Soft Nano Technology
Prof. Rabibrata Mukherjee
Department of Chemical Engineering
Indian Institute of Technology, Kharagpur

Lecture – 30
Dewetting – 1

Welcome back. We are essentially now starting of our 5th module I think, the next module, separate module at least and which is on instability rapture and Dewetting of a thin film, broadly it false in to the thin film instability and Dewetting.

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Course Content

1. Introduction:
   - What is Nano? What is so unique about it?
   - Specific Coverage in the Course
   - Nano Patterned Surfaces
   - Stability of Ultra thin Films
   - Applications of Nano Patterned Surfaces and the Associated Science
2. Some Basic Concepts
   - Surface and Interfacial Tension: Components
   - The Wetting Regimes: Young's Equation
   - Wetting on a Nano Patterned Surfaces ;
   - Hydrophobicity: Cassie and Wenzel State of Wetting
   - Laplace Pressure and Young Laplace Equation

Now if you look at how much we have progressed, we had this discussion on introduction, some of the basic concept we have talked about related to particularly surface tension and waiting.

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Course Content *continued*

3. Patterning Techniques:
    - Nano Fabrication Methodologies
    - Top Down, Bottom up ….
    - Self Assembly, Introduction to Surfactants
    - Brief Introduction to Photolithography
    - Discussion on Soft Lithography
        - Nano Imprint Lithography
        - Capillary Force Lithography
        - Micro Molding in Capillaries
        - Micro Contact Printing etc.

Then we have learned. In fact, spread over 2 modules, 3 and 4 the pattern technique and we would now we are following that photo lithography is the third module and soft lithography is the fourth module.

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Course Content *continued*

4. Atomic Force Microscope
    - Basic Operating Principle including that of STM
    - Different Modes
    - Additional Features of an AFM
5. Thin Film Instability and Dewetting
    - Vander Waal's Interaction between two surfaces
    - Spreading Coefficient
    - Disjoining and Conjoining Pressure
    - Origin of Instability in an Ultra Thin Film: Competition between Laplace and Disjoining Pressure.
    - Hydrodynamics of a Free Surface
    - Morphological Evolution during dewetting of a thin film
    - Dewetting of a Thin Bilayer
    - Dewetting on a Patterned Substrate

We had a reasonable discussion on atomic force microscope which In fact, is the 5th module and now we move on actually to the 6th module, which is thin film instability and Dewetting.

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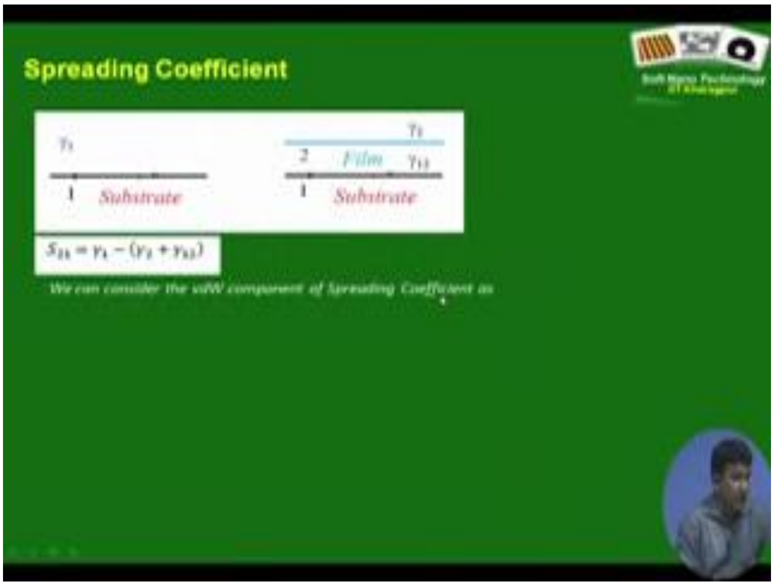

Spreading Coefficient

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

We can consider the vdW component of Spreading Coefficient as

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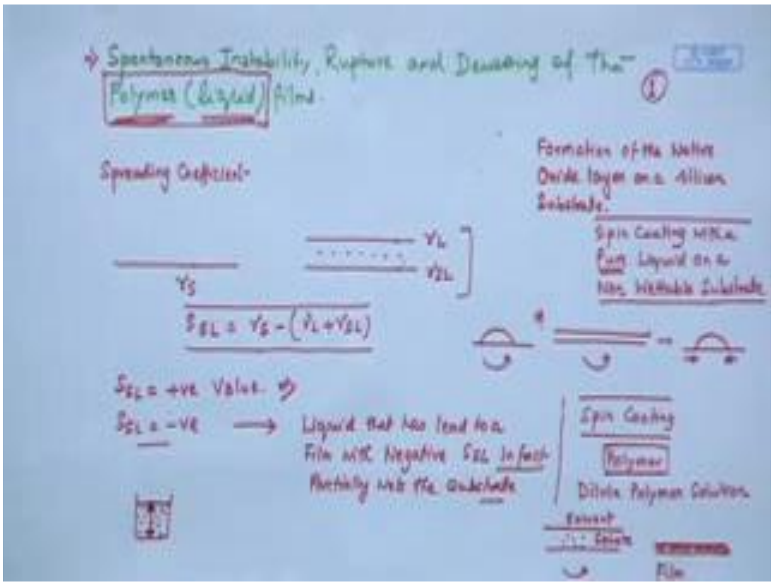

→ Spontaneous Instability, Rupture and Dewetting of Thin Polymer (Liquid) films.

①

Spreading Coefficient

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

S_{SL} = +ve Value ⇒

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

Formation of the Native Oxide layer on a Silicon Substrate.

Spin Coating with a Pure Liquid on a Non Wettable Substrate

Spin Coating

Polymer

Dilute Polymer Solution

Let us sort of quickly recap. In fact, if you look in to the topic, very interesting topic. It is spontaneous instability rapture and Dewetting of a film polymer films, I have also written simultaneously liquid film. Let us write to figure out what we mean to say and when it issue of film instability comes in to picture. We need certain concepts and some of those we have already had make some concepts to one of that concept that we will be needing is the concept of spreading coefficient and we all know the expression of spreading coefficient and see even in front of you and I also prefer to sought of write it down instead of trying to remember it.

So, you have subtract, you have now coated it with the liquid therefore, you have a liquid substrate interface, where inter facial energy is gamma SL and you have the liquid surface tension. So, S SL or SS S to 1 as we can see is essentially this and now you understand a lot on surface energy any things like that. Let us see what a positive value and a negative value would imply. A positive value implies that in fact by way of coating this film, you have reduce the total energy penalty and therefore, this film is going to be stable because, this formation of this film is sort of a natural process.

Like an example of which is the formation of the native oxide layer on a pure silicon substrate. Because silicon has very high surface energy and with the formation of the oxide layer now the surface energy drops; Negative value what would mean is that by way of coating a surface, you have in fact increase the total energy and therefore, thermodynamically the formation of the film is not favor. Question to ask is then what would it imply, it would to essentially imply that, this particular liquid which has to a film with negative SSL. In fact, what can you conclude? In fact, what you should conclude is partially wets subtract it does not wet fully right.

It actually wants to form a finite contact angle and you are forcing it by some means and you also known as what is that some means how you can do that, some means by which you would like you would get a film, continuous film of a partially waiting liquid, you know the technique how you can do that by spin coating. In fact, you supply excess amount of energy in the form of sentry fetal force, which sought of over comes the balance at the contact line forces the liquid to spread right. You can of course, create this, but typically we have seen in the contact of photo lithography, that you form a film of photo legislate that is a polymer, you can in fact create a film of any polymer by spin coating and there is a catch, issue is that is if you take a pure liquid their going to be 2 problems in spin coating.

So, spin coating with a pure liquid on a non wet table substrate. The problems are if you take something like an organic solvent, this liquid will tent to it will spread no doubt and I mean initially you have dispensed it on a surface it is making a finite contact angle, you start spin coating, but if the wiper pressure of the liquid is high, what will happen is the liquid will start to very rapidly evaporate and the rate evaporation will essentially enhance as you spread the liquid because the surface area goes up.

Therefore, after few second or may be few minute, you will be not left with anything. So, no question the liquid has spread like if you take talwin, chloroform, acetone, whatever you can take the liquid has definitely spread even on a non wet table surface, but you cannot do any time result experiments because the liquid has simply evaporated away.

On the other hand, if you take something like water that evaporated very slowly, the problem is that it will spread. So, suppose you have taken water, you now turn it makes a finite contact angle which water in fact makes on most surfaces because water itself is a pretty high surface energy liquid. So, it does not that easily wait a surface. You spread it, its spreads, you rotate it, it spread, but it does evaporate. So, it remains in its low discus state. Now you turn of your rotation, the problem is what is going to reach at back and dewett in to its original configuration.

So, you again cannot get a permanent film, but in what type of material you can get a permanent film and that is while this polymer become a wonderful model system for this type of study. Because what you do you take a dilute solution in an organic solvents let us a which is rapidly operating solvent. You spin coat its spreads solvent evaporates. So, here is the put print of the solvent now during spin coating, you have the solute, the solvent evaporates away and the solute gets deposited on the surface. So, you get a film on an on wet table surface which remains. So, that allows you to makes some experiments. The second thing is what is going to come up very will again realize the utility of having a polymer and also the implication of using these 2 words in heading is the form of spontaneous instability and rapture we are going to talk about. In fact, requires a liquid, but again the same problem, I mean if you really do the experiment with a highly volatile organic liquid, your characterization becomes very difficult because what you see the film to be film disappearing, but whether the film is disappearing due to rapture, instability or evaporation, you cannot be we can valued.

So, the trick is that you take a polymer film, when you want to see the instability and the dynamics you take the polymer in a liquid form and you can very easily do that, we have already learned that, you take a glassy polymer, simply heated beyond is glass transaction temperature, discos in we reduces in many foals, so behave like a liquid, you have all the evolution there we will soon see example and then whatever stage you want characterize you simply cool down the temperature just the way you have close in the structure nano simply lithography and you get permanent structures.

The other advantages is that most polymers have long change to the molecular way is high, therefore the viscosity is high and therefore, dynamic is slow. So, that allows you to sought of track the evolution on many it's or on a realistic time scale sometime it can be even slower. So, these are some of the advantages of using a polymer. But anyway you are talking about the basic concept, so we have this spreading coefficient, that is an important criteria, but reality is that we all we often see water stored in a plastic bucket. Plastic is a reasonable hydrophobic and it does not prefer to have water, but then the water layer it does not ruptured right, why? Because you have adequate thickness and therefore, the I mean sort of the even though locally the spreading coefficient is negative nothing matters because there is too much inertia or too much amount of material present and no instability manifested.

That also brings us to one an answer question. So, far what leads to the manifestation of these instability and to answer to that or to initiated discussion on that I would like to remind you of what we have talked about VDW forces, something that I have not yet talked and is how the scaling changes between 2 surfaces. That something is coming up in the right in the media next lecture. What we know from the 6, 12 potential of the l J potential is that the scaling of the interaction forces is attractive part is r to the power 6 and we have also r good that roughly this separation distance is of the order of 10 nanometer. Well, here comes the question.

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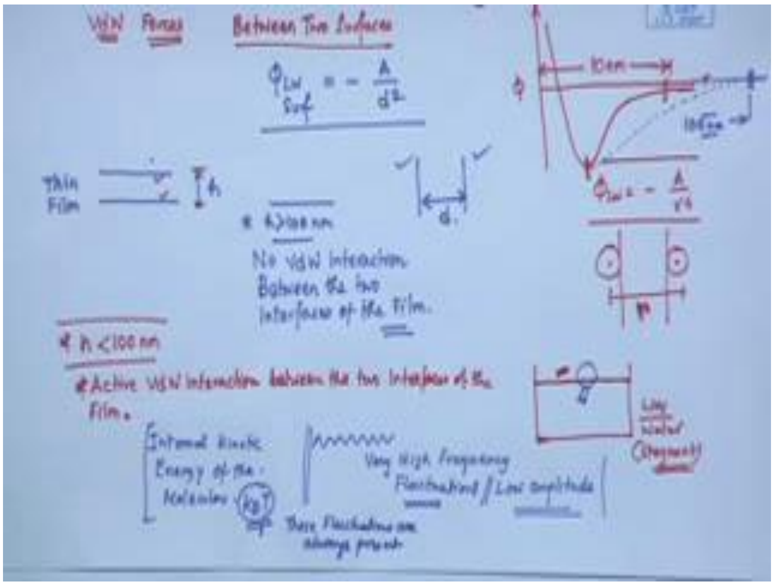

VdW Forces Between Two Surfaces

$$\phi_{\substack{LW\\Surf}} = -\frac{A}{d^2}$$

$$\phi_{LW} = -\frac{A}{r^6}$$

Thin Film

* h > 100 nm

No VdW interaction Between the two interfaces of the film.

* h < 100 nm

* Active VdW interaction between the two interfaces of the film.

Internal kinetic Energy of the Molecules k_BT

These fluctuations are always present

Very high frequency fluctuations / Low amplitude

So, this is between 2 fundamental particles which we have been talking here considering the herds were model, this is the separation distance, what is hertz here I mean this is in fact the point where the outer orbital's of the 2 molecules come in contact and beyond that if they I mean. So, r is equal to 0 is essentially when the 2 nucleic inside and that happens only in the nuclear reaction nuclear efficient reaction in fact.

Other than that what happens is oscillate is a molecule comes too close each other there orbital's starts to overlap. And therefore, you get this strong electrostatic repulsion between in the electrons, but what we are asking is what happens, when you considered the interaction between 2 surfaces which are very close to each other. I have mentioned qualitative we have, for the timing please believe me we will soon see it mathematically that the scaling in fact, changes to 1 by r square d squared d is the separate distention between the two, it does not remain r to the minus 6 it becomes d to the power r to the power minus 2.

So, what is the consequence? Consequence is you can yourself understand the this scale becomes much the slow becomes much relaxed or the d k characteristics become much sluggish or in other words interaction becomes longer range as compare to that between fundamental particles and this is indeed true, that there arguably this is sought of the of the order of 100 nanometer. People have the doubts, but maybe it is 15 nanometer, but it certainly more than 10 nanometer, it is something more like 40, 50, 60 nanometer something like that there is active Van der Waals interaction right.

So, this is another thing that one needs to understand and therefore, again when we are back to a thin film. So, if the film thickness is greater than let us a this 100 nanometer for the sake of argument we are assuming this 100 nanometer to be to be the cut of now when let us take the film thicknesses take and this 100 nanometer what does this picture tell you, that there is no interfaces of the film where enough. So, in our contact in fact, this is a film, I very first day itself I emphasize that we will considered something to be tin film there is active inter facial interaction between the 2 interfaces, that is not the does not really matter.

The film can still rapture, you may not have a uniform film because if there are some surface defect of or something like that. But even if the spreading coefficient is negative, that from the stand point of spreading coefficient you see that this film is unstable, but

Van der Waals force is not going to cause any damage to the film stability. However, if the film thickness is now and each we are marking as film thickness, but it does say, does it immediately tell avail this the condition for a film instability please do not jump on to conclusion all it tells.

Now you have active Van der Waals interaction between the 2 interfaces of the film, where enough you may still ask so what? One quick answer would be so there might will certain things, now it depends we have spurned the interaction is active we have not mentioned, whether the nature of the interaction is attractive or repulsive. In fact, we will see there the sign of the spreading coefficient. In fact, tells you whether the nature of the interaction is attractive or repulsive. It sounds a bit surprising because so far we have always been talking Van der Waals interaction to be attractive and now suddenly I am telling well the interaction may attractive, may be repulsive, we will see that. It in fact depends on certain relative magnitudes of something call (Refer Time: 16:01) constant of the film and the surface which we will discuss soon.

Suppose this interaction is attractive which you are expecting because you are Van der Waals interaction is a attractive. So this surface interaction poor is inter face, but there is liquid. So, what will happen? Does it sought of merge general liquid squeezes out like what we have seen in the let us a in the case of colloidal to colloidal particles joining up it is not like that.

In order to understand what happen and this is a absolutely qualitative discussion I would like to trigger deliberately will had some scientific and mathematical terms, but this is a deep understanding that you will develop and the understanding is pretty qualitative let us see what we can do? Before in order to progress we need to sort of look in to again we layer of stagnant liquid, let us a water which is stagnant fair enough. So, this can be let us a bucket full of water. If I ask you that there is no external force and there is no flow there is no leakage, what to do expect the condition act the interface the liquid there interface and immediately all of you will say this is stagnant liquid. So, UVW that free components of velocity at the interface are all 0.

Which is very logical is a perfectly valid microscope picture, but now suppose I give you a hypothetical tool to sought of exam in this interface at let us say 10 nanometer resolution and why I say it’s a hypothetical tool? Because do not confuse AFM cannot examine this because AFM is capable of only examining a only solid sample, not a liquid sample, it can be analyze a sample under liquid do not highlight that, but there is something it was mentioned as liquid cell.

But, suppose if you sought of allowed to a examine this interface which is apparently static, apparently flat, everything at least a very high magnification and very high you are allow to acquired data at very high time frequency also. What would you see? You in fact see that there are some very high frequency fluctuations, which are also very low amplitude, few nanometers. What is the genesis of this fluctuation? Well this fluctuation, its sounds very surprising, but fluctuations are there and that is no damage to the interface. So, bucket full of water cup of coffee whatever you see stagnant free surface.

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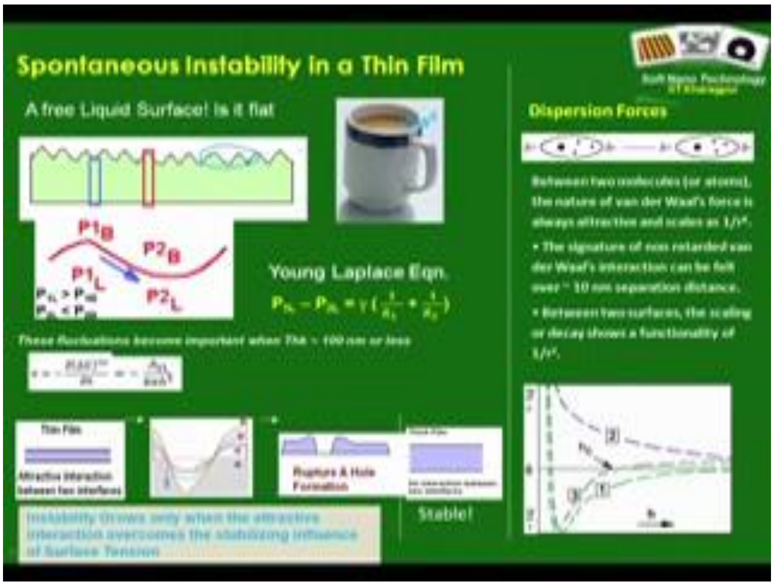

Spontaneous Instability in a Thin Film

A free Liquid Surface! Is it flat

Young Laplace Eqn.

These fluctuations become important when Thk ~ 100 nm or less

Instability Grows only when the attractive interaction overcomes the stabilizing influence of Surface Tension

Stable!

Dispersion Forces

Between two molecules (or atoms), the nature of van der Waal's force is always attractive and scales as $1/r^6$.

- The signature of non retarded van der Waal's interaction can be felt over ~ 10 nm separation distance.
- Between two surfaces, the scaling or decay shows a functionality of $1/r^2$.

In fact, there is some very high frequency fluctuation like what is drawn here right high frequency, low amplitude, what is low? Few nanometers may be. So, what is the genesis of this fluctuation? Well, these fluctuations are attributed to the internal kinetic energy of the molecules. We remember eve every material has some internal energy and this internal energy in fact has several components like internal potential energy which is a essentially the interaction forces, like fundamental forces, internal kinetic energy, there can be vibration etcetera also.

But this is attributed to the internal kinetic energy of the molecules, which is numerically presented as KB in to T. Now you see T is absolute temperature and you have let us a looking at a bucket at room temperature or you are looking at a polymer film which is elevated which is heated beyond its glass transition temperature; so T non 0, KB anyways non 0. So, this term is non 0 always right.

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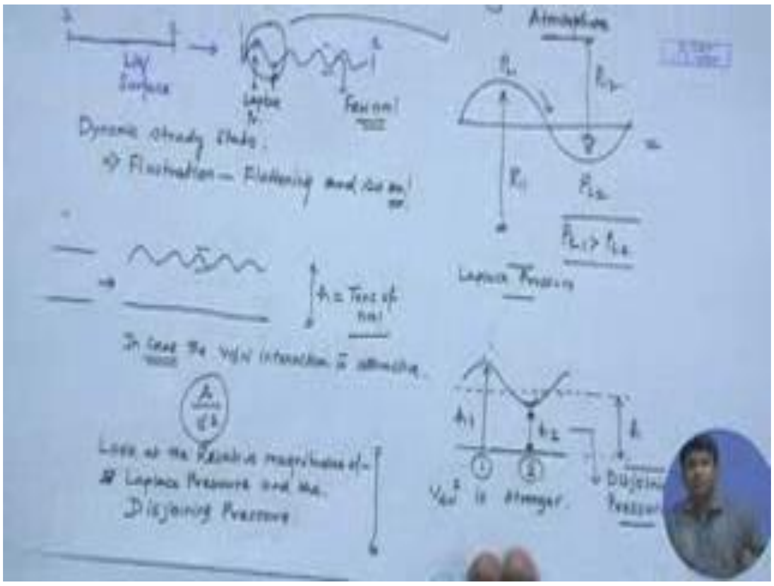

So, the molecule in fact, try to go away with it each other and surface tension of the interaction forces bind them to the. There is the competition that goes on right and this leads to this type of fluctuations. So, in other words this fluctuations are Omni present, unless you are performing your experiment at absolutely 0 of course, then T is equal to 0 and fluctuating goes away.

Now you have a liquid surface and which you understand is not flat, consequence curve liquid surface, what is the thing we have learned? There is Laplace equation. Why? Because let us a if you looking in to this segment of the film and you know between the 2 points 1 and 2, the lowest lent segment will be if the if the film surface is flat that corresponds to the lowest energy a lowest surface energy a configuration. So, the movement there is this fluctuation due to the internal kinetic energy or isolation of the molecules.

In fact, it increase the surface tension and surface tension it increases the surface energy and surface tension of opposes this growth, or in other word what happens you can go once stab deeper and try to explain it. In fact, there is Laplace equation and you can sought of write young Laplace equation we just take an exaggerated view of one single isolation here are this is going to be r one here let us a this is going to be r 1 to 2 this r 11 and you can yourself see in fact that if this is positive with this is going to be negative.

So, the Laplace pressure PL1 assuming it is expose to atmosphere. So, the outside pressure at both the places is same PL1 is going to be grater up then PL2 and this is something I briefly mentioned while I will talking about Laplace pressure. So, we all know that liquid flows from high pressure reign to low pressure reigns. So, what happens? Now liquid simply flows from this area to this area. And therefore, they may discus flat an out.

So, there is a dynamic competition that goes on it is a dynamic steady state, fluctuation flattening and so on. However, contrariety it may sound, but if look you at a flat liquid surface you now understand the there is the nano scale, there is some fluctuation going on continuously right. So, what I mean its fine. So, bucket full of water there is fluctuation, this amplitude is few nanometer may be, even if it is few nanometer nobody knows nobody has visualize it so for till it, but now you start thinking of a thin film, thin liquid film. Like the once we have considered here.

So, this thin film now you are understand that at any time snap short its actually like this, let us a you of film thickness was the order of 10s of nanometer and this amplitude couple of nanometer, few nanometers may 4,5 nanometer and this is lecture 20 nanometer. So, for a 1 meter dip water level in a bucket of water in nanometers nobodies cares 9 water smaller. But when you are film thickness is 20 nanometer and let us a this is amplitude is 4 nanometer, the isolation amplitude is just one order lower and. In fact, is turn out that it can be 5 to 10 percent of the film thickness. So, this is very important and now you since the thickness the overall thickness of the film is lower than 100 nanometers, you are talking of rejoin where essentially there is active Van der Waals interaction.

So, in case now and what is the case we will realize soon the VDW interaction is attractive. An as I told this interaction scales as one by d square d is the separation distance. So, what happens is this is let us says the mean film thickness. At any instant of time this is the fluctuation spectrum. So, what you now observe the ret point 2 the VDW interaction is stronger and remember the nature of the interaction is attractive. So now, what we have discussed here the movement there is a fluctuation the film would ideally flat and outright, but here now we have an additional complexity.

Since, that attraction is stronger here and it is stronger at this point as compare to this one, these two are trying to coming contact with each other due to Van der Waals interaction or in other words the substrate is sought of the pulling, remember that this surface cannot go up because these a rigged surface rigged interface define by the geometry of the substrate, but the liquid free surface is a deformable surface and therefore, it once to deform because it is feeling and attraction towards the surface due to Van der Waals force and this is what is called again there is a flow.

So, there has to be, so this if it if this amplitude grows there has to be some flow there for people time it in terms of some pressure this system at the disjoining pressure, something again we will discuss .

So there is now an additional component, the Van der Waals force rewind disjoining pressure which tries to pull the 2 interfaces and Laplace pressure tries to flat it out. So, now there is an additional competition. So, the movement there is an additional competition now one needs to look at the relative magnitudes of the Laplace pressure and the disjoining pressure.

I will stop here, let this ideas settle in your head I will show a video was to what happen a and then we need for a good understanding of the situation. We need a real good understanding of the disjoining pressure which is something that I will take up in my next lecture.

Thank you.