Instability and Patterning of Thin Polymer Films

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Lecture No. # 03

Some Fundamental Surface Related Concepts - I

So welcome back, after a detailed introduction, I hope which you have enjoyed, it is time for getting into deeper. So, we get started with some of the basic concepts, which are important for understanding the physics that is governing the entire phenomena.

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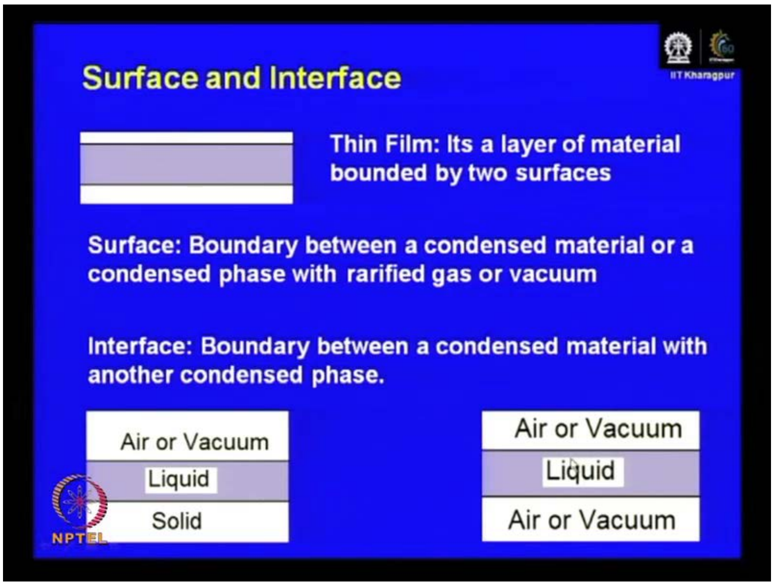

Surface and Interface

Thin Film: Its a layer of material bounded by two surfaces

Surface: Boundary between a condensed material or a condensed phase with rarified gas or vacuum

Interface: Boundary between a condensed material with another condensed phase.

And the most important thing to start off is surface tension, because we have defined a thin film in terms of a layer of material bounded by two surfaces or two interfaces. Therefore, it becomes important to quantify what exactly are these, so called surfaces or interfaces. Very simple definition for the of a surface is it is the boundary between a condensed material or a condensed phase with rarified gas or vacuum. Similarly, the mode of formal definition of an interface is the boundary between a condensed material or a condensed phase with another condensed phase.

So, when we talked about a thin film, let us say it is a liquid film coated on a solid sub state and the other side was exposed to an air or vacuum. So, here we essentially had a liquid surface, this liquid air interface can be regarded as a liquid surface; where as this one the solid liquid contact line or the interface this is going to be marked as a solid liquid interface. When we talked about, let us say a self standing film, we had liquid surfaces on both sides of the film, the example of which we have already told can be so popular.

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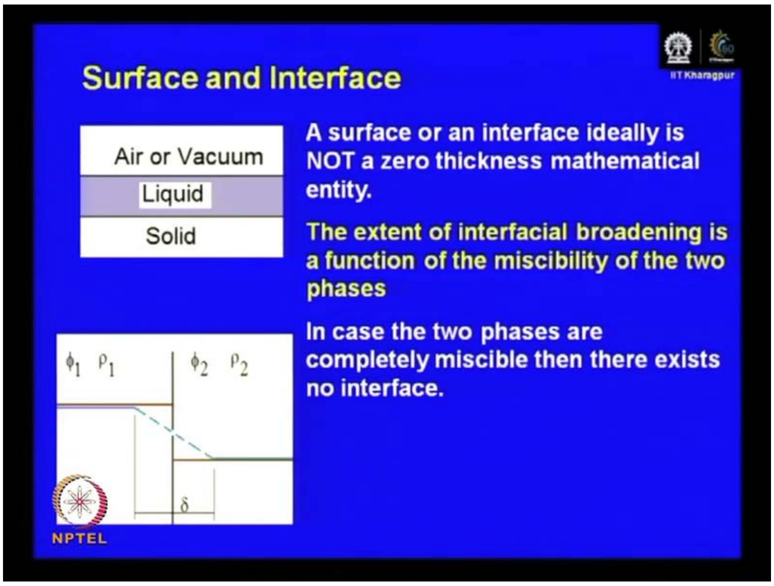

Surface and Interface

A surface or an interface ideally is NOT a zero thickness mathematical entity.

The extent of interfacial broadening is a function of the miscibility of the two phases

In case the two phases are completely miscible then there exists no interface.

In reality, so this is how what you expect the picture of an interface to be; suppose you have two phases, suppose let us say two condensed phases; phase one and phase two, which has two distinct properties, let us say density we have considering rho 1 and rho 2. So, what you do? You would expect that in phase one, the density will be rho 1; right up to here and at the interface you will expect the density to sharply drop a change to rho 2, which is the density of the other phase phi 2. So, however in reality, an interface is not ideally zero thickness mathematical entity as has been shown here; if you consider that there is no variation of rho 1 and rho 2 within the two respective phases. In other words, it stretches up to rho 1 right up to this point and then drops to rho 2. In reality, close to the interface there is a gradual transition of this properties, it can be density, it can be any other internship property, which gradually changes over a link over a special dimension.

So, there is a gradual transition from rho 1 to rho 2 and this distance delta is termed as the interfacial broadening. Now, the simplest thing to understand is the lower is the miscibility of the two phases, in contact with each other lower will be the interfacial broadening. If the two phases are completely miscible, sugar in water for example, then there exists no interfaces or in other words, it is infinitely broaded.

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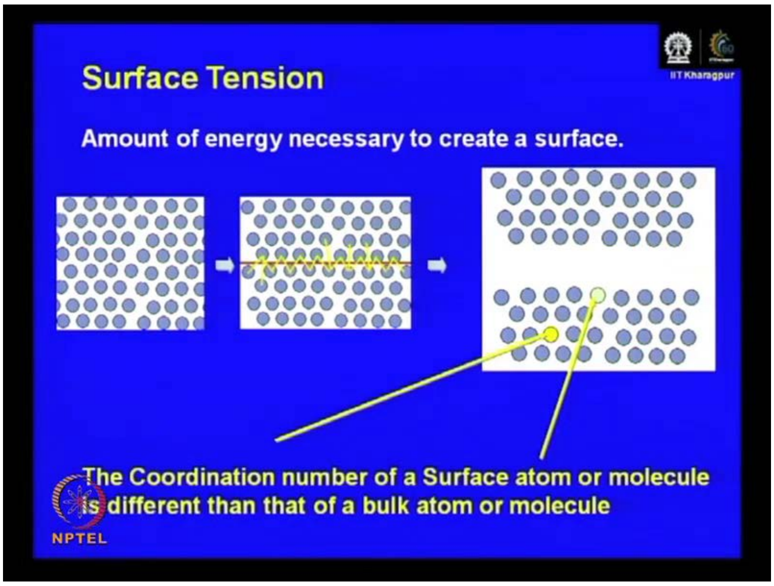

Surface Tension

Amount of energy necessary to create a surface.

The Coordination number of a Surface atom or molecule is different than that of a bulk atom or molecule

Now, we all know the what surface tension? We have started to re detail on internal properties of matter in our school days, along with viscosity probably now what exactly surface tension. Now, without going into a formal definition, let us understand or this can also be a formal definition is in many ways. It is the energy required to create a surface tension has a unit of mile joule per meter square.

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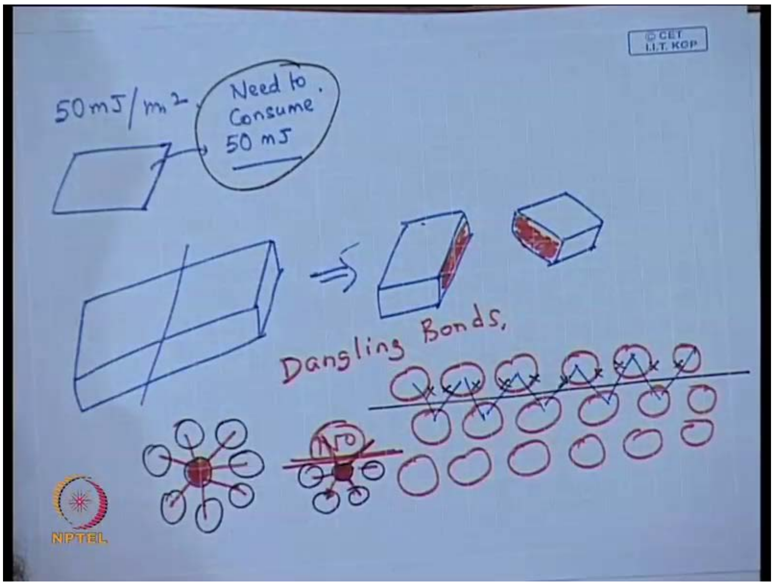

So, if the surface tension of a material is given as 50 mile joule per meter square, what did implies is that in order to create one meter square of that particular a material one meter square area of that particular area, you need to consume 50 mile joule of energy. Now, think of very simple example, which will give you an idea about what surface tension is. Suppose, you have a block of any block, let us say it is a block of batter, which is very, very soft. You take a knife to sort of chop it of from here; and eventually what results is two isolated blocks of butter. Now the question is the when you were applying the knife or cutting it through knife, you have applied some energy to the system by consuming your own metabolic energy. Now, as chemical engineers, we know very well the existence of the mass balance. So, if you look at the total mass of the two blocks after cutting they match with the mass of the initial block. So, what exactly this energy that you have applied externally has done.

There has been no chemical reaction, no heat transfer nothing has occurred, it is not that that you have applied energy and the block has been immediately melted. All what you have done is that by way of cutting you have created these two additional surfaces. So, the energy that you have applied was necessary to create these two additional surfaces. A simple example, the a extended example can be that if you are trying to cut something as soft as butter; and you apply your knife with very high force you will hear that you have not only cut, but you will hear a (( )) on the surface.

So, what it means that the amount of energy that you had supplied, in the form of your own metabolic energy was way in excess as compared to that is necessary to create these two additional surfaces. So in other words, you can look into this concept of creation of a surface; suppose, this is a bulk object, where you want to cut it into two, and create these two additional surfaces as a as shown here. So, this is more of a molecular level picture of a material or of a surface. So, by way of creating the surface what are you actually doing? You are overcoming all these interactions which are shown in yellow, over this particular picture, if it is not clear. So, suppose these are some of the molecules or atoms present; and there is interaction between these molecules or atoms, the all these interactions are present. And if you want to sort of create a surface out here, you are breaking all these interactions.

So, these interactions can be in the form of bonds, these interactions can be in the form of the induce dipole interaction we have talked about. But since you have these fundamental particles or atoms or molecules, they are ease interaction between them, because we now know that it is not mandatory to have electron sharing or polarity has to be present; in order to have interaction even for charge neutral particles or neutral particles there can be induced dipole induced dipole type of interaction. So, whenever there are fundamental particles like atoms or molecules present, there is interaction in some form of the other. So, whenever you want to create a surface, you are overcoming these interactions. So, your energy needed to overcome or create a of a surface, these actually, if you multiply, if you can locate the number of interactions present and you multiply with number of such interaction on the surface, you will get to that amount of thing. So, this is what exactly is known as surface tension. This is a many faced tension of surface tension or it is the energy needed to create a, some unit area of unit new area of a material.

Now, if you look into this figure carefully what happens is that suppose if you investigate, if you now look at one molecule this is the same material; do not forget this you have you had a uniform bulk material which you have cut into two. So, all the molecules are same, the material is same, the ordering is same, but if you now investigate in details; two particular molecules, one molecule which is present at the surface, and one molecule which is present at the bulk.

You can see that the co ordination number of the bulk molecule, coordination number by the probably most of you know coordination number is, very loosely speaking the number of molecules that is around a specific molecule. You can see that the coordination number of a bulk molecule is different as to that compared to a surface molecule. Now, what it means that even if there is no polarity things are charged neutral, the interaction, even if it is dispersion interaction it is sort of balanced from all sides for a molecule in the bulk. In contrast to that, if you now consider a surface molecule, this interaction is not balanced, because there is no interaction on this side. What it means? We have just understood that the vanderwall's force between two fundamental particles is attractive in nature.

So, what it means that not only a surface molecule is under coordinated, but as a consequence of that there is a net inward attraction, that is surface molecule experiences, which is absent in a bulk molecule. So, a bulk molecule remains a sort of stable in its equilibrium position; while a surface molecule is subjected to continuous inward attraction, because of this unbalanced interaction. Sometimes, if you are overcoming physical bonds, while creating the surface and this bonds are I mean this bond these electrons, which could have participated in bond formation; which are now free these are referred to as dangling bonds.

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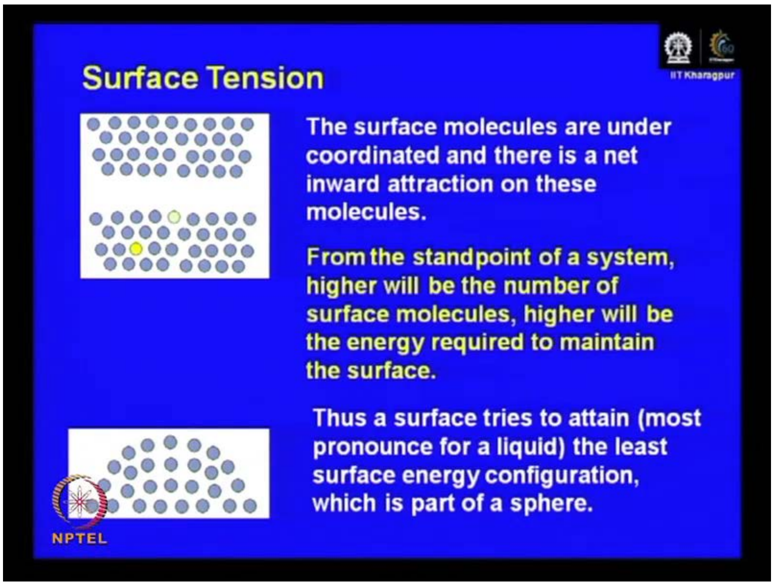

Surface Tension

The surface molecules are under coordinated and there is a net inward attraction on these molecules.

From the standpoint of a system, higher will be the number of surface molecules, higher will be the energy required to maintain the surface.

Thus a surface tries to attain (most pronounce for a liquid) the least surface energy configuration, which is part of a sphere.

So, the surface molecules are under coordinated and there is a net inward attraction on these molecules. From the stand point of a system of course, we know that every system tries to minimize its level of energy; from the stand point of a system higher will be the number of surface molecules, higher will be the energy required to maintain the surface. So, surface molecules have some sort of, in order to maintains maintain its integrity or overcome the inward pool its experiencing, because of under coordination. If the molecule has to remain at the surface, the system has to consume some energy. Which is manifested, the summation of which is manifested as the surface tension, the total surface tension that is the other way you can look at surface tension. Thus a surface tries to attend, this effect is most pronounced in liquids, the least surface configuration which in which often if the there is no significant influence of gravity and other body forces; which is part of a sphere.

So, this is something we all know that if we dispense a drop of liquid irrespective of its initial shape, it eventually tries to take a spherical shape. Why it tries to take a spherical shape? Because if it try, if it goes for a spherical shape, then its surface area is minimum; what it means that you have minimum number of molecules present on the surface. Since, you have a surface there will be some number of under coordinated molecules which are experiencing this inward pool or inward interact inward pool, because of the attraction from the inner molecules, which are absent on the other side of the surface. However, if you have the minimum number of molecules present on the surface, this energy penalty is going to be minimum. So, a liquid where reconfiguration is possible, because the molecules are not that tightly bound as in a solid, always tries to take a minimum energy configuration, which is in the form of a part of a sphere. Now, do not feel that solids do not try to attain this minimum energy configuration. The only problem is that the solids cannot reconfigure easily cannot deform to these type of forces, because of its structural rigidity. So, if suppose you do a thought experiment, you heat up a solid, so that it becomes molted or things like that there will be very several phenomena, a solid surface will also try to contract to a part of a sphere.

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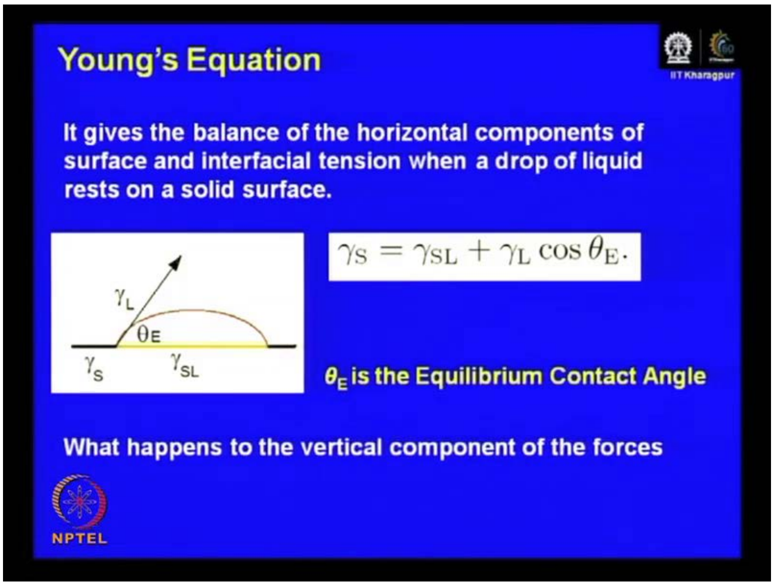

Young's Equation

It gives the balance of the horizontal components of surface and interfacial tension when a drop of liquid rests on a solid surface.

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta_E.$$

θ_E is the Equilibrium Contact Angle

What happens to the vertical component of the forces

Now, this is again something we all know that if you dispend a drop of liquid on a solid surface and it eventually forms a part of a sphere. The balance of the horizontal components of surface and interfacial tension gives you, as what is known as very famous young's equation. So, here you have a liquid drop dispensed on a solid surface, your solid surface is surface tension of gamma S; the areas of the drop which is covered by the liquid is no longer exposed to air. Therefore the surface, it is now not part of the solid surfaces alone or a solid interfacing in contact with air. It is the same solid; however, now it is in contact with the liquid. So, this is now a liquid solid interface, where do you have the interfacial tension gamma SL.

Of course, the liquid surface tension is gamma L and if it makes an angel theta E, which is known as the equilibrium contact angle. The balance of the horizontal component of surface and interfacial tension, which is very very simple you just simply balance gamma S equal to gamma S L plus gamma L cos theta E, this is known as the young's equation. Important thing to remember is that theta E is what is known as the equilibrium contact angle or it is a static contact angle. Now, if keen listener would definitely think of that we consider the horizontal component of surface tension, but what happens to the vertical component of surface tension. What becomes the force that is significant there is the gamma L sin theta E component.

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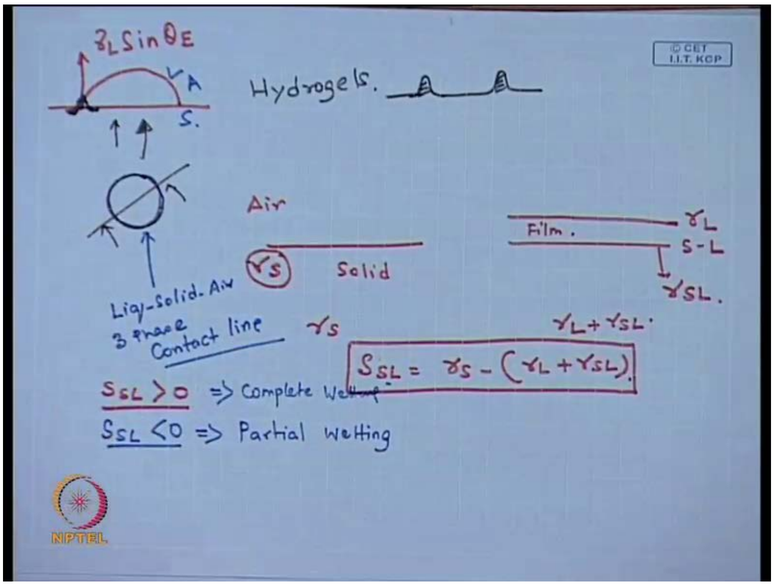

$$\boxed{S_{SL} = \gamma_S - (\gamma_L + \gamma_{SL})}$$

$S_{SL} > 0$ ⇒ Complete Wetting

$S_{SL} < 0$ ⇒ Partial wetting

Well the reality is that this as you can see hypothetically from the, I mean the direction of this force would be acting outward. So, this will be gamma L sin theta E. So, this will try to sort of cause some sort of a deformation on to the solid surface here. So, it will probably try to pull the surface here, but if it is a solid sub state you are using is a rigid solid, surface probably this force becomes too weak to cause any deformation. However, there has been experiments performed on soft solid surfaces, for example, an example of which can be hydrogels which are gels very soft solids contains lot of water.

One can dispense a drop of a liquid and one can see after the drop has completely evaporated some signatures like this, which correspond to the contact line. These types of humps are caused by the vertical component of the surface tension. Now, this figure if you see from the top, it is we told that it is part of its sphere. So, this is what you are seeing from the top, it is actually part of a sphere, this is a liquid droplet, but this if you take the section like this corresponds to this. So, this is something very very simple and many of us probably know, there let us have a look I mean. So, later I mean we will discuss certain aspects in detail over young’s equation.

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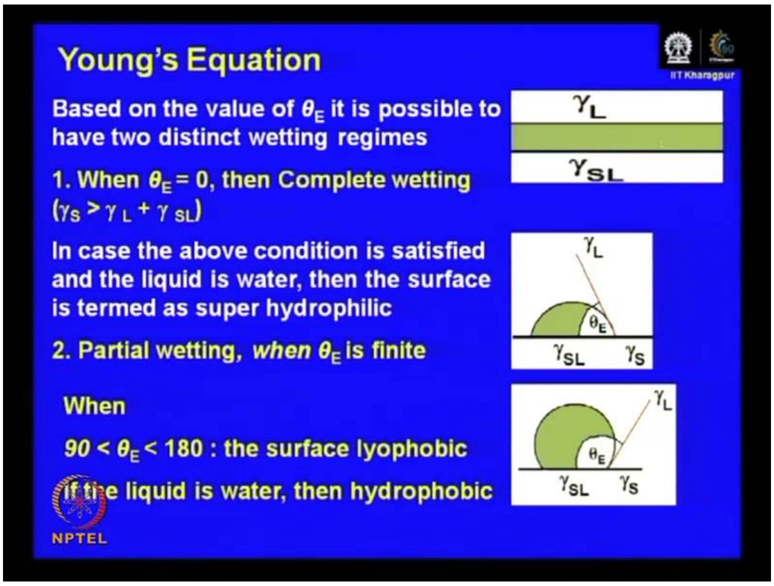

Young's Equation

Based on the value of θ_E it is possible to have two distinct wetting regimes

1. When $\theta_E = 0$, then Complete wetting ($\gamma_S > \gamma_L + \gamma_{SL}$)

In case the above condition is satisfied and the liquid is water, then the surface is termed as super hydrophilic

2. Partial wetting, *when* θ_E is finite

When

90 < θ_E < 180 : the surface lyophobic

if the liquid is water, then hydrophobic

Now, based on what you can see immediately that based on the value of theta E, it is possible to have two distinct wetting regimes. One possibility is when I seem to limit is that theta E is equal to zero. What does a theta E equal to zero configuration look like? Well, it looks likes nothing other than this; where the liquid spreads fully on the solid sub state without forming any contact angle. So, this is a regime which is termed as complete wetting. In contrast to that, if theta E is finite and what can be the likely values of theta E; if it is finite, it is greater than zero, but it can be all the way up to 180 theoretically. It is termed as a partial waiting. Let me just add, in case one sees complete wetting and the liquid is water, this is important; then the surface can be termed as a super hydrophilic surface.

So I repeat, in case you have complete wetting and the liquid that is wetting the solid surface is water, then the surface can be termed as a super hydrophilic surface. In contrast with theta E is non zero, that is it is finite, then you have partial wetting. But even in partial wetting, as you can see from these two figures, you can have in a way two slightly distinct scenario. So, what is the difference between these two figures? Well, both of them actually refer to a scenario, where you have partial wetting; in contrast to this figure which refers to complete wetting. However here in this particular case, theta E is acute. What it means that it lies between 0 and 90. In contrast to that in this particular case, theta E is obtuse that is it lies between 90 and 180.

So, when theta E is finite and theta E lies between 0 and 90, the surface on which the liquid is making such a contact angle is termed as a lyophobic surface. And if the liquid is water, then the surface is termed as a hydrophilic surface. So, what does hydrophilic means? It means that the surface likes the water to preferentially spread though it is not fully spreading. It is partially wetting, but since the angle is acute, so it still prefers preferential wetting. In contrast to that, when theta E lies between 90 and 180, the surface is the termed as a lyophobic surface; and if the liquid is water it is regarded as a hydrophobic surface.

So, what it means that the surface does not really want your liquid to spread on the on it and it tries to contract it to as much extent possible. Looking at the expression of the young’s equation, you can immediately find out yourself that lower is the value of gamma S the surface tension of the solid higher will be the angle theta E. So eventually, if we consider the liquid to be water, a hydrophobic surface is one, which typically has lower surface energy. In contrast, a hydrophilic surface as the surface energy of the substrates gradually increases theta E also becomes lower. So, hydrophilic substrates essentially have much higher surface energy.

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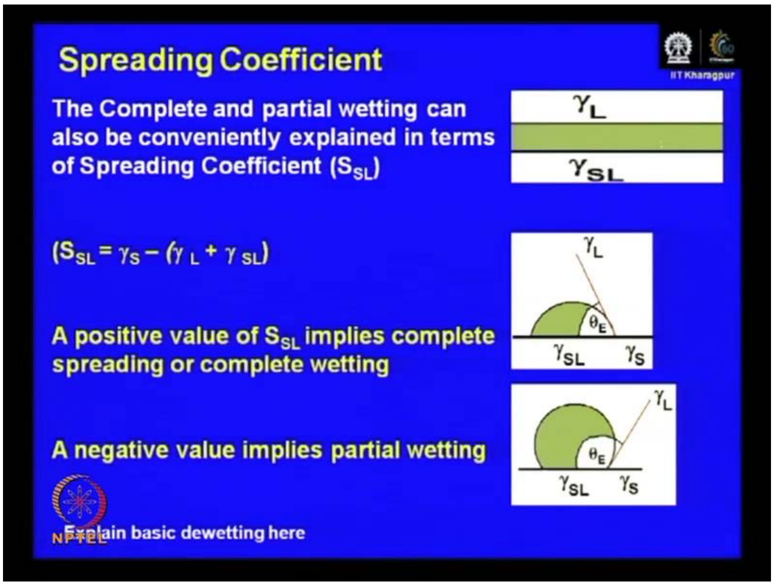

Spreading Coefficient

The Complete and partial wetting can also be conveniently explained in terms of Spreading Coefficient (S_{SL})

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

A positive value of S_{SL} implies complete spreading or complete wetting

A negative value implies partial wetting

Explain basic dewetting here

This concept of partial wetting or complete wetting can also be termed or discussed or understood from another stand point that is the stand point of spreading coefficient. Well, the complete and partial wetting can well spreading coefficient is essentially defined as S SL equal to gamma S minus the summation of gamma L plus gamma S L. So, what it essentially means is very very simple; if you just configure the way you get a film. So here is a bare substrate, which has a surface tension gamma S; suppose this is solid substrate it is in contact with air. So, you have a solid air surface or the solid surface which corresponds to a surface tension gamma S. Now, you coat it with a liquid. So, you have a liquid; so, this liquid now has a surface leap here which corresponds to energy gamma L, but the solid air contact line is now replaced with a solid liquid interface; so, which corresponds to an interfacial tension gamma S L. So for unit area, if you consider for the system, the total energy was gamma S into a; for unit area is gamma S here the total energy is gamma L plus gamma S L

So, the if you look at the expression for S SL, which is given as, this actually gives you the difference in energy before and after coating the film on a surface. Now, if S SL is greater than zero, what it means that you initially had higher energy ascribe to the solid surface and by way of coating the film on top of it, you have actually reduced the total energy. So, we know that any natural process would prefer to sort of tend to its lower energy configuration. So in this case, where the spreading coefficient is greater than zero, what you have done is by way of the coating, you have actually reduced the total energy of the system. Therefore, in such a case the spreading of the film on the solid surface is preferred. So, you can have complete wetting. In contrast, if you have S SL to be less than equal to zero. What it means that you have some definite energy ascribe to the solid surface, but after you have coated, the total energy that is now attributed to the solid liquid interface and at the liquid surface is actually higher than this. Therefore, by way of creating the coating, you have increased the total energy. Therefore, such a case the spreading of the liquid is not favored; the surface will prefer to remain bare rather than getting covered with the liquid fully and therefore, creating higher energy.

So, this corresponds to a scenario where you have partial wetting, while the previous one corresponds to scenario, where you have complete wetting. The other important thing to notice that, this is the view of the drop from the top, so this line is known as the liquid solid air three phase contact line; where all the three phases (( )). So, you have A there you have liquid, you have solid. So, this is what is known as the three phase contact line. Now, I will give you a very simple example of this, where you can microscopically see the validity of this young's equation. This is I am sure most of us have done at some point or the other, you pour some water on the table for example, or on a on a surface and you try to wipe it with your hand; and you see that at certain locations the water meniscus is retracting back.

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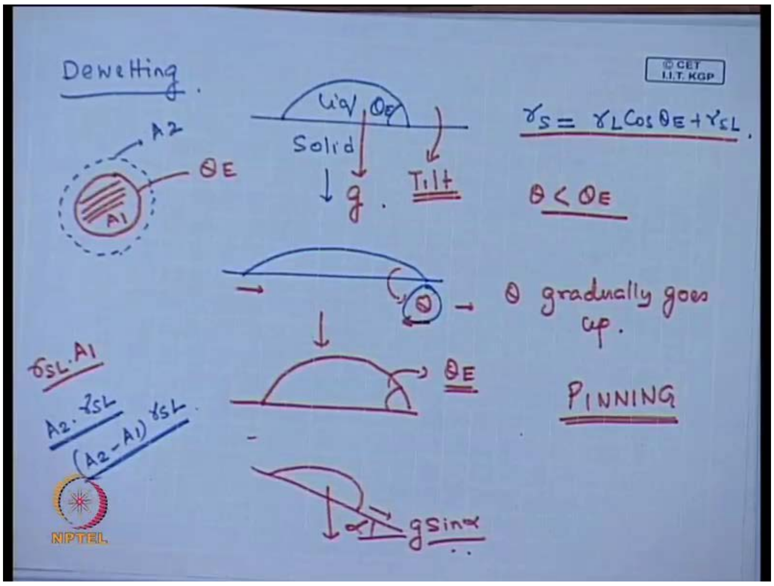

I am sure many of you have seen it at some point or the other; this is what is known as Dewetting, in the simplest form. Now, what exactly happens? What exactly happens is this you know that for a specific liquid solid combination the gamma the young's equation is going to be valid. So, this is let us say the initial drop, now what have you done? By way of spreading, you have actually applied some energy externally and you have spread the liquid. You have spread the liquid means, now it makes an (( )) angle theta; let us say which is smaller than theta E. So, if you now substitute this value of theta in this equation, what happens is you will find that this equality is no longer valid. Or in other words, we know that theta reduces cos theta tends to one. So, eventually the right hand side has become larger as compared to the left hand side.

So, there is an imbalance; and this imbalance in energy eventually results in the retraction of this contact line up to the extent. So, it retracts what it means that theta starts gradually goes up. And when does the retraction stop it stops, when theta gets back to theta E. So, when theta becomes equal to theta E, what happens is this equality gets validated again gets valid again, so the retraction stops. So, this is Dewetting, but in comparison to the types of flows you have studied in fluid dynamics, where it is in most cases triggered by a pressure difference or by a hydrostatic head or in some cases by (( )) type flow by triggering a flow artificially. Here is a scenario of a flow which is triggered by surface tension forces.

So, this is something I guess, you have all seen or you can try it out after listening to this; if it is interesting to you. Of course, on a dirty table or on a table you will see that the droplet may not be spherical at all times; it may not be part of a sphere, but those are attributed. Those are, because the physics is absolutely valid those happen, because you may have imperfections or impurities on the surface; which sort of acts as additional pilling sites or something like that, some of the issues which we will talk later. So, if you revisit this problem from again; so, this is corresponds to the size of the droplet corresponding to the equilibrium contact angle theta E. So, let us say this area is a one; so the balance this is now the liquid solid interfacial contact area. So, the energy is gamma SL into A 1.

Now, by way of spreading you have reduced the theta; so, essentially the contact line has shifted over here. So, let us say the area is now A 2 and the liquid is covering the solid surface; so now, it is a two times gamma SL, which is we have already seen unbalanced. So, the we know that in order to have any flow there has to be some sort of a driving force; and in this particular case, the driving force is actually A 2 minus A 1into gamma SL. This excess energy is unbalanced due to this change of theta E to that theta that intrinsic theta. So, this is the driving force that triggers to this retraction of this drop back to its equilibrium configuration. So, this is the phenomena of Dewetting, in its simple simplest form; we see if you go by the dictionary meaning its opposite of wetting, but this is something that is very very simple, and you can explain it or you see it yourself that you can explain based on whatever little thing you have learnt so far in this course.

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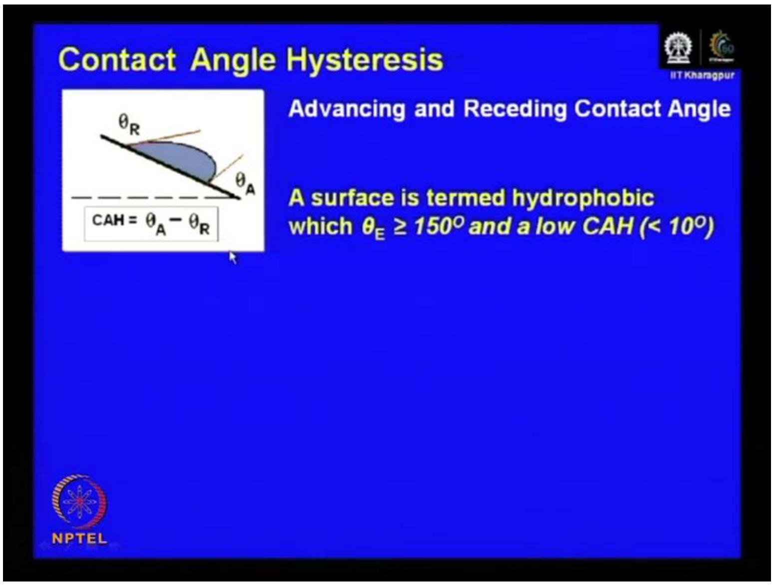

Contact Angle Hysteresis

Advancing and Receding Contact Angle

A surface is termed hydrophobic which $\theta_E \geq 150^o$ and a low CAH (< 10^o)

There is another concept that I would like to introduce you here which is known as contact angle hysteresis. Well, the in the young’s equation what we have seen so far, if we talk about the equilibrium contact angle or the theta E over here. Now, suppose you want to tilt, so you have a liquid drop sitting on a horizontal surface and you want to suppose gradually tilt the surface. What would you expect? The movement you actually tilt; so gravity is acting in this direction. The movement you tilt it gravity extends this direction, so there is a component, if alpha is the angle of tilt which is g sin alpha, which provides the driving force for this flow. This is very well known, in the case of flow over a tilted inclined plane; for example, that is pretty well known.

Now, you might see that the movement you tilt. So, ideally you would expect the movement you tilt; however, small the value of alpha the angle, tilting angle alpha might be the you would expect the drop to start moving. But in many cases that does not happen and you have to tilt it to substantial angle, when all of a sudden the drop starts to move. Now, if you gradually tilt it, what you will see? That the contact angle on the both sides which are essentially the same, because you are looking at the section now change. So, before tilting while on both sides, it was theta E; now, it take the drop it takes a shape like this. And at the particular combination of angles, where the drop starts to roll or starts to climb down, if you note the two angles; now, the drop is going to move in this particular direction, so this is known as the advancing contact angle; and it is going to sort of come down in this direction, so this is known as a receding contact angle.

So, the difference between theta A and theta R at the critical condition, when the drop starts to move is known as the contact angle hysteresis. So, this is slightly counter in (( )), because if only the horizontal components of the surface and interfacial tension are balancing the stability of the drop or the location of the drop. Then you would expect that whatever small the inclination angle alpha may be the drop should start rolling off, but this does not happen. There are additional effects which one of the key effects or key terms related to that goes by the name pinning, we will try to explain what pinning is in our subsequent talks which lead to this contact angle hysteresis.

We have already talked about the hydrophobic surfaces in the context of structural super hydrophobicity or the lotus leaf effect, etcetera etcetera. A surface when the liquid is water is conventionally calmed as super hydrophobic, when it should be super hydrophobic in the slide I am sorry I missed it out, is termed super hydrophobic. When the equilibrium contact angle executed on a solid surface is close to around 150 degree and it also exhibits a low contact angle hysteresis of around 10 degree of 10 degree or lower.

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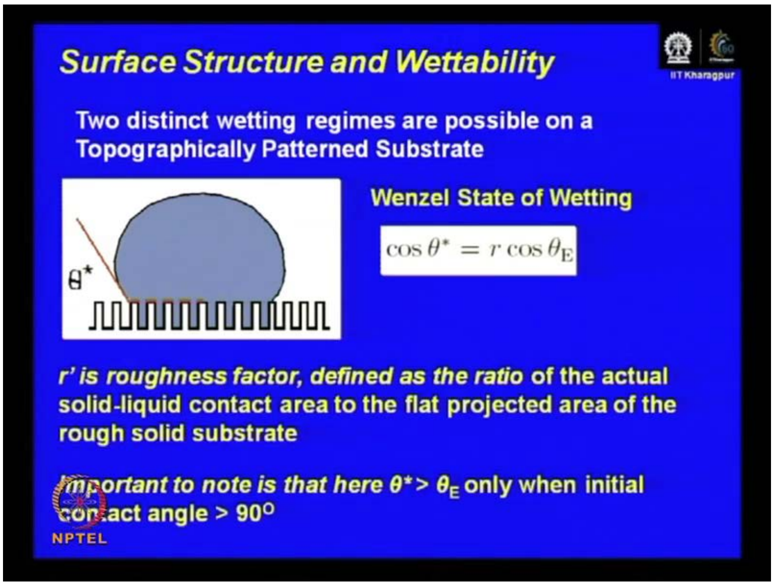

Surface Structure and Wettability

IIT Kharagpur

Two distinct wetting regimes are possible on a Topographically Patterned Substrate

Wenzel State of Wetting

$$\cos\theta^* = r\cos\theta_E$$

r' is roughness factor, defined as the ratio of the actual solid-liquid contact area to the flat projected area of the rough solid substrate

Important to note is that here $\theta^* > \theta_E$ only when initial contact angle > 90^o

NPTEL

Now this brings us, since we are discussing about the young's equation and we have already talked about the effect of structural super hydrophobicity in the initial slides, where we talked about the lotus leaf effect etcetera etcetera. So, let us also take a quick look as to what happens there.

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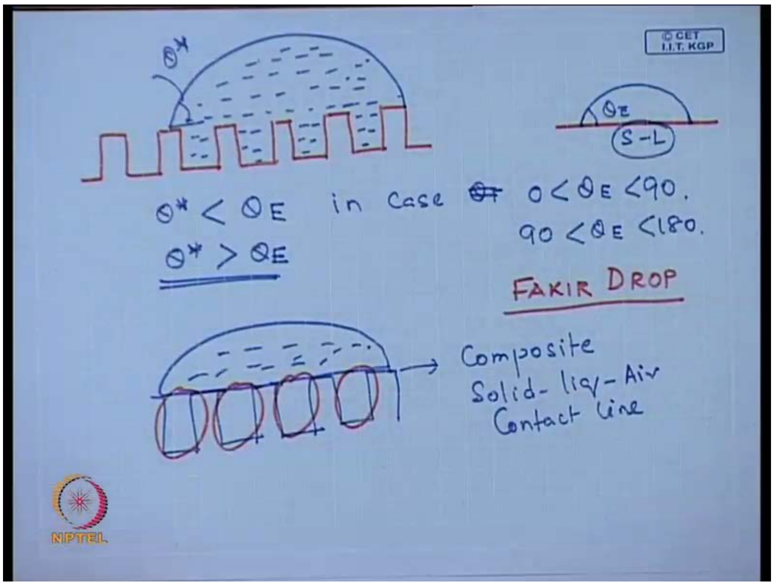

So, we now know what exactly is a pattern surface. So, you have some a structured surface like this which can be topographic patterns; which can be greetings, which are array of parallel lines or can be different type of structures. So if you now in contrast, so in comparison to that we have so far considered a flat surface for understanding the young’s equation, where the drop makes an equilibrium contact angle theta. Now, let us say we have a surface which is structured and we dispense a drop on top of that. There can be two distinct wetting regimes, one of that is that you have a solid which is structured, but the liquid sort of gets within the valleys on the structure and it wets fully. So, this time of a wetting regime is known as the wenzel state of wetting. And here, you see that there is an contact angle, it you can have an acute angle you can have a obtuse angle does not really matter. You can you have a contact angle theta star, which is given by the equation cos theta star equal to r times cos theta E. Where cos theta E is the equilibrium contact angle between the liquid and a flat surface of the same material. Now, theta star is the effective contact angle on a topographically patterned surface of the same material.

Now, r is defined as the roughness factor which is defined as the ratio of the actual solid liquid contact area to the flat projected area of the rough solid surface. So because of the topographic structure, you have the contact area has actually increased. These are the additional areas where there is contact had it been flat; this was the only area over which it was in contact. So, you can find that r is always going to be greater than 1.

Now, we have talked about this is one important aspect that, we have talked about topographic patterning to increase the level of hydrophobicity that is what we have talked. But here you can see for the equation, that theta star can only be higher than theta E, when theta E is greater than 90 degree, because the way r is defined, r is always greater than 1. So, in case you have a lyophilic liquid, a situation corresponding to lyophilic liquid or a hydrophilic liquid where theta E is finite, but lies between 0 and 90 degree; multiplying it with something which is higher than 1 will effectively make theta star lower than theta E.

So in other words, theta star here becomes less than theta E; in case, theta E lies between 0 and 90 degree. However, if theta E lies between 90 and 180, then you can do the calculation yourself; theta star is going to be theta higher than theta E. So, a structural surface, if it is in a wenzel wetting regime, if or if it is undergoing a wenzel state of wetting, then whether the effective contact angle increases or not depends on the initial equilibrium contact angle. So, for the important message that goes in here is there is no point in binding pattern in something. If you have a surface which is hydrophilic, suppose the liquid is water, then if you pattern it; and if you are having an wenzel state of waiting, then you are not going to achieve any bit of hydrophobicity or any bit of enhanced contact angle, but you are going to make the scenario even worse than that.

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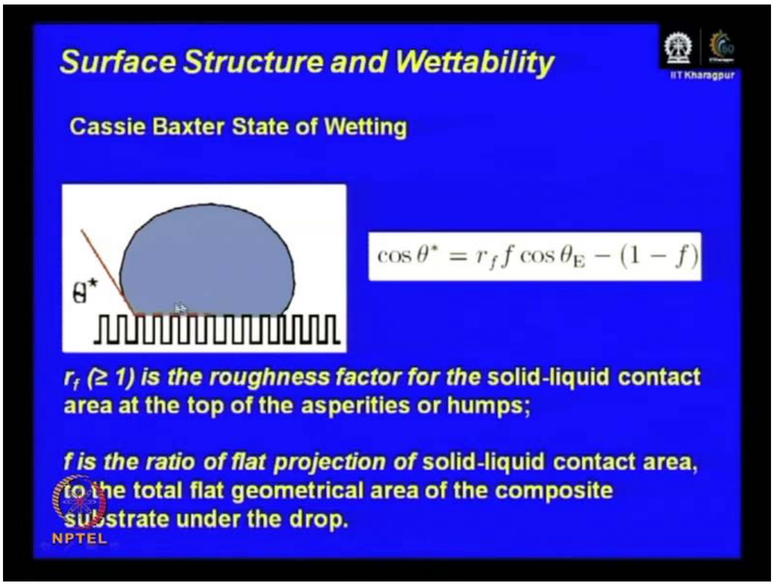

Surface Structure and Wettability

Cassie Baxter State of Wetting

$$\cos\theta^* = r_f f \cos\theta_E - (1 - f)$$

r_f (≥ 1) is the roughness factor for the solid-liquid contact area at the top of the asperities or humps;

f is the ratio of flat projection of solid-liquid contact area, to the total flat geometrical area of the composite substrate under the drop.

In contrast, the other type of a wetting state can be the, so called cassie baxter state of wetting or in many cases, it is referred to as cassie state of wetting. So, if you now compare this figure with the previous the figure that was shown for the wenzel state of wetting, here is something very interesting. Here also you have a structured surface, as you had in the previous case for wenzel wetting. But in case of wenzel state of wetting, a liquid went inside the grooves or the valleys and filled it properly; however, here the liquid does not go inside the grooves or inside the valleys. It sort of rests or sort of floats on isolated air pockets which are along these grooves.

So, the typical case of a liquid solid contact line the way we understood young's equation is now. So, this is a solid liquid contact line here. In case of cassie state of wetting, a solid liquid contact line is actually replaced with a composite solid liquid air contact line. So, the liquid stays over here, it does not penetrate inside the within the valleys, which remain where there are air pockets where air pockets remain there. And these sorts of leads to the additional affects of hydrophobicity, which will come in a minutes time. Now, the way sort of, so as if this drop here floats on the structured surface; so, this is what exactly occurs in many naturally occurring leaves which we have already talk. This is what is a lotus leaf effect, how it is explained or this is what is known as a lotus leaf effect. This also has a name which is accepted by the international scientific community, but which has a very indian origin, because these type of this configuration is often known as the fakir droplets.

You may be knowing that our indian fakir's perform all sorts of strange activities, including they would some time lye on a bade of nails or something like that; so, it is exactly similar to that. So, this cassie baxter state of wetting is also referred to as fakir drop configuration. Now, here if you look at the equation, mathematical equation the cos theta star is given as r f into f cos theta E minus one minus f; where r f is the roughness factor of the solid liquid contact area at the top of the asperities or humps. And f is the ratio of the flat projection of the solid liquid contact area, to the total flat geometric area of the composite substrate under the drop. So I repeat, f is the ratio of the flat projection of solid liquid contact area to the total flat area. It is the projection of solid liquid contact area to the total flat geometrical area of the composite substrate under the drop.

So, essentially one minus f refers to the fraction of the solid surface that is actually in contact with the liquid and f is the ratio f is the remaining part, which is the projected area which is not in contact with the liquid. So, this part, these fractions of the part which is not in contact with the liquid is sort of taken care by f and one minus f takes care of the rest of the stuff. r f pretty much similar to what was defined for in the in the context of wenzel state of wetting, which corresponds to the roughness. So, one important thing even in wenzel state, as well as in cassie state is that for example, if you have the wenzel state of wetting and you want to you have a situation or a scenario where your initial theta E is in the acute angle domain, then you want to increase it higher. So, higher value of r is going to help that help lead to that increase in theta star. So, that the how can this r be at the what essentially leads to this higher value of r.

Well, it can be seen that higher is the feature height higher will be the value of r. So therefore, it becomes important to create structures with higher values or higher aspect ratios rather than the going in for structures with very fine periodicity, but we just shallow; this is one of the limitation. So, this brings us or focuses on notice to one critical factor or one important factor that it is important to have higher aspect ratio structure or taller structures to achieve higher levels of hydrophobicity. Similar is the concept for cassie baxters state; however here, the relative values of f and one minus f, which falls under the category of what is exactly the duty ratio of the of the topographic structures; something a term that will be explained in details later. We will also have a significant influence on the wetting regimes as well as the wenzel state.

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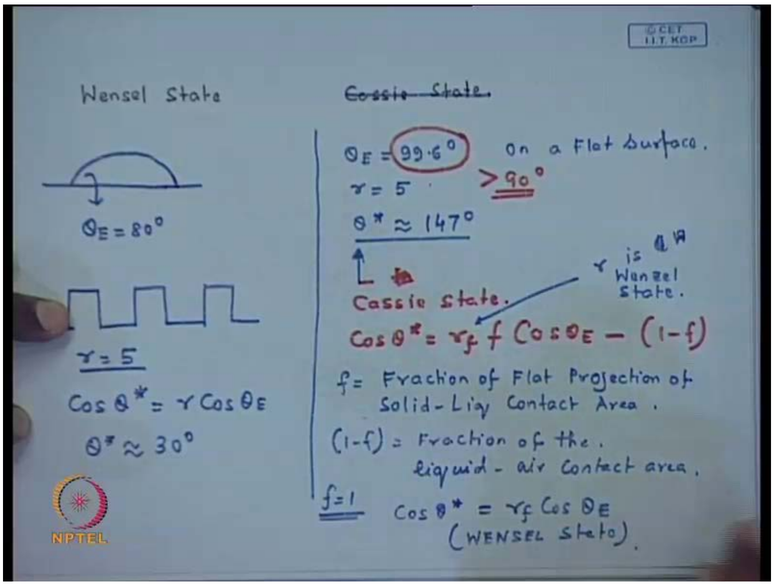

Wensel State

$\theta_E = 80^\circ$

$r = 5$

$\cos\theta^* = r\cos\theta_E$

$\theta^* \approx 30^\circ$

Cassie State.

$\theta_E = 99.6^\circ$ On a Flat Surface.

$r = 5$ $> 90^\circ$

$\theta^* \approx 147^\circ$

Cassie state.

r is Wenzel state.

$\cos\theta^* = r_f f \cos\theta_E - (1-f)$

f = Fraction of Flat Projection of Solid-Liq Contact Area.

(1-f) = Fraction of the liquid - air Contact area.

$f=1$ $\cos\theta^* = r_f \cos\theta_E$

(WENSEL State).

So, let us look at some practical examples. Suppose, we have a scenario where a liquid on a flat solid surface makes an equilibrium contact angle of 80 degrees. So, this is a regime where the equilibrium contact angle is acute, so essentially, it is a regime of preferential wetting. Though the wetting is not much favored, because the contact angle is close to about 90 degree. Now here, if you have if you replace or if you have a rough or a structured surface of the same material, where let us say r is equal to 5. So in that case, based on the formulation we have for the wenzel's state which shows that cos theta star is equal to r cos theta E; you can calculate for yourself that theta star sort of drops to roughly 30 degree. So, instead of achieving a higher contact angle as we have already mentioned this example shows that in wenzels state, if you have a rough surface as well as the equilibrium contact angle on the smooth surface is less than 90 degree. You actually reduce the effective or the intensive contact angle and you have actually favor spreading. In contrast, let us say we have in the wenzels state another system where theta E is close to 100 degree on a flat surface.

Now, for the same roughness, you can calculate that theta star trans out to be around 147 degrees. So, this is what we have told; now you can see numerically also that in case of wenzels state, enhancement of the equilibrium contact angle is possible, only when your initial equilibrium contact angle is higher than 90 degree. So, if the liquid is water on a particular surface. So, you can achieve higher equilibrium contact angle only when the surface is hydrophobic.

In contrast, in the cassie state, we have cos theta star is r f, we have already talked about what are the definition of r f and f. r f is nothing but has been termed as r in a wenzel state. Now, f is as we have already talked, it is the fraction of flat projection of solid liquid contact area and naturally one minus f is going to be the fraction of the liquid air contact area. Now you can see, in case f is equal to one, that is there is no air interact or the fraction of flat projection of the solid liquid contact area is equal to one, which means one minus f is equal to zero; therefore, this term contributes to zero. And immediately, what you see that cos theta star reduces to r f cos theta E which is nothing but, I guess you understand by now is the wenzel state.

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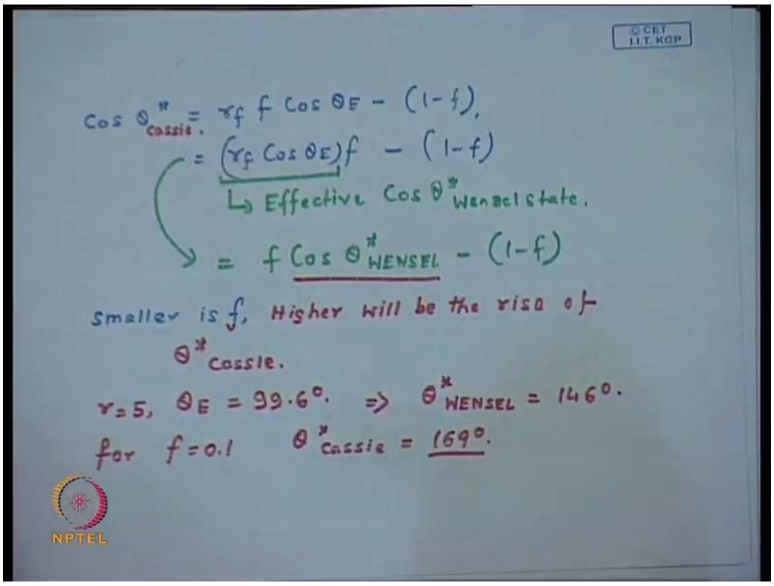

$$\cos\theta^*_{cassie} = r_f f \cos\theta_E - (1-f),$$

$$= \underbrace{(r_f \cos\theta_E)}_{}f - (1-f)$$

↳ Effective $\cos\theta^*_{\text{Wenzel state}}$.

$$= f \underline{\cos\theta^*_{WENSEL}} - (1-f)$$

Smaller is f, Higher will be the rise of θ^*_{cassie}.

$r=5$, $\theta_E = 99.6°$. $\Rightarrow$ $\theta^*_{WENSEL} = 146°$.

for $f=0.1$ $\theta^*_{cassie} = \underline{169°}$.

So, the other way of writing; so, if you look at the equation, let us write the equation again for the cassie state. So, what you actually get, you can look at this term to be the effective contact angle, you obtain from the wenzel's state. So, one can write this equation in a rather neat form, its f cos theta star wenzel minus one minus f. Now, it can be seen very clearly that smaller is the value of f, higher will be the rise of theta star. So, if we are if we now sort of, in order to distinguish the two, we write this as theta star cassie and this to be the theta star wenzel. We can clearly see that the smaller is the value of f higher will be the rise of theta star cassie.

So, now let us look at the previous example with r equal to 5 cos theta or theta E equal to 99.6 degree; we have already obtained that theta star wenzel is equal to around 146 degree. Now, if you see that for f equal to 0.1, we get theta star cassie to be around 169 degrees. You can see for yourself that you vary the value f in the above equation, there will be a gradual reduction in theta star cassie and the values will vary from this range of 169 degree to what is given through the wenzels state thats 146 degree.

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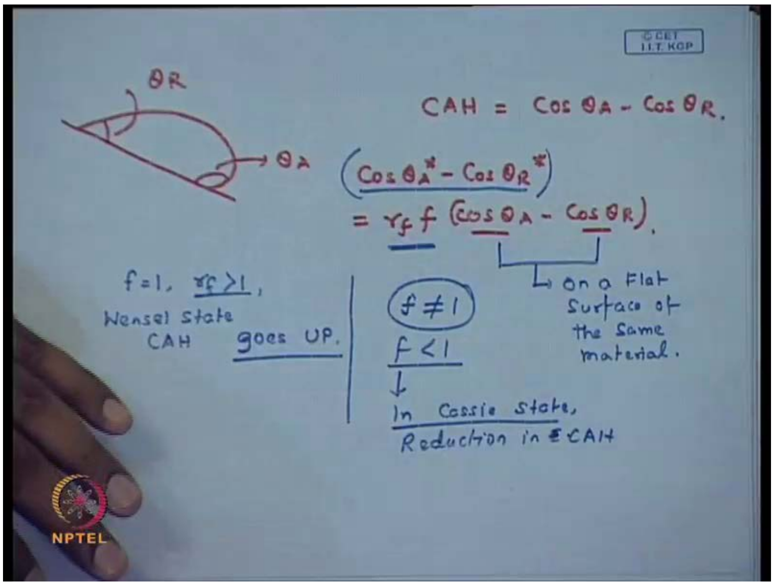

$$CAH = \cos\theta_A - \cos\theta_R.$$

$$\underline{\left(\cos\theta_A^* - \cos\theta_R^*\right)} = \underline{r_f}\, f \left(\underbrace{\underline{\cos}\,\theta_A - \underline{\cos}\,\theta_R}_{\text{on a Flat Surface of the Same material.}}\right).$$

$f = 1$, $\underline{r_f > 1}$,
Wensel State
CAH $\underline{\text{goes UP.}}$

$\boxed{f \neq 1}$
$\underline{f < 1}$
$\downarrow$
In Cassie State,
Reduction in CAH

Now, the other question we had talked about the contact angle hysteresis. So, the other question to ask is, if you are looking now at the contact angle hysteresis on a rough surface does it change? Does it increase or does it reduce? So, the way we have defined we have defined contact angle hysteresis initially to be this is the advancing contact angle, this is the receding contact angle and we have defined CAH to be the difference between. Question to ask is what is going to be the value? In case you have a structured surface. So, if you write it in terms of the wenzel equation, in terms of the cassie equation, because that is the more general equation; because we have seen that by substituting f equal to one in cassie baxter equation, you can get back to the benzel equation. So, let us write in terms of that. So, what you get is. So, this theta A and theta R are the advancing and the receding contact angles, please remember on the on a flat surface of the same material. So, the essentially the hysteresis are the energy required to move the drop whether it goes up or comes down it is to be seen. You can see that if f is equal to 1, r f is always higher than one for a rough surface.

So, in wenzels state actually the difference is higher than this difference; or the contact angle hysteresis goes up irrespective of, so this is interesting. So, in wenzels state we saw that if the liquid is water at least for a hydrophobic surface, you effectively see an enhancement of the equilibrium contact angle. Or for any general liquid, if the equilibrium contact angle of that liquid on a flat surface is higher than 90 degree; then on a structured surface, even if you have a wenzel regime, the equilibrium contact angle goes up. In contrast in wenzel regime, if the equilibrium contact angle is lower than 90 degree, then it actually favors spreading.

Now here, irrespective of whether your initial equilibrium contact angle was higher or lower than 90 degree, what we see that in wenzel regime, your contact angle hysteresis goes up goes up always. Now, if you remember in one of our a early lecture, we had defined a super hydrophobic surface not only a surface which sort of exhibits a very high equilibrium contact angle, but where the equilibrium the contact angle hysteresis is also very low. So, if you are sort of relying on your wenzel sort of wetting to create a hydrophobic super hydrophobic surface, this is going to be an inherent problem. It is very very difficult, even if you achieve a higher degree or higher effective contact angle by wenzel regime of wetting, your contact angle hysteresis will actually go up. Now, you can see from the equation that f can, if f is not equal to 1 and f is less than 1, then it becomes possible to obtain or achieve values of the left hand side or this term can be lower than this. So in other words, in cassie state by a suitable design by design what you were actually teller is you vary the value of f as well in addition to r, you can achieve a reduction in the contact angle hysteresis.

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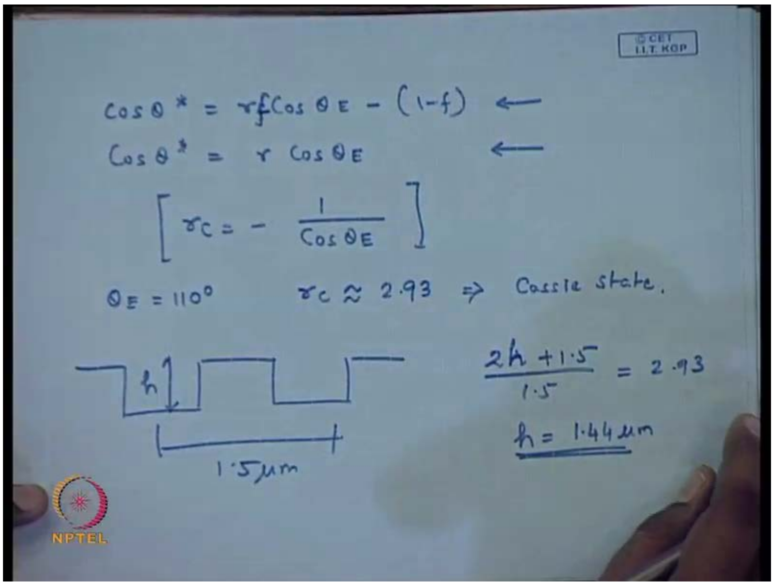

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$\cos\theta^* = r f \cos\theta_E - (1-f) \leftarrow$

$\cos\theta^* = r \cos\theta_E \leftarrow$

$\left[r_c = -\frac{1}{\cos\theta_E} \right]$

$\theta_E = 110^\circ \qquad r_c \approx 2.93 \Rightarrow$ Cassie state.

$\frac{2h + 1.5}{1.5} = 2.93$

$\underline{h = 1.44\,\mu m}$

Now, one can also look at for a specific surface or for a specific material, what can be the critical roughness above which or at which you can see a cassie to wenzel transition; or in other words, if you have if your material is sort of prefix, what is the minimum roughness you require in order to positively have a cassie state from an wenzel state. Well, this can be found out by sort of looking at the equations and. So, this is the equation for the cassie state; this is the equation for the wenzel state, for all practical purpose I have instead of r f I have written r. So, if you are looking at the transition between the two states what you can actually do? You can equate these two. And you can find out accordingly the critical roughness that is necessary or above which you can guarantee a wenzel a cassie state of wetting can be can come out from can be given by this relation. So, suppose if you have a material, let us say about (( )) theta E is 110 degree, you can see that your minimum r c required is close to 2.93 to positively have cassie state of wetting. So, the one can look into it from another angle. Suppose you have a grating, whose periodicity let us say it is 1.5 micron; so, one can design the structure geometry of the strictures like this, suppose you have height of the structure to be h. So, what you for this material which exhibits a water contact angle and it will be a equilibrium contact angle of 110 degree.

So, what you can write is that 2 plus 2 h plus 1.5 divide by 1.5 is 2.93 and you can solve for h to be equal to roughly 1.44. So, if you have a grating structure of this particular material which and you want to have a structure a periodicity of 1.5 micron, then the minimum feature height should be 1.44 micro meter, in order to achieve a cassie state of wetting.

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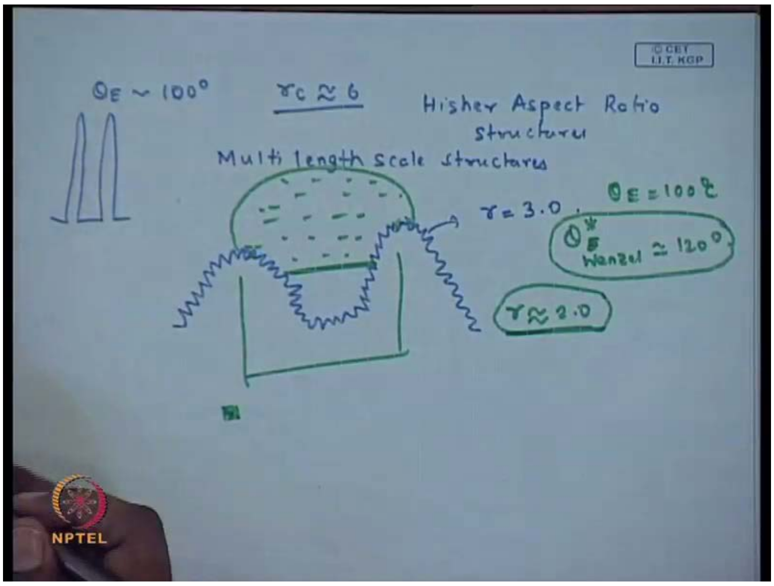

So, this actually leads to the concept that in many cases, if and here the contact angle was 110; so, if you have a lower contact angle, let us say theta E is roughly equal to 100 degree, you can see that r c is close to 6; which means that this requires the fabrication of rather tall structures or higher aspect ratio structures. Now so, it is going to be something like this. Now, these type of tall structure or higher aspect ratio structures are mechanically weak; exactly like anything that is very, very narrow and tall, they are prone to abrasive damage, and they are rather fragile. So, the latest trend is not to go in for a very tall structure, which are again from the paradigm of fabrication, which we will see in one of our subsequent lectures is difficult to fabricate. So, the present trend is to go in for multi length scale structures. So, let us quickly talk of a structure like this, where the nano patterns over here has an r of 3.0, and you have a cassie wetting, a wenzel wetting here. So, that will give you if so, you are equilibrium contact angle is roughly 100 degree. So, this will give a local wenzel angle of roughly 120 degree.

And now, if you have for this micro structure this the larger protrusions or the periodic structures of r is roughly equal to 2, you can sort of, here you have a cassie state of wetting, you can easily have a cassie state of wetting now with the effective contact angle of 120 degree, and in order to achieve cassie state all you need is r equal to 2. So, which sort of makes the structures much, much shorter, as compared to some structures had in wanted to go in for structures with single length scale. So, this is multi length scale or hierarchical structures, and again we will see in some of our subsequent lectures, how this type of structures can be made.