which are

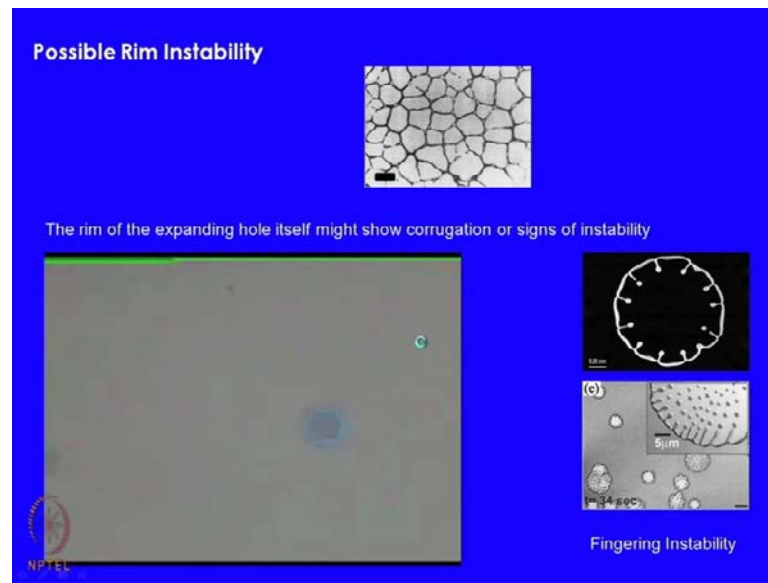
forming, and these ribbons or this polymer threads break down due to Rayleigh instability, forming isolated polymer droplets.

So this is, what you see is the polymer ribbons and then these ribbons break down into droplets, which can be arranged along the threads of the ribbons or there can be a morphology, where the droplets can be completely random, which is associated to what is known as the fingering instability or not associated. In case, there is fingering instability along the rim during hole growth, then one gets a completely random array of the holes. If else, if there is no fingering instability, we will see what is fingering instability in detail; then typically, the holes arranged along the polymer threads. So, this is a very typical configuration which was first seen by (( )) writer in 1992. So, you have the hole coalescence, the adjacent holes grow, they coalesce resulting in the ribbon formation stage; and these ribbons eventually break down in to isolated droplets due to Rayleigh instability.

Part of it, you can also see in this particular movie, so these are the polymer threads or the ribbons, what you have; some of them have already broken down this is captured from an intermediate stage, I would to say by in our lab by my students and what you can see very clearly is that with time, some of the threads, you track any one of the threads for example; it, lets you track this one. You can see that it sort of breaks down, see here you see this two makes occurring and this making is due to the Rayleigh instability and resulting in final droplets. Here is a situation, where it is more of a random droplet array not as well organized as this one.

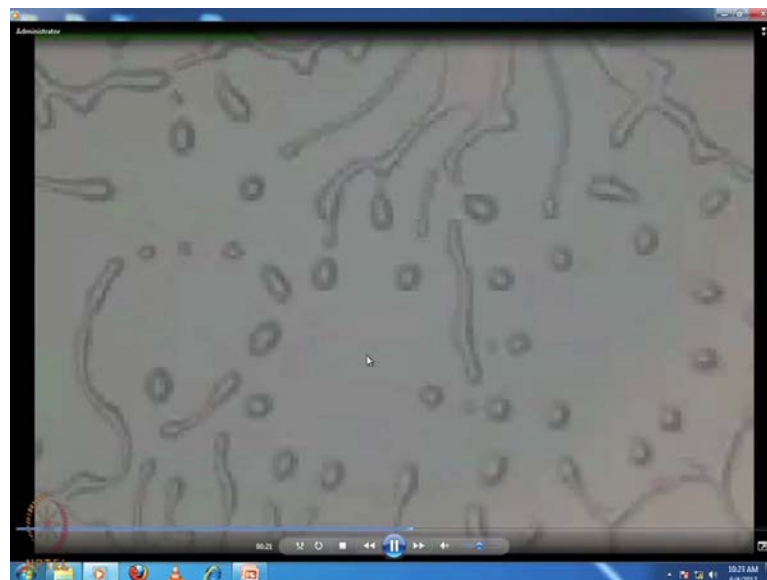


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So, there can be a signal, there a situation where you have possible rim instability or the fingering instability in a rim, which you can see in this particular video, it is not working this movie, but. So, let me just show you the movie

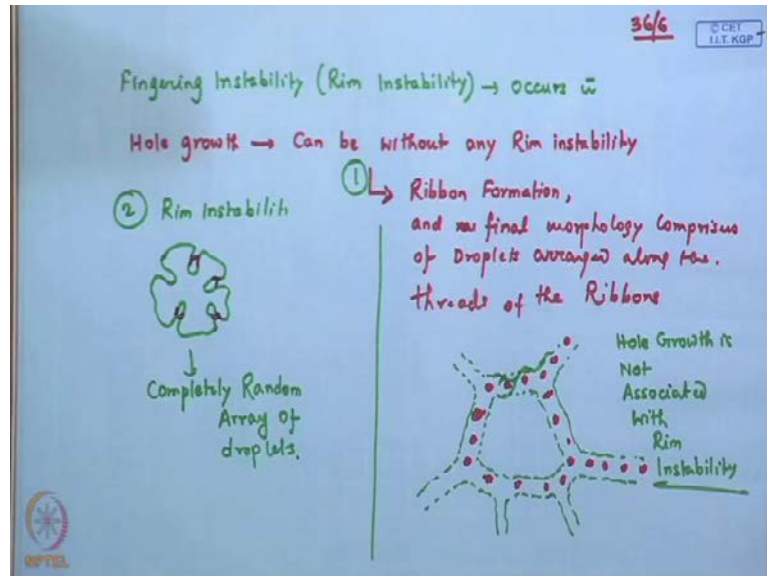
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So, here you can see that a hole is growing, and the growing hole, the growth of the hole is sort of not uniform, but it sort of shows some fingering instability and along the periphery of the hole. And as the hole grows, it sort of lives behind some droplet. So, this

is a very interesting movie, you can see that here you see the early stages the hole are growing.

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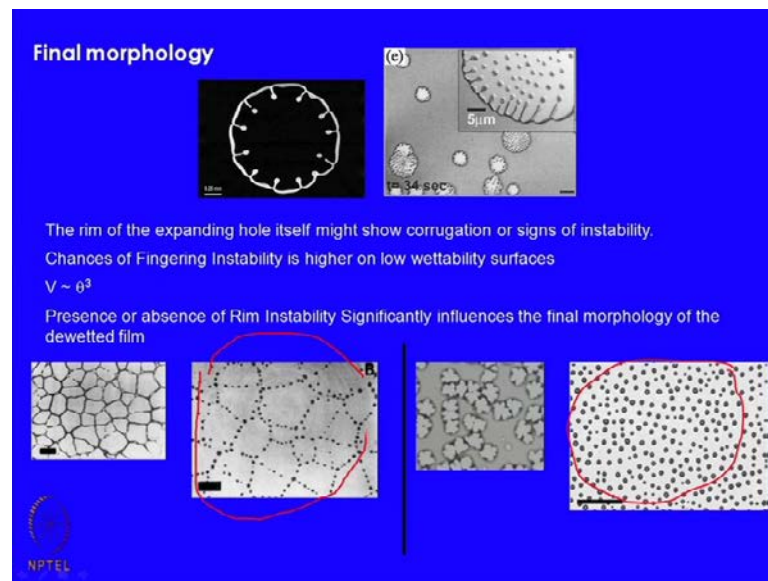


So, ideally the way we have discussed that hole should grow nicely circular hole the growth should be circular, but in certain cases, particularly fingering instability, as this is known or often it is also called the rim instability occurs. It is still under investigation, so people are still speculating what exactly leads to these two distinct morphological evolution sequences. So, hole growth can be associated, can be without any rim instability. In that case, one gets to the stage of ribbon formation and final morphology comprises of droplets arranged along the threads of the ribbons.

So, your final morphology in this case is something like this. So, you essentially what you can conclude by looking at the structure that you had let say, some threads like this and which has sort of broken due to the in plane Rayleigh instability forming droplets. So, this is the situation where the hole growth is not associated with rim instability. In contrast, when you have rim instability; so, this is the first possible root, this is the second possible root. So, this root is observed more in case of thinner films on lower molecular weight polymers; so, particularly on the other root with where you have rim instability, the hole growth itself there are some undulating fingers in a growing hole and these eventually ruptured detach from the retracting meniscus. So, finally, what you get is a completely random array of droplets.

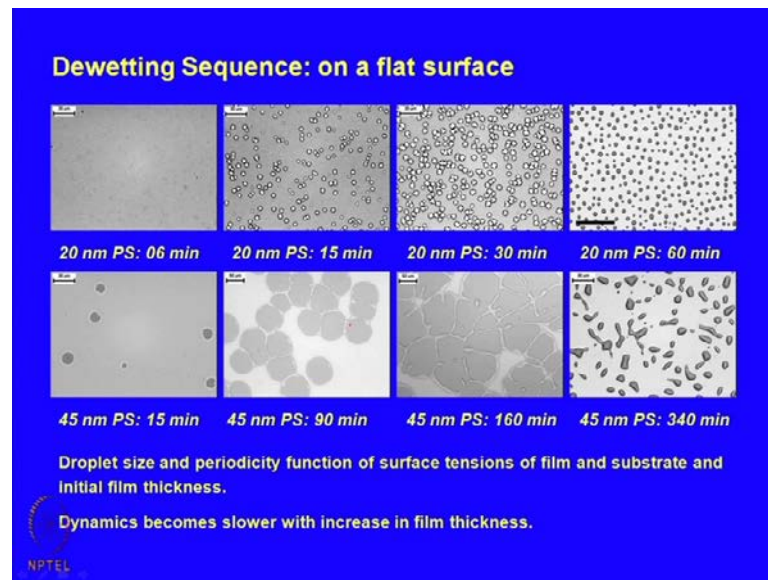
So, let us have the look at the video again. So, here you see a very clear contact line you can see from the height difference that you have the rim formation and see these are the droplets which are the fingering instability, so that breaks into the droplets. And you see that over all morphology comprises of a completely random array of droplets, no threads nothing. So that is the key difference, when you have a rim instability and you do not have a rim instability.

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So this is, if you have a rim instability or fingering instability this is the lightly morphology to get. You get a completely random array of the droplets, in contrast in cases where there is no rim instability; it is lightly that your droplets will be arranged like this.

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So, this is the Dewetting sequence we have already talked about

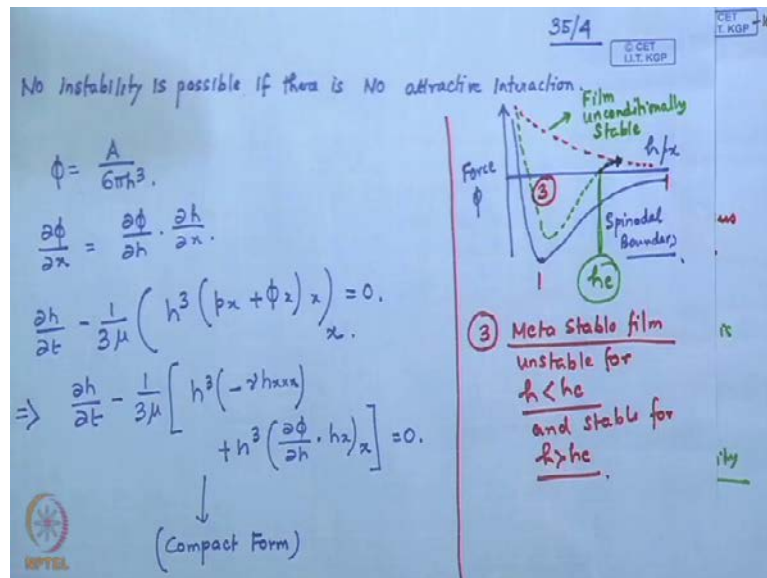
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And other mysteries include that the mechanism that we have suggested is for a spontaneous instability, which is available or possible only in case of a thermodynamically unstable film. But there can be issues, where one sort of can see dewetting in thicker films also, which is primarily due to what is known as heterogeneous nucleation. So, you have some surface defects or micro cavities on the surface, where the local film thickness might not be, so where the film may not be uniform and it can

preferentially ruptures. So, during the spin coding phase itself, for example, it can rupture or even after it is coated. So, what happens is a heterogeneity essentially acts as a zone, where locally the film thickness is a lower than the spinodal limit, particularly in a Meta stable film. So, you can have heterogeneous nucleation, but we are not going into that much amount of details. You can also have what is known as homogeneous or thermal nucleation, which is pretty prominent case of Meta stable films. We talked about Meta stability, so these are films there is a critical thickness above which the film is thermally stable. So, above which the film is thermodynamically stabilize same **sorry** for that. So, what happens is that, if your film thickness is close to the spinodal boundary.

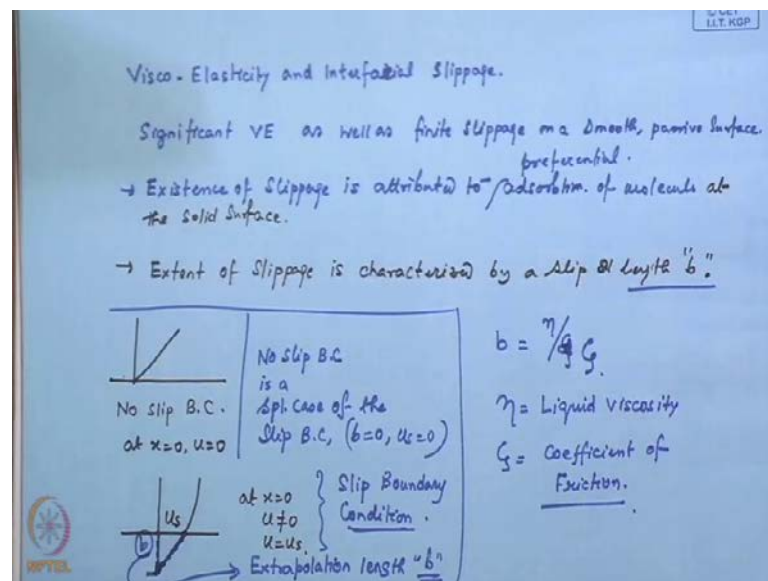
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So, here is the spinodal boundary you will say, which is  $h_c$ . Why the spinodal boundary, because if the film is thinner than  $h_c$ , it becomes spinodally unstable, thermodynamically unstable or it should exhibit spontaneous instability. But often in a Meta stable film, you see a spinodal light deviating even for thicker film. So what happens is, beyond  $h_c$ , but very close to it; you have a film thickness which is beyond  $h_c$ , but then you have this surface undulations. So as a part of this undulation, sometimes these undulations, since they are associated with a couple of nano meter amplitude. Locally at certain locations, the film thickness can drop below  $h_c$ , and then it just sort of follows this spinodal Dewetting root.

So, this is not a true nucleation, because you do not have to overcome any activation **(C)** which is very important for any heterogeneous nucleation. This is more like an homogeneous nucleation, which is an unique case that happens. So sometimes, this resume is also known as the defects sensitive spinodal resume by professor Sharma, but, let us not get into these very complex and complicated things. The other important thing that we need to discuss is that since, we are talking about polymer mills; so, there is a significant role of visco-elasticity and the interfacial slippage.

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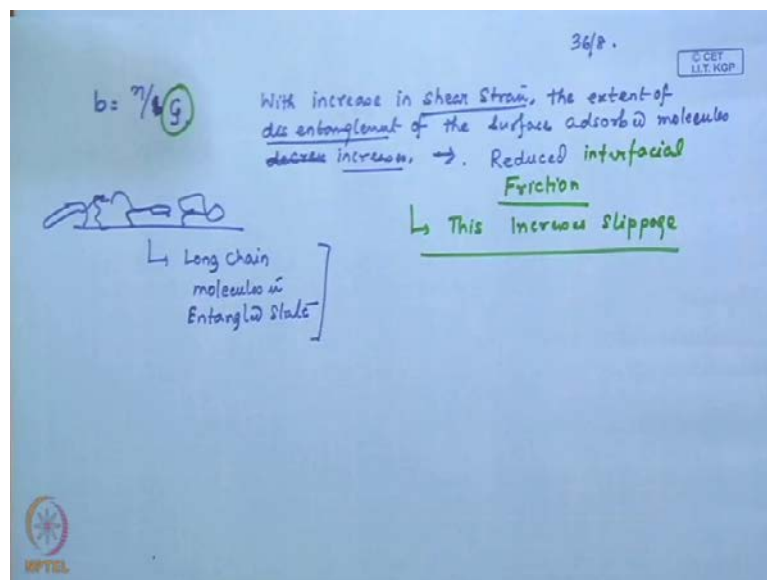


So, thin films of long chain polymers typically exhibit significant visco-elasticity as well as finite slippage on a smooth passive surface. The existence of slippage is attributed to adsorption of molecules or it is a preferential adsorption, adsorption of molecules at the solid surface. The extent of slippage is characterized by a slip length b. Now, going back to a fluid mechanics concept, so this is what is in a no slip boundary condition, where at x equal to zero, u is equal to zero; this is what is your slip boundary condition. So, at x equal to zero u is not zero, but u is something finite u is u s. So, this is what is u s, this is what is known as the slip velocity and the extent of slippage is sort of identified or quantified in terms of this hydro dynamic extrapolation length b, so this is sort of the extent of slip. So this is, I am sure in your fluid dynamics you have come across; this term, this slip boundary condition and which is a consequence of interfacial slippage, what we are discussing now.

And one must also understand that no slip boundary condition is a special case of the slip boundary condition. So, as  $b$  tends to zero,  $u_s$  is also equal to zero. So this is not a slippage, which is very, very common, but it is often encountered in long chain molecules with polymers. And so the extent of slippage, even here is characterized by a length  $b$ , which can be calculated in terms of  $\eta$  by  $\zeta$ ; where  $\eta$  is the liquid viscosity and this the coefficient of friction.

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So, what happens is when with increase in shear strain, the extent of disentanglement of the surface adsorb molecules decrease, increases and this in terms; so, what happens is you have a surface to which this polymer molecules are adsorbed as we have already discussed that this is attributed to the adsorption of the molecules. So, these are long chain molecules and they are in an entangle state. So, as there in a entangle state, so what happens is with increasing shear strain, there level of entanglement reduces of their extent of this angle, this entanglement increases; and these results in reduced interfacial friction. And therefore, since the coefficient of friction is at the denominator, therefore what happens is, this increases slippage; so, this is about slippage. We are running out of time in this particular class, so we will stop here this class.

In the next class, we will get started with a little bit about the visco-elasticity, and then primarily what we will talk is how the signature of visco-elasticity and slippage alters the morphological Dewetting path way of a polymer thin film. And then, we will move on two more very interesting things, but we will very briefly touch upon them. One is the Dewetting of a boiler polymer boiler, so instead of one interface, deformable interface you now have a two deformable interfaces. And the other important thing is that well, this Dewetting spontaneous instabilities perfectly fine for understanding the physics, but as we have told repeatedly that from the stand point of coating ,this is disastrous. So, we will talk about some of the strategies which can be adopted to suppress this deviating, even in ultra thin films. Thank you.