**Lecture No. # 31**

**Spontaneous instability and Dewetting of Thin Polymer Film – I**

Welcome back. In the previous lectures in the last module, we try to understand the different interaction forces and also saw, how these forces become significant for a very thin film. And we talked about the concept of Hamaker constant and then, gave some initial examples were we could correlate how the stability of a system or a thin film is dependent on couple of things, one is the spreading coefficient and one is the Hamaker constant.

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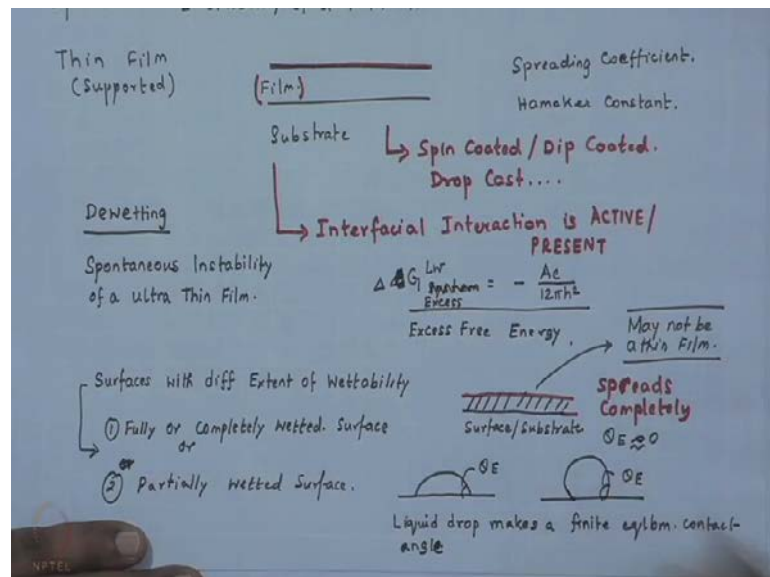


So, what we will do today, we will extend our concept in in terms of the spontaneous instability or understanding the situation, which leads to a spontaneous instability in an ultra thin film.

So, this is the next module that we are going to start (Refer Slide Time: 01:28), where we talk about the spontaneous instability and dewetting in a thin polymer film. Before that

let us try to find out what exactly we mean by a thin film. Of course, thin film we have yesterday understood that the easiest way to define or we talk about essentially a supported thin film, which is coated on a substrate which is the easiest system to sort of identify. It can be sort of spin coated or dip coated or there are other mechanisms also, one can drop cast such a thin film, there are various ways.

So, we have identified something to be a thin film, when we understand that the interfacial interaction is active or present. So, essentially we talked about the, if we are talking about the Van der Waals interaction, this interaction is present in the system (Refer Slide Time: 02:52). So, you can immediately see that, higher is the value of h this will eventually this excess interfacial energy or let us write the excess energy excess free energy of the system will tend to 0.

Now, couple of important keywords we are going to pick up in today's lecture and one of them is the word of dewetting. Now, let us try to (( )) our concept on, what is Dewetting? Dewetting is a phenomena which has sort of a, a it can be observed in macroscopic world as well, it is not that, that you really have to go down to nanoscopic (( )) to observe Dewetting.

So, we will first talk about bulk dewetting of a liquid drop let us say on a solid surface and then, eventually extend this idea in understanding the spontaneous instability (No audio from 03:59 to 04:09) of a ultra thin film. So, the bulk dewetting of course, we have already talked about surfaces, which have different levels of wettability (No audio from 04:30 to 04:45), so based on that, a surface can be distinguished as a fully wetted surface or partially wetted substrate. So, this is what is a fully wetted surface? So, this is the surface or the substrate (Refer Slide Time: 02:25). If you dispense a liquid, it will spread completely, so the equilibrium contact angle is eventually close to 0.

And this may not be a thin film, this can be a thick layer of liquid also (Refer Slide Time: 05:54), this can be a thick layer of liquid also partially wetted substrate of course, there were a liquid drop makes a finite equilibrium contact angle (No audio from 06:20 to 06:39). And we have also argued that, based on if the liquid is water, so this is the equilibrium contact angle over here (Refer Slide Time: 06:52).

And we have argued that, if the liquid is water (No audio from 06:59 to 07:10), then depending on what is the magnitude of theta E we may identify a surface, which is hydrophilic or hydrophobic.

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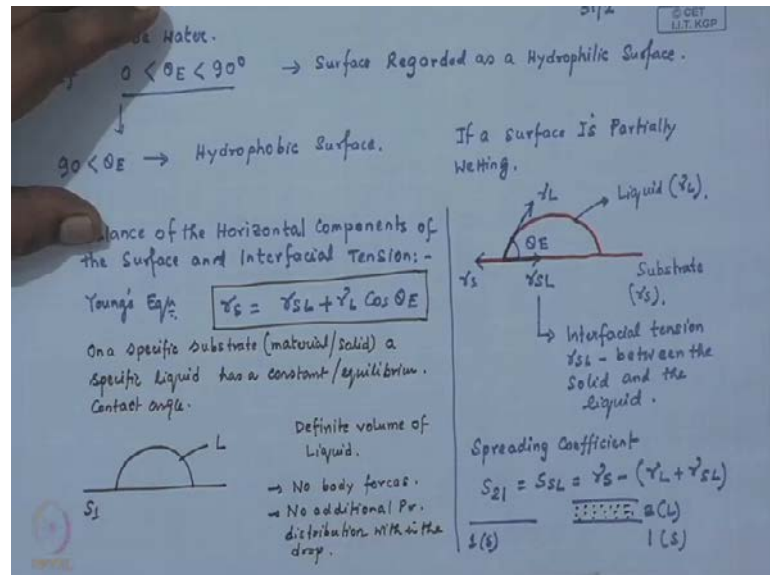


So, the general idea is that, for the liquid to be water (No audio from 07:32 to 07:42), if theta E lies in this range (Refer Slide Time: 07:50), that is it covers both these two classes, this is completely wetted, as well as this configuration, the surface is regarded as a hydrophilic surface (No audio from 08:02 to 08:14).

In contrast, if theta is greater than 90 degree all the way as high as possible it is a hydrophobic surface. Irrespective of that, if a surface is partially wetting (No audio from 08:38 to 08:48) I will just we will just repeat the concept that, we already know it is something like this let us say (Refer Slide Time: 08:56) or even it does not matter, if theta exceeds 90 degree.

So, let us say this is the surface or the substrate as we often referred to, which has a surface tension gamma s (Refer Slide Time: 09:12), this is the liquid which has a surface tension gamma L and of course, this is the interfacial tension (No audio from 09:28 to 09:48) liquid. So, based on this we know that, one can write a balance of the horizontal components of the (No audio from 09:58 to 10:16) of the interfacial tension and this also we know to get the Young's equation as gamma s is equal to gamma S L plus gamma L cos theta E.

When the previous lecture we had also defined the spreading coefficient. So, may not be a a bad idea to quickly recap its expression S 2 1, where where we just use the notation like this (Refer Slide Time: 11:15), the film material was regarded as 2 and the solid was the (()) was regarded 1. So, the notation we are using today is essentially S S L or it was identified as gamma S minus gamma L plus gamma S L.

And based on whatever understanding we developed yesterday in terms of preferential wetting and spreading coefficient you can immediately now understand that, for a system like this (Refer Slide Time: 11:53), where there is complete wetting, the spreading coefficient is greater than 0, it is positive. Because what happens is you have a high surface energy substrates on mutual lower surface energy spread completely.

So, if you are taking water let us say, which has a surface tension of 72 milli joules per meter square the obvious thing is that, if you take a surface which has higher surface energy then water will automatically spread entirely. And this will be manifested with a spreading coefficient.

In contrast, if you have a surface or if you take a substrate for which the surface energy is lower than the liquid, the liquid surface tension is higher than that, then of course, the liquid will not try to spread entirely or it will try to form a isolated droplets. We will revisit this problem, while understanding dewetting. And this is actually the fundamental point from which the concept of dewetting comes in.

So, in a system where you have a partially (( )) drop, it is reasonable to understand or or do that spreading coefficient is negative. But please realize that, spreading coefficient is based on a hypothetical situation, where irrespective of what surface energy of the liquid and the solid you have, you are able to create a continuous film.

So, you can calculate a spreading coefficient for a system like these. But remember, spreading coefficient is essentially defined for this type of a scenario and from this to this (Refer Slide Time: 13:38). So, the transition from if you can create a continuous film down to a partially wetted drop with making a finite equilibrium contact angle.

Depending on the sign of spreading coefficient, depending on the value of equilibrium contact angle is nothing but, the physics of dewetting which we will talk about. So, coming back to the Young's equation, what these gives that, on a specific substrate or

material a liquid has a constant contact angle. Thus, if you dispense or if you take a specific substrate let us say S 1 and you sort of define a you take a definite volume of liquid L and if there are no significant.

If the volume of the drop is not large enough that, there are significant body forces or gravity acting on it and there are no additional pressure distributions, then the geometry of the drop will be governed by the balance of surface and interfacial tensions, this we all know. What in simple terms? It means that, the shape of the drop may be I will shift to the new page.

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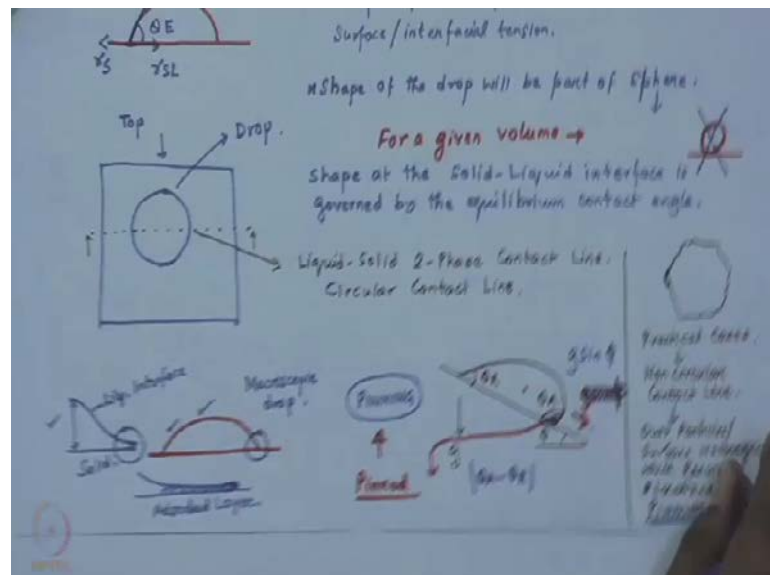


So, the shape of the drop governed by balance of surface and interfacial tension and in absence of body forces that is the gravity role of gravity can be neglected and no additional pressure distribution or temperature gradient within the drop. This droplet shape will be part of a sphere, because for a given volume a sphere the spherical geometry we all know, this has the minimum surface energy.

But, it cannot take a configuration like this (Refer Slide Time: 18:30), because it is sort of limited its geometry or its shape at the liquid interface is governed by the equilibrium contact angle. So, this much we understand and it depending on the nature of the wettability, nature of the liquid. This equilibrium contact angle can vary between any I mean it can be acute it can be obtuse, whatever it is.

Now, so what it means that, for a given volume of a liquid once you dispense it and based on the balance of gamma S, gamma S L and gamma L, the equilibrium contact angle is fixed. So, for a definite volumes of if you now see from the top, you see the droplet to be like this (Refer Slide Time: 19:47), so this is the drop, this is what is known as the liquid solid 2-phase contact line you also know this, because I think we have if not imply directly or explicitly talked about these concepts in while discussing hydrophobicity we all understand this.

So, essentially what where does this picture originate from, if you take a section of this drop along this plane you get to this picture. We already have argued that, it is a part of the sphere, so you get a circular contact line. In many practical examples of course, you see a contract line like this (Refer Slide Time: 20:54), non circular contact line, this is attributed to dust particles or surface heroginites, which result in something called localized, there is an important word pinning of the contact line.

So, as if at these locations this contact line is stuck up, there is some additional force which is holding the contact line we will be talking about pinning a little bit may be, it is an important phenomena and to a large extent responsible for various unique properties that is observed in in flow involving droplets.

And one of the thing that, we have already sort of introduced you to in one in our earlier modules is the a concept of contact line hysteresis. So, you take a drop like this and gradually tilt the surface and you see that, as soon as you tilt the drop, it does not flow. Though the reality is that, if g is acting in this direction and you have an angle phi making with the horizontal, the reality is the moment you tilt a drop, there is now a net force of g sin phi on this drop and the drop should sorry its illegible (Refer Slide Time: 23:18), drop should immediately move, because there is any driving force, but it does not happen.

And we know the difference in the magnitude between the advancing and the receding contact angle is actually a critical parameter in defining or determining or identifying the nature of a surface. For example, if you have a (( )) to fabricate a super hydrophobic surface, not only your equilibrium contact angle has to exceed 150 degree, but you must have a very low contact angle hysteresis, which is typically of the order of less than 10 degree. Super hydrophobic surface particularly, if you are a looking for application like

self cleaning application, this contact angle hysteresis is becomes a very critical parameter.

But, important thing to realize is that, what is responsible for this contact angle hysteresis and the the scientific reason that is given or the argument that is given, it is actually this pinning which is responsible for the contact angle hysteresis or in other words, the contact line at the advancing side of the meniscus over here is as if this is pinned (Refer Slide Time: 24:35).

So, there are some additional interaction that arises which may not be all the always because of dust or heteroginites, but there can be some localized interaction localized additional enhanced forces, interaction forces, because what one has to understand that, if one is looking at a geometry like this (Refer Slide Time: 24:58), the interaction the interfacial interaction let us say over here, and this is a macroscopic drop.

So, this is a macroscopic drop nothing like 10 nanometer, 20 nanometer nothing like that but, eventually close to the contact line it sort of, (( )), so this is the liquid interface, this is the solid and though here, the separation distance is much much higher let us say, it can be few hundreds of microns or may be couple of millimeters. What happens is? Over the close to the contact line, actually these two interfaces become very come very close to each other, before they actually merge.

There is of course, a theory some people sort of grossly visualize a contact line to be a discreet entity, where it just comes and merges at a fix point, but there is a view, which was first proposed by (( )) and there are many people, who sort of subscribe to this view, is that well the contact line is not a 0 thickness (( )) 0 thickness entity. At the point of contact it sort of a stretches forming a very thin adsorbed layer ahead of the liquid meniscus, and which sort of merge with the substrate only at an infinite separation distance.

So, what happens is over this part of the film you are now back to the regime of the thin film, so ultra thin film, so this is very very thin. There are some experimental procedures based on which these type of films can be the thickness of these adsorbed layer has been measured. Optical interferometer using an optical microscope platform is one such approach. And then you have, so what happens is, as compared to the remaining part of

the drop, where there is no interfacial interaction all you look at the or if you take a bulk view like this, you are only interested in taking the balance of the surface tension forces.

But, close to the contact line you now have a regime, where there is interfacial interaction. So, these type of interactions might be a responsible for imparting these additional forces, but and resulting in pinning. So, we will not elaborate our discussion on pinning any further, because that is not the intension of this module, but it is important to note that, pinning does exists; and also for our way of understanding dewetting and as well as, spontaneous instability and how the dynamics is governed we will take a picture of the contact line like this.

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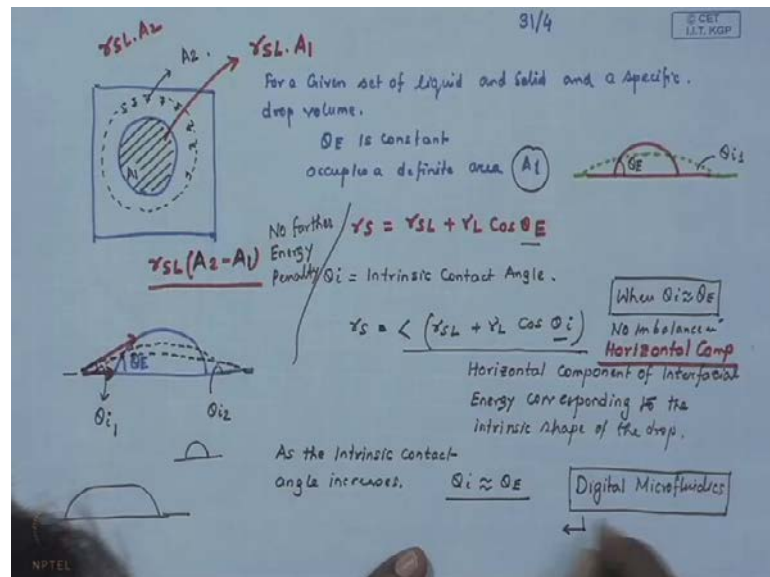


So, coming back to this particular figure (Refer Slide Time: 28:02), what we understand that for a given liquid solid set for a given substrate given liquid and a given drop volume or a specific drop volume, since theta E is fixed (Refer Slide Time: 28:22), so (No audio from 28:31 to 28:53) drop volume, theta E is fixed therefore, the drop if you look from the top occupies a definite area let us say, A 1.

Now, so this is the same picture. So, this we are looking at the elevation and this is at the plane. Now, if we do, so if we now take a drop which is making an equilibrium contact angle with the solid surface and then, some how (( )) this block, which can be like you try to artificially spread it. And this is something you can do, it is a very simple experiment. What you can do is? You can pour some water on a smooth table in front of

you and then, you just try to wipe it with your hand. So, that is very very simple I mean I typically when I take a class I just put put some splash some water on the board I will just spread it with your hand. And this is something you I mean I am sure all of you have seen.

So, if you spread it what you see that, a spread a drop the contact lines some of which some how retracts back at certain locations, this is what is dewetting nothing else. So, it is exact opposite of spreading and this is what is known as dewetting. Of course, if you do an experiment like this on your study table or your dining table in most cases you will see a contact line like this (Refer Slide Time: 30:47), it will not be circular. So now, you understand why it is not circular. Ideally the contact line should have been a part of the circle, but due to heteroginites present on the table or on the substrates, you will see a non circular contact line.

But even, if you spread it with your hand you will find that, at certain locations it might be retracting back, now that is what is macroscopic dewetting. So, let us see what the phenomena occurs, so you have this drop which is making this equilibrium contact angle and by way of spreading you have actually made it like this (Refer Slide Time: 31:37).

I am assuming that, you have (( )) it in a fashion, so that it still retains its symmetry. So, let us say, this is now the new projected geometry of the contact line of the spreader out drop, this was let us say occupying an area of A 1 the initial area was A 1. Now after spreading let us say, it is occupying an area of A 2 and it is making a intrinsic contact angle of theta i.

So, if you now again write the Young's equation, what you will find the left hand side remains the same gamma S, the right hand side now is cos theta i. So, this is the total component of interfacial energy, vertical component of interfacial energy corresponding to the sorry not vertical the horizontal component (No audio from 32:54 to 33:14) corresponding to the intrinsic shape of the drop. And as we know that, cos theta increases with the lowering of value of theta, so since theta i is lower than theta E therefore, this side is now higher as compared to the this side.

So, the left hand side is now smaller than the right hand side, which means that there is an imbalance in the surface tension; and this imbalance also gets manifested with the fact that, earlier the amount of area that was covered by the liquid was gamma was A 1. So,

the total surface energy of this part was gamma S L into A 1, because this A 1 is the part of area, which was below the drop. So, therefore, the total surface energy was gamma S L into A 1. And now, by way of spreading this liquid actually covers an area now of A 2.

So, the total area that is, so the energy that corresponds to this is gamma S L into A 2. So, this is that additional energy penalty, this is the additional energy penalty, the drop has to sort of is occupying, because of getting spread it and which also is manifested in this imbalance (Refer Slide Time: 34:45). So, what is the consequence? This additional energy has to be released and that release is through the retraction of the contact line (Refer Slide Time: 35:00).

So, what will happen? This contact line will start retracting towards the centre and as it retracts, what happens is, theta i progressively increases (Refer Slide Time: 35:08), so this was theta i 1, at an intermediate stage this will be theta i 2. And as the intrinsic contact angle increases therefore, what happens is this? Imbalance progressively starts reducing and when the retracting contact angle, the theta i sort of matches the equilibrium contact angle the dynamics of the retractions stops, because then these two sides become equal; and concurrently A 2 also becomes equal to A 1.

So, there is no further energy penalty as well as, no imbalance in horizontal component of surface and interfacial tensions. So, this is like an iterative solution procedure, you can say many of few are well conversant with programming and numerical solution of let us say, non-linear equation where you sort of go on iterative. And when your solution matches the convergence criteria your software programs stops, this is something we all know, how it operates and we routinely do it.

So, exactly the same way this intrinsic contact angle, when it retracts and sort of this progressively goes on reducing with theta i gradually increasing it, when it matches theta E the dynamics controls, the dynamics stops. And it so, what is the whole sequence we talked, we had taken a drop which was making equilibrium contact angle, so you dispense a drop on a surface and it will automatically take the shape of a perfect sphere, if the effect of gravitational field, if the effect of body forces is negligible. And, if there are no other additional temperatures or pressure gradient within the fill itself within the drop itself.

So then, what we have done as I taught experiment or is a real experiment is we part of this drop which was making an equilibrium contact angle theta E, when intrinsic contact angle let us say, theta i 1 this resulted in an imbalance in the horizontal components of surface and interfacial tension in Young's equation. As well as, the drop is now or was now occupying more area on the surface on the solid surface, which it is than what it is supposed to occupy based on its dispense volume and the balance of its surface and interfacial tensions.

So, this excess area that was getting covered corresponded to this much amount of energy penalty, which was also sort of a different way of representing it is the imbalancing the right hand side of the Young's equation, which was now higher. So, this led to the motion of the contact line towards the centre; and as the contact line started to be retract, the intrinsic contact angle sort of started to increase.

So, as theta i started to increase this cos theta i started to reduce, so the imbalance between the right hand side and the left hand side started to reduce and when theta i sort of matched with theta E, the retraction stop completely. So, this is what is the phenomena of macroscopic dewetting.

We all sort of have seen it or if you have not seen it, I would suggest that you pour some small amount of water on your on on a surface on a table or on a glass plate or wherever you want to do and just spread it with your hand a little bit of course, you will firstly if you dispense a lot of water you would not see a spherical droplet forming, you will see a rather flattish film it is because of the fact that, we now understand that if the drop volume is high, then you cannot neglect the body forces. So, the gravitation due to the presence of gravity, you will have some flattening, it will not the part of the part of a sphere.

But even with this, so you now must understand or you you are now in a position to understand that, why if you take a drop a very small drop you will see it is a part of a sphere. But, if you take a large amount of drop, it is not part of a sphere, it is something like this, it its it gets (( )). And then, if you spread it with your hand you will see that, at certain locations the contact line retracts back and takes close to this original morphology. So, this is what is dewetting.

But, what is interesting to note that here also, you have observed a flow, because typically we the way we study fluid dynamics or something like that, we know that a flow is typically triggered by either a difference in the height, which is the the gravity driven flow or like flow over an inclined plane or you use a pump or a blower or something to force the liquids.

So, you had lot of centrifugal force, which gets which which sort of leads to the flow or you have a situation like (( )) (( )) plate is moving and the liquid layer adjacent to the plate, because of the no slip boundary no slip condition sort of moves. But here is you can see, it is an unique situation, where the flow has been triggered entirely due to the surface forces. So, this is also an interesting class of a flow problem. And there is a whole branch of microfluidics, which goes by the name digital microfluidics, which essentially talks about the flow of a droplet. And there are additional handling tools to trigger or actuate, stop the flow of a drop.

So, this is in a (( )) the basic concept of dewetting the I would say, this is the macroscopic dewetting of a drop, which involves which can be observed on a surface we of course, important to note is that, this type of dewetting you see varies largely on the wettability of the surface.

In other words, if you have a situation, where you have complete wettability you would not see dewetting, because by way of spreading. What you are doing? You cannot increase or reduce the equilibrium contact and the intrinsic contact angle. If your equilibrium contract angle is already close to 0 by spreading your just allowing the liquid to spread more and occupy more area and that is all, nothing in more you can do.

But, in practical setting there can be additional effects for example, when we talked about this film spreading of a film or the dynamics of the liquid we have neglected one specific factor, which is always present if you are talking about real settings. That, we have in none of our derivations or wherever we have completely neglected evaporation.
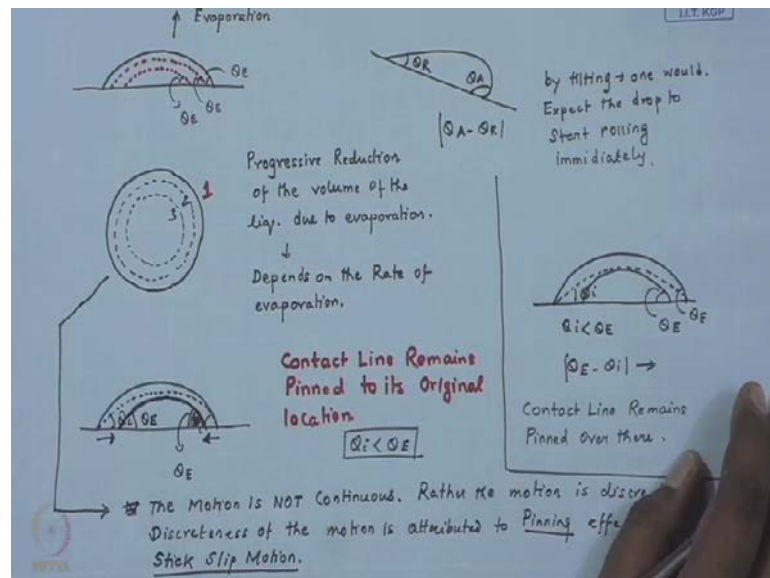
In fact, there can be whole lot of experiments with a partially as well as, completely evaporating surface, where evaporation plays a very critical role. And I will not go into the details, but even if you have a partially wettable surface and you you just leave it like that you do nothing, you do not spread nothing at all. And you have evaporation, which is the case if you just dispense a drop of liquid even like water on a on a flat surface under ambient condition.

If you dispense an organic solvent, the evaporation is much higher, because of the lower vapor pressure, but even for something like liquid water, there will be progressive evaporation; and you might eventually see that, with time the drop becomes smaller and smaller under ideal condition the drop should always retain. So, what happens is? The volume now shrinks, so reduces because of the evaporation.

So, we argued here, that that the amount of area that a drop is suppose to cover depends on its volume as well as, the combination of gamma S, gamma S L and gamma L. The combination of the surface tensions and the interfacial tension determines the equilibrium contact angle, but the exact area the drop is going to occupy is a function of the drop volume, assuming the density remaining constant or in other words, its it is a function of the mass of the drop also.

Now, what happens is, if you have evaporation this contact line here also, progressively you will find that, the drop size is becoming smaller. So, if this was my initial location of

the contact line you might see that, it has become like this after a while and after a while it has become like this (Refer Slide Time: 46:17). So, this this results due to progressive reduction of the volume (No audio from 46:30 to 46:42) of the liquid due to evaporation. And the the dynamics are, how fast or slow this retraction occurs depends on the rate of evaporation.

Ideally, just like tilting of a drop on a solid surface one would expect (No audio from 47:15 to 47:30) drop to start rolling immediately, but that does not happen and there is a critical contact angle hysteresis only beyond this occurs. A similar thing can be observed in the dynamics during the dynamics of this evaporating drop also, one would expect that the movements some part of the liquid evaporates, it would immediately sort of continuously move to its next location, thus the diameter will progressively get reduced.

But many times what happens is, this is what is your equilibrium contact angle (Refer Slide Time: 48:10), part of the drop has evaporated, but you still see that, the contact line remains pinned to its original location (No audio from 48:25 to 48:42). What does it mean? It means that, now your theta i is less than theta E, but still you do not see any dynamics. And then all of a sudden you see that, the drop suddenly moves by a large extent to its new location making a contact angle like this (Refer Slide Time: 49:06), so this where again it sort of the equilibrium contact angle matches with theta E.

So, you see that, this motion from the first to second to third pin location is not a continuous motion. So, this is another very interesting class of problems, which is also very well investigated upon (No audio from 49:34 to 49:42) the motion is not continuous, rather motion is discrete. And which is, this discreteness of the motion is again attributed (No audio from 50:03 to 50:16) to pinning effect and this type of a discrete motion is often referred to as the stick slip motion.

In this course, probably I would not go to any greater detail with stick slip motion, but this is a very interesting class of motion. So, what you see that, even after evaporation though there is a, so this is your initial drop and there might be some evaporation, so the volume increases, the volume reduces. So, you are now in a shape like this, where your theta i is now smaller than theta E. So, there is an imbalance now.

And this imbalancing in the Young's equation again in the right hand side, there is an imbalance, so it should retract, but it does not retract instantaneously and it sort of which,

so unlike this rolling of a droplet or sliding a movement of a droplet on a microscope on a on a on a tilted surface it depends on the difference of theta A and theta R.

Here, there is a difference critical difference between theta A and theta i after which, the drop starts to move and and then it moves moves to a location, where again it sort of goes back to (( )), when intrinsic shape corresponding to theta E and then again as if the contact line remains pinned over (No audio from 51:59 to 52:12) there till again this dynamics occurs. So, this type of a motion is again attributed to what is known as a pinning. And in this type of motion is called the stick slip motion.

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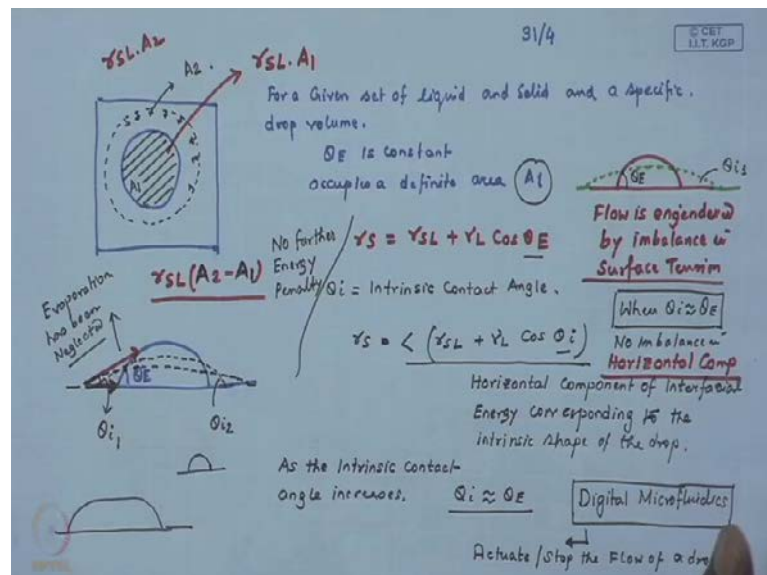


So, both these as well as, the example we talk, where we take a drop initially making an equilibrium contact angle with the surface and then, we part (( )) by way of forcing it to spread and see the dynamics, this is both are sort of flow, which are triggered by the surface effects of the imbalance in the horizontal component of surface tension. And these are examples of dewetting, which we will talk in in, which have sort of introduced (( )). The important thing to note here, for a setting like this is the flow is engendered by imbalance in surface tension the horizontal component.

So, this is what is bulk dewetting and based on this, we will now start talking about the dewetting in an ultra thin film. And we will be talking about the dewetting in a polymer thin film in a liquid form, but this phenomena is possible in a in any ultra thin liquid film. Of course, we will argue why research is more oriented towards polymer thin films

and not with other types of thin films of simple liquids like water or any organic solvent, thank you.