Soft Nano Technology
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Lecture – 35
Dewetting – 3

Welcome back. We talked in detail about the Van der Waals interaction or the free energy of interaction due to Van der Waals sources between two surfaces or two blocks. And we are now convinced that indeed as compared to two fundamental particles, where the interaction scales as 1 by r to the power 6 between two surfaces the interaction is 1 by d square.

In addition to that we have now realized that there can be excess free energy in a thin film, we have derived an expression for that. And we have also found out another criteria for understanding whether a film is stable or not and that is based either the effective inter phase potential or the disjoining pressure whichever is its essentially the same thing.

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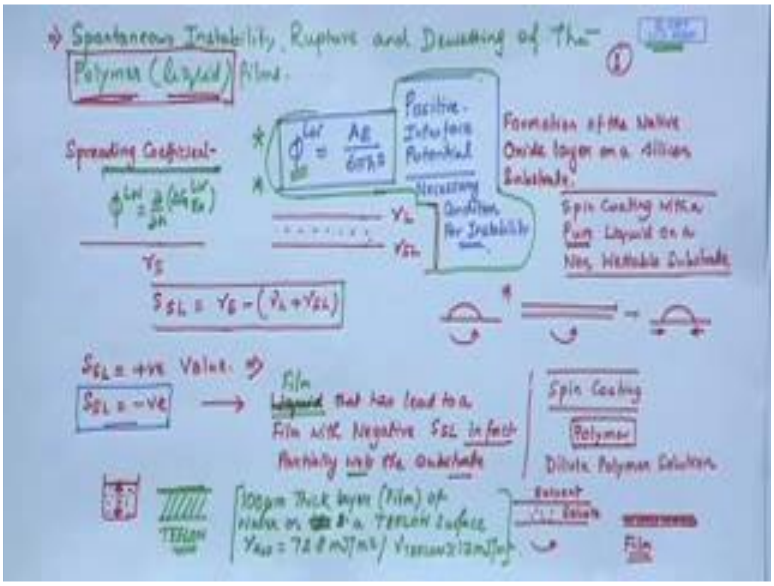


⇒ Spontaneous Instability, Rupture and Dewetting of The Polymer (Liquid) Films.

Spreading Coefficient

$S_{SL} = \gamma_S - (\gamma_L + \gamma_{SL})$

$\phi^{LW} = \frac{A_E}{6\pi h^3}$ Positive Interface Potential. Necessary Condition for Instability

Formation of the Native Oxide layer on a Silicon Substrate.

Spin Coating with a Pure Liquid on a Non Wettable Substrate

S_{SL} = +ve Value ⇒

S_{SL} = −ve → Film that has lead to a Film with Negative S_{SL} in fact Partially wets the Substrate

Spin Coating

Polymer

Dilute Polymer Solution

100 µm Thick layer (Film) of Water on a TEFLON Surface

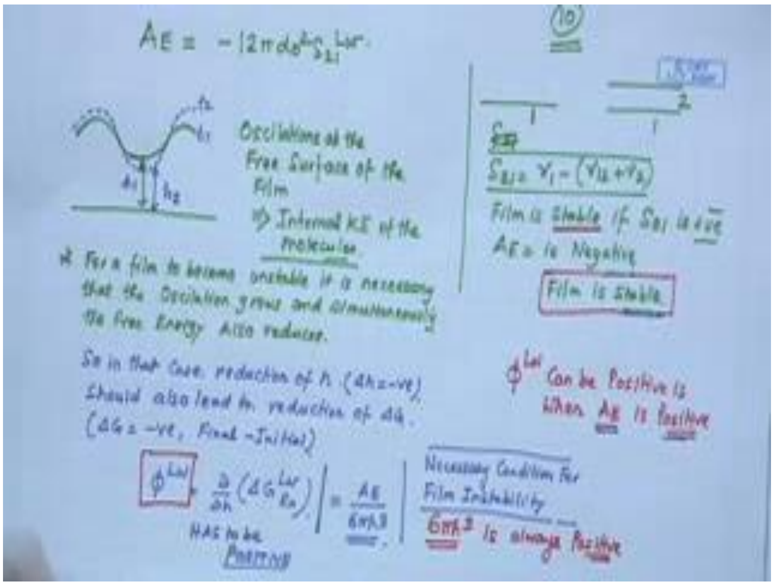
So, this is a hand written slide which is used to sort off trigger the discussion on spontaneous in stability. And if you look into that lecture, what you will see that only this part I have added based on what we discussed in the previous three lectures, only this part. So, what is it? While I discussed about the stability and instability at this level right, I talked about or tried to explain it only in terms of spreading coefficient. What I implied or emphasized if the spreading coefficient is positive; that means, that by coating the film we have been in fact reduce the total surface energy. Therefore, the film is unconditionally stable.

What on the other hand, if the spreading coefficient was negative, then what it implies that coating the film or rather I would replace this liquid with film has led to in fact, the liquid partially wets. So, by way of coating the film you have in fact, increased or we have increased the total energy. And therefore, thermo dynamically this film is not stable. But there was a limitation or there is in fact, a limitation of this spreading coefficient based approach and that is the expression of spreading coefficient does not consider the film thickness.

So, based on spreading coefficient you will get that if you try to have a 100 micron thick layer of water on a surface of Teflon 100 layers which we have no harm in marking that as a film, thick layer of water on a Teflon surface. Why I am giving this example because water any of you would know by now gamma H 2 O is 72.8 mille Joule per meter square. Teflon is of the order of 12 mille Joule per meter square.

Plug in the values even if you assume gamma interfacial attention is of the order of five or something like that. You are going to have a significantly negative value of spreading coefficient. So, based on spreading coefficient what you will get that this thick layer of Teflon, a thick layer of water on Teflon is going to be unstable right. That is what your spreading coefficient alone will tell you. But reality is this film will remain there nothing is going to happen to this film because a film is two thick and those surface fluctuations will never get adequate help from interfacial Van der Waals interaction to growth. They will always be flat and down because of Laplace pressure.

However, if you now look into this effective Hamaker effective interface potential, what we have got from the consideration of the excess free energy, how the excess free energy. So, let me also write down its expression as delta delta h of delta G LW excess. So, what does it give? It actually gives you an idea how the free energy, the excess free energy of a thin film changes with change in the film thickness. So, what it means that because of this fluctuation there is change in the local thickness of the film and as a consequence or as a result of that the excess free energy also changes. (Refer Slide Time: 05:43)



$A_E = -12\pi d_0^2 S_{21}^{LW}$

Oscillations at the Free Surface of the Film

⇒ Internal K.E of the molecules

* For a film to become unstable it is necessary that the oscillation grows and simultaneously the free energy also reduces.

So in that case reduction of h ($\Delta h = -ve$) should also lead to reduction of ΔG. ($\Delta G = -ve$, Final − Initial)

$\boxed{\phi^{LW}} = \frac{\partial}{\partial h}(\Delta G^{LW}_{Ex}) = \frac{A_E}{6\pi h^3}$

HAS to be POSITIVE

Necessary Condition for Film Instability

$6\pi h^3$ is always Positive

$S_{21} = \gamma_1 - (\gamma_{12} + \gamma_2)$

Film is stable if S_{21} is +ve

A_E is Negative

Film is Stable

ϕ^{LW} can be Positive is when A_E is Positive

Now you understand or what we very nicely discussed towards the end of the previous class is that for the film to become unstable it is necessary that the oscillation grows and simultaneously the free energy also reduces. Otherwise the process will not evolve because it is a spontaneous instability. And that gives you a necessary condition for film instability or the film to become unstable is effective Hamaker effective inter phase potential phi LW must be positive. What is the advantage? Advantage is and that becomes positive only when your Hamaker constant is also positive. The effective Hamaker constant is also positive because of the fact that this particular term 6 phi h cube is always going to be positive.

And therefore, effective inter phase potential will be positive only when Hamaker constant is positive that is fine. But what is the advantage of looking into effective interface potential as compared to let us say spreading coefficient. The advantage is its expression contains h and therefore, if you look into this type of a system right, you might have A to be positive, but since the expression contains h it will not indicate a positive value, but it will indicate phi LW to be equal to 0. And therefore, you know that you have failed to satisfy the necessary condition of instability right.

So, I would put it and as we are sort of strengthening our concepts based on slowly from spreading coefficient to effective Hamaker constant to now the effective interface potential or the conjoining and disjoining pressure. This is in fact, probably the best bench mark to identify or examine whether a film is thick or thin. Of course one of the necessary conditions is AE is positive for the film to become unstable.

We have had enough discussion on that I am not going to repeat it. But then you can have situations where AE is positive, but the film eventually remains stable it is simple because of the fact that h is too high, to large and therefore, this term because the denominator becomes so large tends to 0. And then you know that well you have a thermo dynamically unstable film, but it is actually stable is stabilize by gravity. There is too much amount of thickness, there is too much amount of material and your Van der Waals sources are too week to grow by dislodging so much amount of material.

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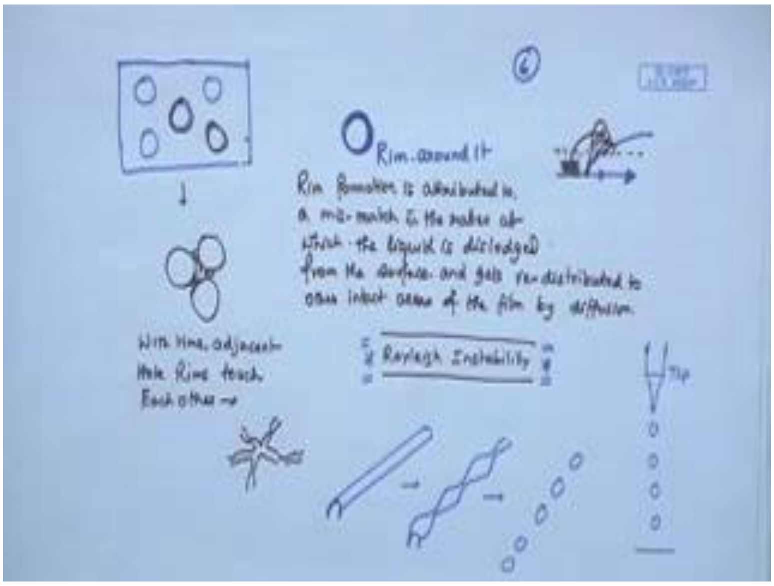
Rim formation is attributed to a mis-match in the rates at which the liquid is dislodged from the surface and gets re-distributed to other intact areas of the film by diffusion.

With time, adjacent hole Rims touch Each other →

So, now coming back to the issues related to dewetting, what we had discussed? We are discussed quite a few points. In fact we now know that the spontaneous in stability observed in a liquid film is in fact, long wave instability. We also know that before the film raptures there is in fact, a competition between disjoining pressure which tries to destabilize the film and Laplace pressure surface tension given Laplace pressure which rise to stabilize the film.

So, essentially as long as the film has not ruptured, surface tension has a very nice role trying to maintain the film integrity. However, the movement the film has ruptured in fact; the whole growth is favored by surface tension.

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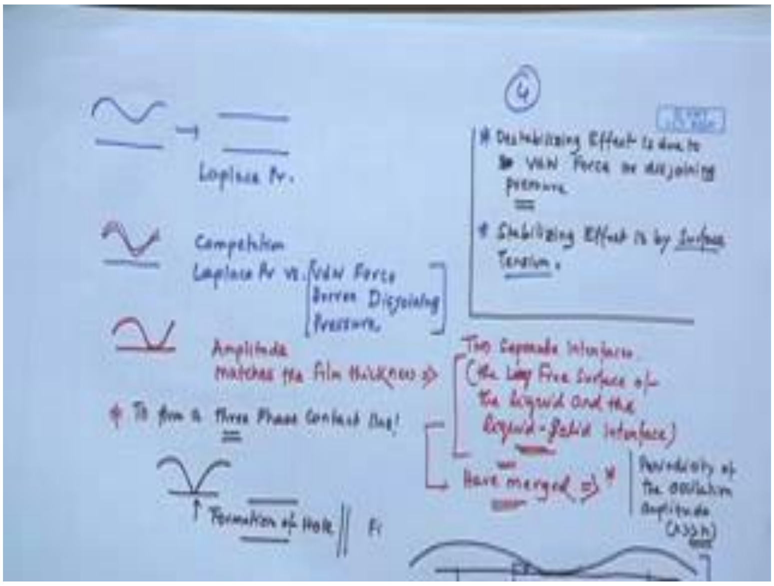

So, there is in fact, a role reversal of surface tension before and after the ruptured of the film. We also know that whole formation is not that simple as we have talked about a particularly the retraction and the dewetting part. Because there is a miss match in the rates at which the material is dislodge from the surface are which distributed to the intact parts of the film and that often leads to the formation of a rim around a growing whole.

And in fact, it turns out to this rim profile sort of gives lot of idea about the viscoelasticity of the film. So, if you have long chain polymer which is due to entanglement affects more viscoelasticity in fact, the rim profile becomes very very skew terminate becomes very sharp in one of the two side inside and outside it is pretty slanted I will skip all the details from the time being.

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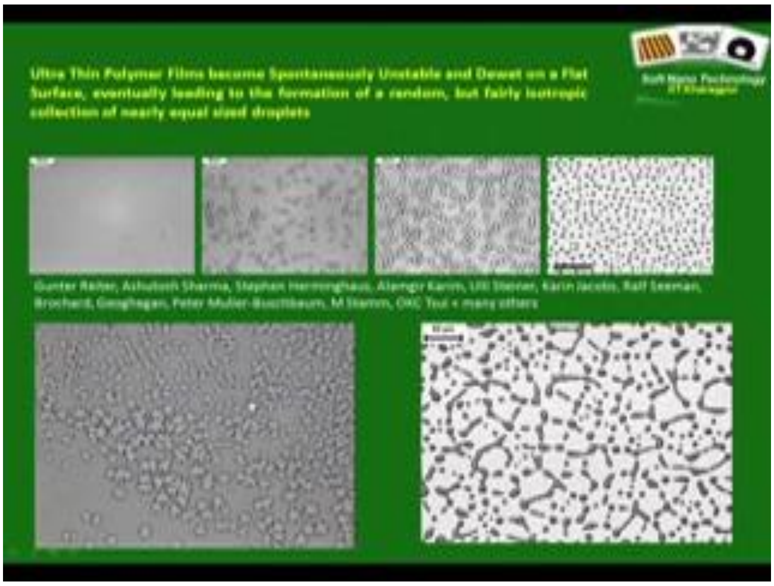

Ultra Thin Polymer Films become Spontaneously Unstable and Dewet on a Flat Surface, eventually leading to the formation of a random, but fairly isotropic collection of nearly equal sized droplets

Soft Nano Technology IIT Kharagpur

Gunter Reiter, Ashutosh Sharma, Stephan Herminghaus, Alamgir Karim, Ulli Steiner, Karin Jacobs, Ralf Seeman, Brochard, Geoghegan, Peter Muller-Buschbaum, M Stamm, OKC Tsui + many others

Anyway so, let us have a quick relook at these two videos. So, what are the things you now? You know that the film is rupturing. Therefore, you know the spreading coefficient is negative, you know the effective Hamaker constant is positive, you know the effective interface potential is positive etcetera etcetera. You see that it and this is the late stage thing where we also talked that. In fact, the adjacent rims join up. These rims lead to a cellular structure comprising of very tall high aspect ratio threads which eventually break down to you to what is known as Rayleigh instability.

You are more than welcome to check in the net about a little bit more detail about Rayleigh instability. I will not get the time to cover it in the course, otherwise something very very interesting. So, it is essentially if you have a long liquid trade like this, it tends to become oscillating and undulating because of effects of surface tension. And it eventually this integrates then to droplets. In fact, if you can very simple experiment with a regular tap, if you try to turn of the regular tap or if you sort of make the flow very very thin and its sort of and to I mean just ahead of closing the tap. You see that so, this is let us say the tap, the flow is much reduced. So, you see the meniscus become like this and then you observe that water is falling in drops.

So you have a feeling, well I have all most closed the tap nearly fully. So, the supply is intermittent and therefore, we are seeing drops. That is not the case. In fact, the supply is continuous, but it is say very low supply and then ideally it should form a long cylinder of very tiny thread or cylinder of water which in fact, disintegrates due to Rayleigh instability into these droplets. You can try it out yourself.

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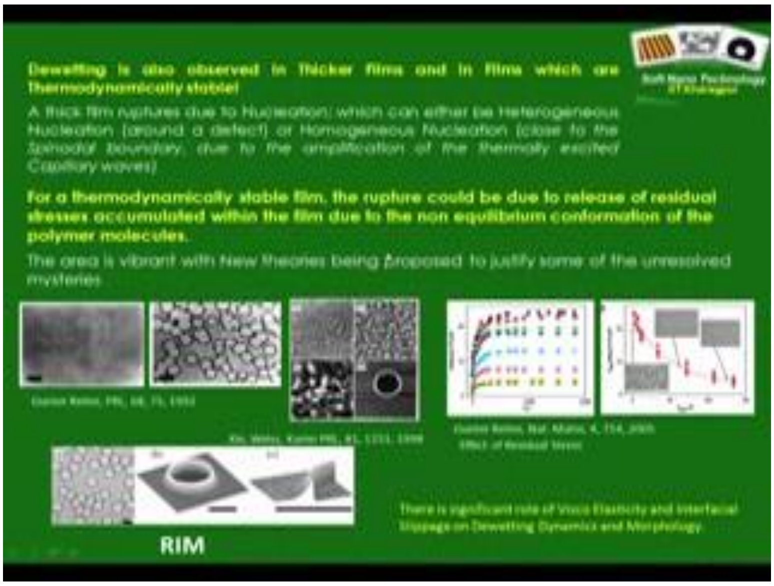

Dewetting is also observed in Thicker films and in films which are Thermodynamically stable!

A thick film ruptures due to Nucleation; which can either be Heterogeneous Nucleation (around a defect) or Homogeneous Nucleation (close to the Spinodal boundary, due to the amplification of the thermally excited Capillary waves)

For a thermodynamically stable film, the rupture could be due to release of residual stresses accumulated within the film due to the non equilibrium conformation of the polymer molecules.

The area is vibrant with New theories being proposed to justify some of the unresolved mysteries

Gunter Reiter, PRL, 68, 75, 1992

Xie, Weiss, Karim PRL, 81, 1251, 1998

Gunter Reiter, Nat. Mater, 4, 754, 2005

Effect of Residual Stress

RIM

There is significant role of Visco Elasticity and Interfacial Slippage on Dewetting Dynamics and Morphology.

So, as I mentioned there are certain issues related this dewetting like this, rim profile is important. The whole lot of other stuff which I do not want to really complicate things and make things difficult for you, but some of the observations is that one many times observes that films which are thermo dynamically stable. So, let us say where the spreading coefficient is positive right or the effective interface potential is negative based on the value of Hamaker constant. These types of films are also showing dewetting and following almost the similar mechanism.

So, people started to argue, there must be some additional feels that are responsibilities not only the Van der Waals force driven growth. And people have come up with lots of arguments like one often argues that hydrogenous nucleation is responsible. But nucleation typically requires surface in homogeneity and why across almost very sample the surface inhomogeneity is uniform is a matter of debate. So, people also came up with more creative thoughts for example, like there is accumulation of residual stresses during spin coating which slowly get reduced and as a film is reheated beyond its class transition temperature depending on the magnitude of the residual stresses stored within the film, it can ruptured.

So, there are some pioneering works in this particular area. I will as I mentioned these are too much of research level areas where contributions are coming in last five six years or may be last two three years. So, I will not going to too much of amount of details and I will focus on something that is bit more general.

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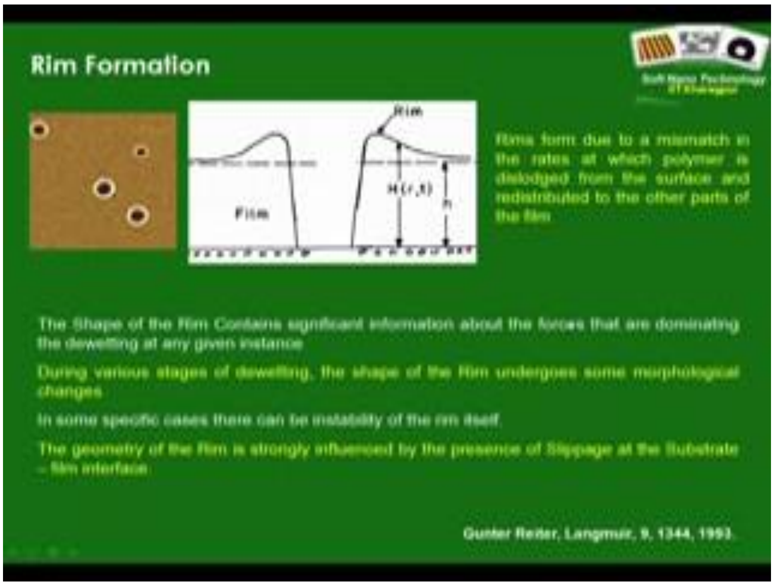

Rim Formation

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.

Gunter Reiter, Langmuir, 9, 1344, 1993.

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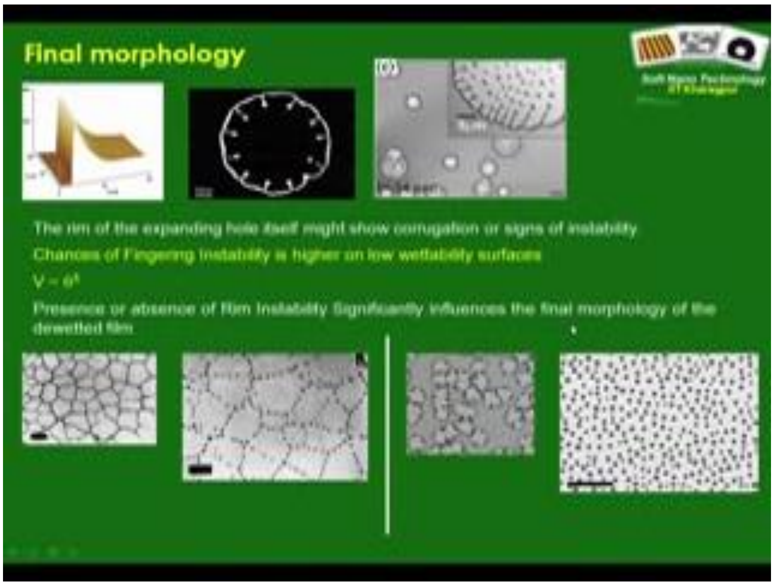

Final morphology

The rim of the expanding hole itself might show corrugation or signs of instability

Chances of Fingering Instability is higher on low wettability surfaces

$V \sim \theta^3$

Presence or absence of Rim Instability Significantly influences the final morphology of the dewetted film

So, there can be other issues like, so this is that cellular structure I was talking about. So, you see if have these cellular structures that the drops are not completely isotropic like what you see here. Here it is like a completely random collection of droplets, but here you see the drops sort of arranged according to the sort of contours of the cellular patterned. But here you see that the drops are completely random. Well it turns out that in this latter case, while retracting the rims themselves sort of started to show some short of an undulation and was leaving behind secondary droplets as the whole was growing.

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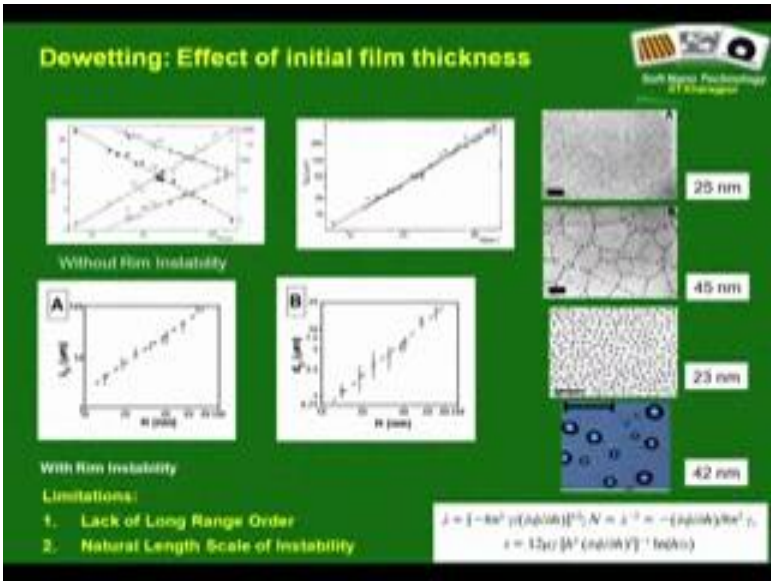

Dewetting: Effect of initial film thickness

Without Rim Instability

With Rim Instability

Limitations:

1. Lack of Long Range Order
2. Natural Length Scale of Instability

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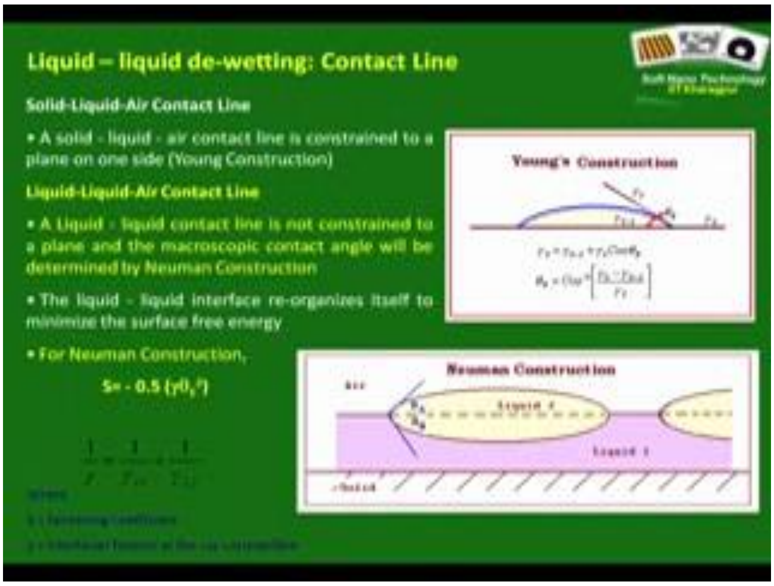

Liquid – liquid de-wetting: Contact Line

Solid-Liquid-Air Contact Line

- A solid - liquid - air contact line is constrained to a plane on one side (Young Construction)

Liquid-Liquid-Air Contact Line

- A Liquid - liquid contact line is not constrained to a plane and the macroscopic contact angle will be determined by Neuman Construction
- The liquid - liquid interface re-organizes itself to minimize the surface free energy
- For Neuman Construction,

$S = -0.5\,(\gamma\theta_c^2)$

So, there are lots of issues like this and which I really do not want to get into. In this course may be if I offer a second level advance course on dewetting, I will talk about all this issues. This is again something I will skip. I will not talk about a very fascinating situation that is if, it is a liquid liquid bilayer and what happens if a liquid forms or if a liquid partially wets a liquid.

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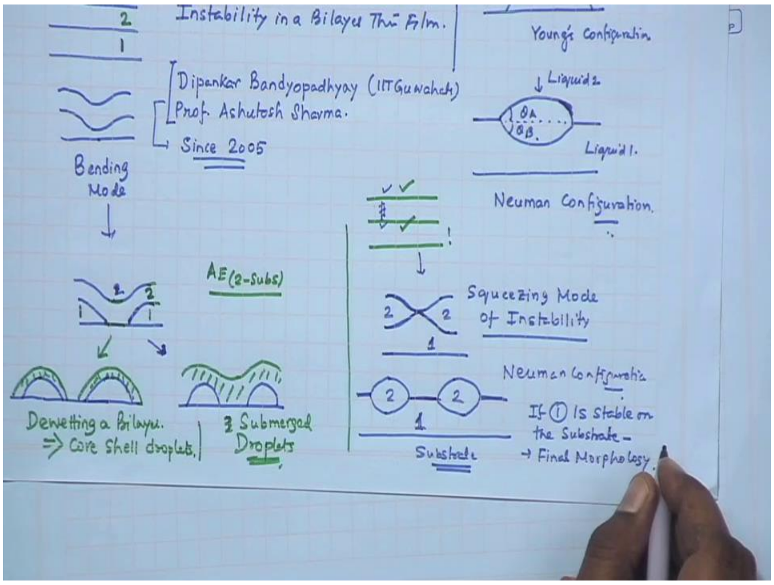

So, if a liquid partially wets a solid, you know this is the configuration, Young’s configuration this is what is called two well conversant with it by now. But if it is a liquid then what happens if the bottom layer is also liquid and you can do that you can put some let us say, water on some glycerin or some honey or something like that. The top layer liquid in fact, the vertical component I just briefly mentioned what happens to the vertical component. In fact, the vertical component does not manifest in anyway on a rigid surface. Because the surface is do stiff to sort of exhibit any effect of this vertical component surface tension.

But that is not the case when we have a liquid because it is a deformable liquid liquid inter phase therefore, you observed some deformation on the bottom layer also. And this is typically the equilibrium configuration of a drop of liquid 2 on an intact layer of liquid 1. And it is sort of given by a, I mean let us not I will not talk about it leave it. But this configuration is called the Neumann configuration. And important reason why I talked about this particular example is, an important class of problem is instability in a bilayer. In fact, where both the layers are adequately thin and both can deviate.

So, you see instead of a single layer film, now there are three inter faces and two deformable inter faces. And there is absolutely no reason to believe that all the three inter phases will become unstable of both the layers will become unstable together. In fact, it turns of that one of the layers becomes unstable first and that sort of dictates the initial evolution path way. So, easiest way to think about it, it is very nicely written here shown here.

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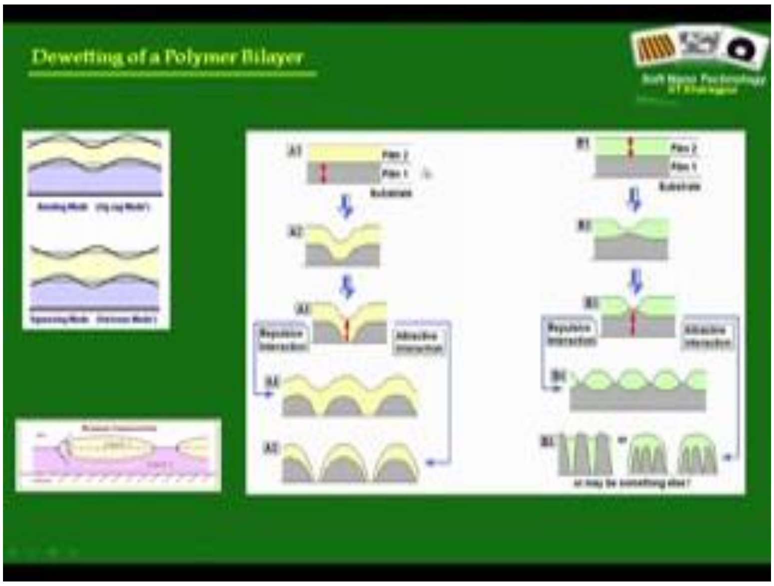

Dewetting of a Polymer Bilayer

Suppose you have a bilayer comprising of two films, on the left hand frame what you see is a situation where you can read a lot of literature on bilayer dewetting by wonderful theoretical worked by professor Dipankar Bandyopadhyay at IIT Guwahati, along with professor Ashutosh Sharma, who have contributed immensely into this field ever since 2005. Initially they contributed lot of experimental, a theoretical papers and then some of them have been experimental validate. Because doing experiments with the bilayer is extremely difficult because tracking an interface with an f m, you now understand an f m.

So, you know understand that if you have a bi layer, the f m will only give you an information about the top layer. It will not give you information about the submerged interface. And therefore, tracking a bilayer dewetting is an extremely difficult thing. However, there have been experiments on bilayer dewetting and that those experiments are going on from nineteen mid ninety's, but it is this particular group from professor Sharma's group that the theory of devoting bilayer has almost emerged.

So, what can happen in a quick way we can let us investigate? It is that in this particular case, the strength of interaction between the film film interface and the film substrate interface is stronger than the interaction between film layer interface film layer, the free surface of the liquid two and the film interface. And as a result of which this layer bottom layer becomes unstable first and as a consequence of that the top layer simply follows that. This mode of instability is known as the bending mode of instability.

After the bottom layer has ruptured, so bending mode you know understand what I have drawn, the bottom layer has ruptured. So, this let us mark this as 1 this as 2. So, what happens over these areas, now the film two comes in direct contact with the substrate. And again now one means to look into the sin of the effective Hamaker constant between 2 and the substrate. If depending on whether this is positive or negative, if it is positive then there is a possibility that this particular layer will also ruptured and as a result you are likely to get structures like this. Or there is a possibility that the interaction here is repulsive between these two surfaces of 2 and the substrate and therefore, this is the permanent or this is the final morphology. Either of which from the stand point of fabrication is very exciting because see, here by simply dewetting a bilayer one has led to some core shell droplets. And here one has led to some submerged droplets right.

You have learnt adequate amount of nanofabrication in terms of soft lithography, photolithography. Fabrications of both are very difficult. So, therefore, instability is not only scientifically very exciting and interesting to study, but it has the potential to fabricate some novel structures which are difficult to realize by classical or conventional top down lithography techniques. What is the only problem? The only is something you have already seen and that is the structures are random.

Therefore, what we will learning in our next class is how to align this structures, but before that let us look in to the other possibility that can happen with a bilayer and the other possibility is, the interaction between this surface and this interface is stronger than this one. And in that case what will happen? The evolution will be like this.

This is what is known as the squeezing mode. It in fact, is bit interesting because here both the interfaces are deformable and as a consequence of that you see that the top free surface sort of comes down. But since there is an attractive interaction, this liquid liquid interface also goes up which is not the case here. Because here this surface, the one of the surface that is the film, the liquid solid interface that is participating in the initial instability is rigid and therefore, it cannot deformed.

However, here since the interaction is initial, interaction is stronger between these two interfaces, it deforms like this and resulting in initial structures which look like this. Did you see them somewhere? Of course, you actually have drops of 2 restring on a layer of 1 following the Neumann configuration right. Now of course, the question comes whether a film of 1 is stable on the substrate or not. You can understand it very easily. And if the effective Hamaker constant is negative which means the 1 is stable on this surface then of course, this is the final morphology. If not then of course, there are other issues in fact; they are even if this is stable there can be other consideration. So, let me just spend a couple of minutes on that.

So, after the initial rupture and dewetting has taken place, this is the configuration and may be one of the assignments we have is to find out the conditions Hamaker constants under which this thing happens.

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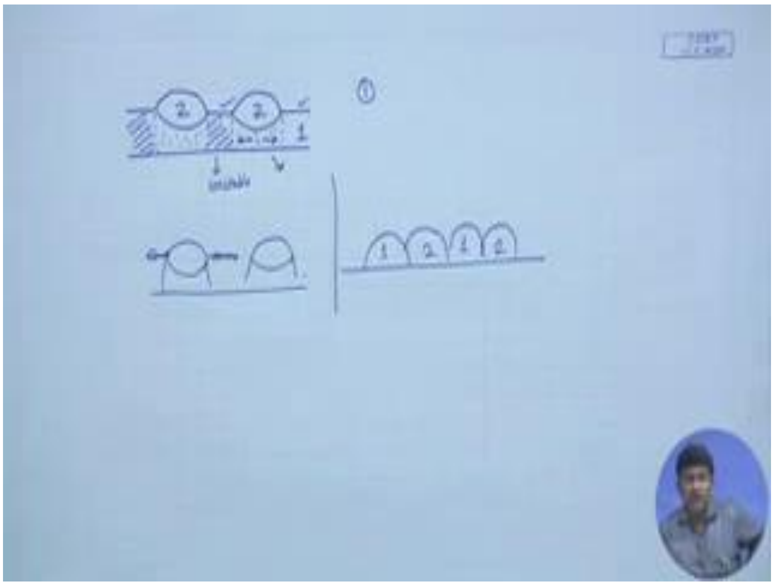

So, now there can be three possibilities, simplest one this film is stable everywhere. So, you see this film 1 in fact, has two different types of areas right. One area is you only have a layer of this under area. The other area is where it is submerged between drops of two. So, if the film 1 is stable at both locations then this is the final morphology. But there can be other possibilities that these areas it is unstable and these areas it is stable.

So, then it might lead to some eventual structures like this, some sort of structures like this or if there is a possibility that these areas it is un stable and these areas it is stable then it can lead to some coexisting structures in fact, liquid can squeeze out from here and 2 might in fact, eventually come in contact with 1.

So, all these possibilities are there in a bilayer and it depends on the strength of the interaction forces across the different interfaces at different times. Film thickness of course, is a critical thing because if one of the layers is thinner than the other one of course, the possibility of that particular combination, that particular film rupturing ahead of the other one is more. But there are issues like wettability, relative wettability, relative spreading coefficients and Hamaker constants and also the viscosity because other film might be unstable, but if the viscosity is too high, the molecular weight is to high, the dynamics might be to slow.

Anyway so, bilayer dewetting again is a topic in itself and I just gave you a glimpse of some of the exciting possibilities that are there. How the complexity sort of increases manifolds when there are two deformable interfaces which involved their coupled deformation. But one thing we have realized that bilayer dewetting or dewetting as a whole has the potential to offer a novel nanofabrication technique. Because all you do is you start off with a thin film and you eventually result, all lead to some structures which you otherwise do with lot of difficulty.

But the problem is the limitation is these structures. The utility of these structures are severely limited by the randomness and next therefore, what we are going to talk is the possibility of aligning this dewetting structures typically on a pattern surface which can be a topographically pattern surface, fabricated by any one of the soft lithography techniques we talked about or may be even chemically pattern substrate. So, that is the next thing that is going to come up next.

Thank you very much.