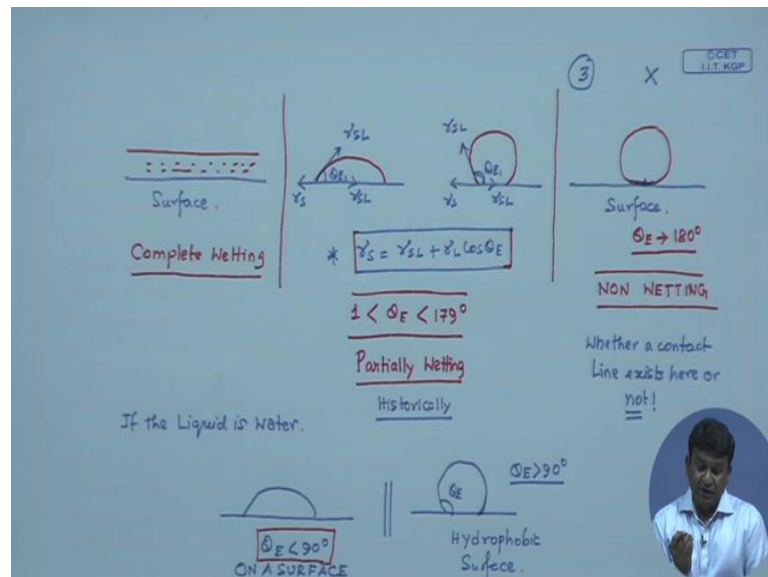


**Soft Nano Technology**  
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**Lecture - 05**  
**Fundamental Concepts**  
**Related to Surface Tension- 02**

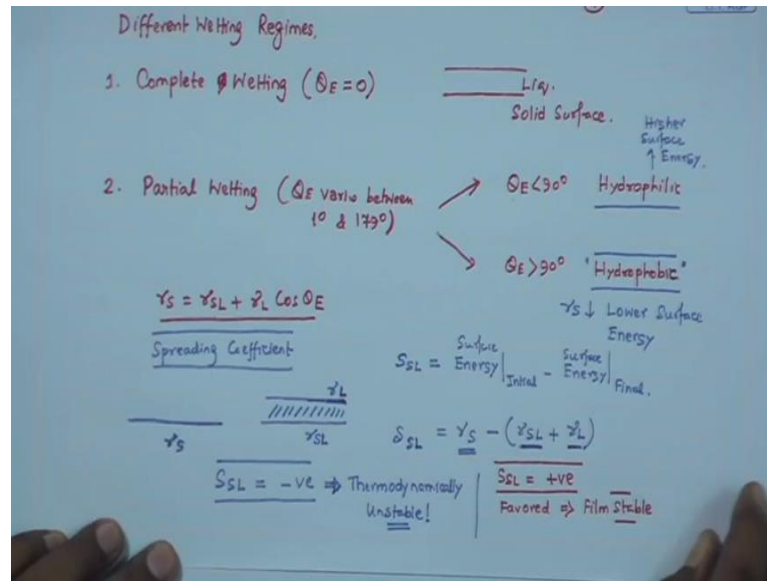
We have been discussing about some of the basic concepts are related to surface tension and surface energy.

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And we have just realized that several things. Firstly, we have learned the Young's equation, which is valid when you dispense a drop of liquid on a solid surface and it makes a finite equilibrium contact angle. We also realized how to discriminate between the different wetting regimes on a flat surface.

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And they are complete wetting and I am deliberately going a bit slowly because this is a new course of many of you. Where, theta E is essentially 0, you actually get a film, liquid film fully covering the solid surface and the second possible regime is the partial wetting where, theoretically or in principle theta E varies between. Experimentally people have shown values close to 165 degree with water and here if the liquid is water, depending on whether theta E is less than 90 degree or theta E is more than 90 degree, you term a surface to be hydrophilic or hydrophobic.

From the Young's equation, by doing a simple balance you can. In fact, convince yourself that hydrophobic surfaces or surfaces on which equilibrium contact angle is higher actually has lower values of gamma s, lower surface energy and on the other hand surfaces on which water or any liquid spreads as higher surface energy. As I have already told, water has a pretty high surface energy; that is 72.8 milli joules per meter square. So, there are it is possible to make various surfaces particularly surfaces coated with Teflon, which is known to be one of the lowest surface energy material, on which waters exhibits significantly high contact angle. But an interesting thing is that most of the organic liquid. So, solencies like alkenes they have very low surface energy. Their surface energy itself is in the range of 25 to 30 milli joule per meter square and.

Therefore, they tend to spread almost over anything, any surface. So, for example, one perennial problem of this particular phenomena, you have use that all your the touch

screen devices like your smart phone or whatever. You will invariably see that after using it for few days you have marks of finger print on them. What happens is that, finger print actually contains oleic acid; oleic acid is a pretty low surface energy material and therefore, it spreads on almost any surface and dislodging it, is rather difficult.

Anyway, we will look in to certain additional aspects, but before you move on. So, one of the things is, as we have discussed in the introductory classes; that hydrophobic surfaces are pretty important or artificially creating hydrophobic surfaces actually makes lot of sense because you might want to have self cleaning surfaces or you would like to. Let us say because of rain, water drop accumulates on a surface and you definitely like to remove the water. So, that the surface becomes dry and fresh and all that essentially requires that water should not spread on this surface.

1 of the essential or necessary conditions of this so called self cleaning surface is to have a hydrophobic surface. Before we move on to which the concept of hydrophobicity further I would also like to introduce the concept of, what is known as spreading coefficient. It is a very simple concept, but a very powerful concept considering a very basic concept or fundamental concept of thermodynamics. That any process any natural process leads to minimization of free energy. So, what is spreading coefficient? You just remember, you do not have to sort of remember anything by heart. It is represented as SSL; that is a solid liquid spreading coefficient. All you need to remember is, this particular picture.

Suppose you had a solid surface which had a surface energy  $\gamma_s$  and then you take a liquid or put a liquid on it. In a manner as if the liquid forms a film. Do not worry about what is the equilibrium contact angle, when you are talking about the spreading coefficient or defining the spreading coefficient of course, all the considerations are valid.

If the liquid spreads fully on the solid surface what are? So, this is going to be the configuration. So, you just need to subtract the energy per unit area. The initial configuration minus the let me put it a surface energy, total surface energy or the total energy ascribed at the surface in the final configuration and that gives you this expression. Just remember this picture and the expression automatically forms. What is the utility?

Suppose you have SSL to be negative. What does it mean? It means that after creating the film, it numerically means that the summation of this term and this term exceeds this.

What does it mean? That after creating the film their art techniques, trust me will learn and one of the spin coating, let me also tell where it is possible? In fact, to overcome the equilibrium contact angle by applying excess amount of external force and can force a liquid to spread on a non wettable surface it is there. So, irrespective of whatever is the value of your theta E, you can theoretically or in even in experiments, in practically also you can get to this configuration, but even if you create film like that what a negative value of spreading coefficient gives, is that by creating this film you have. In fact, increase the total amount of energy ascribe at the surface and.

Therefore it is very lightly that you have gone in the opposite direction of a natural process and you have created a film that is thermodynamically, on stable. You can still to do menu worse and maintain the stability of the film over a period of time. So, you can do some kinetic stabilization or you can do so some other clever things to make a film stable, but the thermo dynamically this type of a film on stable. In contrast, if you now have a situation where you are SSL is positive. What does it mean? It means that by creating the film you have. In fact, reduce the total energy that is ascribe at the interface and therefore, it is thermo dynamically favored and the film is going to be unconditionally stable.

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Silicon Wafer      Silicon  $\rightarrow \gamma_S \approx 428 \text{ mJ/m}^2$       5      SCEY I.I.T. KGP

$\gamma_S$        $\Rightarrow$        $\overline{\text{SiO}_2 \text{ Layer}}$        $\gamma_S \approx 55-60 \text{ mJ/m}^2$   
 $S_{SL} = +ve$        $\approx 1.5-1.8 \text{ nm}$       < Native Oxide Layer >

Hydrophobicity  $\rightarrow$  Taking a clue from the Natural World  $\Rightarrow$  Lotus Leaf.

$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta_E$       Possible means of increasing  $\theta_E$  is  
 Reduce  $\gamma_S$ .

$\theta_E \approx 120^\circ$  | Not more than that!  
 $\gamma_{Teflon} \approx 10 \text{ mJ/m}^2$

I do not know how many of you have seen a silicon wafer, that something that the heart of microelectronics and the photolithography we talked about, the photolithography patterning will be perform non silicon wafer we will discuss. Silicon as a material has very high surface energy. Its gamma S is if the order of 428 milli joule per meters square. This is extremely high surface energy.

See when you are talking about spreading coefficient, surface energy is very high. So, what happens is the moment you bring out silicon to atmosphere, it actually under goes some surface oxidation. The oxygen present in air immediately attacks this, their silicon and forms a very thin oxide layer, which has a thickness and it can be measured of order of 1.5 to 1.8 nanometers. This is called often called the Native Oxide Layer and what is the consequence? Why does this layer form? In fact, if you now take a silicon wafer from your laboratory and try to measure it is surface energy, you will always get gamma S is of the order of 55 to 60 mili joule meter per square.

There we go by way of forming this oxide layer, there is a significant reduction in the total surface energy or the spreading coefficient into this particular case of this oxide layer is very very high and trust me, removing this particular layer from silicon, which is necessary for doping is very very difficult.

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**Surface Structure and Wettability**

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  $> 90^\circ$*

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This is the concept of spreading coefficient; now what we would be interested to look in to certain aspects of Hydrophobicity in somewhat detail. Primarily, for various types of

engineering applications and taking a clue from the natural world particularly a lotus leaf.

From the Young's equation, we already know that one of that ways, increasing theta E is reduce gamma S. However, please be informed that Teflon, Chlorophyll, Chlorocarbon that is sort of the lowest surface energy that is available till day and its surface energy is of the order of 10 milli joule per meter square. So, it turns out of the order of 10 milli joule per meter square. It turns out that if you plug in a value of 10, you cannot really go often two values more than, let us say of theta E, is somewhat in the order of 120 degree not more than that.

What does one do? One takes the clue as I already told. Let us say from the lotus leaf where, you can just search the micro structure of lotus leaf in Google and you can see that there are some micron scale structure, unfortunately I do not have an image. Next lecture or some lectures I will show it definitely, present on the lotus leaf and it turns out that it is also covered with a wax like material. It is obvious that this wax like material is responsible for the low energy part of the surface energy low energy coating, but there are these additional presences of this structures, which also contribute to the effective hydrophobocity and let us find out how the presence of the structure can effect.

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The image shows handwritten notes on a blue background, divided into two columns. The left column discusses the Wenzel state of wetting, and the right column discusses the Cassie state of wetting. Both columns include diagrams of a droplet on a textured surface and a flat surface, along with mathematical equations for contact angle and surface energy.

**Wenzel State of Wetting**

Question 1: Does  $\theta_E$  remain the same?

Question 2: What is the Configuration of the Drop?

$\theta_E^* \neq \theta_E$

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

Where  $r$  = Roughness of the Surface.

$\theta_E < 90^\circ, \theta_E^* < \theta_E$

$\theta_E > 90^\circ, \theta_E^* > \theta_E$

**Cassie State of Wetting**

Air Pockets

Flat Surface

$\theta_E$

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

$r_f$  = Same as  $r$  in Wenzel state (Roughness)

$f$  is the fraction of Solid-Liquid Contact Area under the drop.

$1-f \rightarrow$  Liquid-Air Contact

What can happen if you actually have a structure surface? So, what we are considering is, we have a structure surface or a pattern surface and I just draw it here again explain to

you, what can happen. Roughly same pattern, different pattern whatever if you now put so, compare this we are comparing this with the situation of putting a drop of liquid on a solid surface. Now what we have taken is structured surfaces of the same material. So, these are essentially structured surfaces of the same material over which a liquid, let us say water was exhibiting an equilibrium contact angle of  $\theta_E$ .

Now, the question to ask is, if you sort of dispense a drop of liquid on these structured surfaces. Question number 1; does  $\theta_E$  remain the same and question number 2; bit non obvious what is the configuration of the liquid? This is a very obvious question, but may be to some of you the question number 2 itself is little hazier at this point of time let us see what I mean. Suppose you put a drop and it is only obvious, that this drop will flood the areas between the patterns right and that is exactly what is shown here and. In fact, you can still identify some sort of an equilibrium contact angle, equivalence which is not equal to  $\theta_E$  for sure and there are certain expressions which we can calculate we will do that, but let us look in to the other possibility before we right down the expression.

The other possibility is more exciting, but it happens and the possibility is under appropriate condition and you will have some idea about what this so called appropriate condition is? The liquid fails to penetrate into the gap within the patterns or in other words there are. So, these are the structures and what you have here? You actually have air pockets. Again here you can have a equivalent equilibrium contact angle, but well these two, in the two cases are not same. This is something new that you all probably learning, some of you are learning. This is what is known as Wenzel state of wetting. This is what is known as Cassie or Cassie Baxter State of wetting. This and this are rather similar in the sense that in both the cases, the contact angle is the area under the liquid drop is fully a liquid solid contact area. In this case it was flat.

However in this particular case it is not flat it is structured, but the liquid conformably add here to the surface structure. In contrast here something more exciting takes place here. The contact area is no longer the solid liquid contact area only, but it is sort of a composite solid liquid air contact area. So, what is the utility of where exactly it will show up? The most logical thing is, to assume at this stage is dislodging a liquid on a surface like this is probably going to be easier. This is intuitively what you can say. We will see that, but before that let us take a look what are the values of  $\theta_{star E}$  we get

and here it is given as this equivalent equilibrium contact angle on a structure surface for a Wenzel state is given as this where,  $r$  is the roughness of the surface.

This is interesting because apparently we started this discussion with the basic understanding that you make a surface patterned or structured and immediately your contact angle will increase or the level of Hydrophobicity will increase, but if you see here if your initial  $\theta_E$  is less than 90 degree. In fact, what turns out is  $\theta_{E^*}$  is lower than  $\theta_E$ . That is very interesting. If you now have an hydrophilic material structure it and the wetting regime is Wenzel you. In fact, end up reducing or you end up spreading the liquid more on that surface.

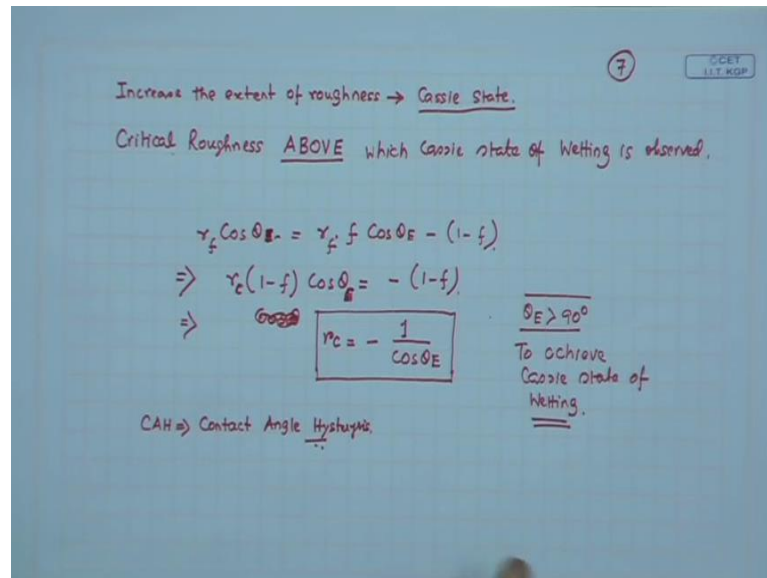
Therefore it is very important that you know, the initial equilibrium contact angle only then patterning the surface might help you, in increasing the effective or equivalent contact angle; obviously, you can also see if  $\theta_E$  is greater than 90 degree,  $\theta_{E^*}$  is going to be  $\theta_E$ . Why and how it happens? You just take a value of  $r$  that is greater than 1 of course, rough surface will have a roughness value greater than 1, you simply plug in some number. So, you multiplied this with the factor that is greater than 1.

If the value is positive, if you are in the first quadrant and therefore, your  $\theta_E$  reduces,  $\theta_{E^*}$  reduces the  $\theta_E$  if you are; however, in the second quadrant you get a negative value and therefore,  $\theta$  is increases are compare to  $\theta_E$ . A bit more complicated relation is given for or one can also write  $\theta_{E^*}$ . You can write this as  $\theta_{E^*}$ , that is the more common notation. What is given as, is another new factor if comes in I will explain it in minute,  $r_f$  is the same roughness and  $f$  is the ratio or is the fraction. In fact, fraction of solid liquid contact area under the drop, so  $1 - f$  in fact, refers to the liquid air contact area.

There areas in the picture contribute to  $f$  and these areas contribute to  $1 - f$ . Now how can one do that? In fact, I can show that or I will show it, that if you increase the value of roughness it is possible to go, to have a transition from Wenzel state to Cassie state. What are the advantages I am coming into it, but when does a transition.



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Statement I make is; increase the extent of roughness. There is a possibility of heading towards the Cassie state and is there critical roughness? Yes, there is. Simply plug in the 2, equate these two equations. So, you have a critical roughness theta star or theta C where, the equilibrium angle the effective contact angles from the two relations is going to be same.

Simply put  $r \cos \theta_E$  is going to be  $r$  because  $r f$  and  $r r$  same into  $f \cos \theta_E$  minus  $1$  minus  $f$ . So, if you do a transposition, what you get? And or let me right  $r f$  in both the cases and what are we looking at? We are looking at a sorry this remains  $\theta_E$ . So, what you get? We are essentially looking at  $r C$ , a critical roughness. So, what you get, is  $\cos \theta_E$ . Please understand the roughness is not negative. You need to have  $\theta_E$  has to be greater than  $90$  degree to achieve Cassie state of wetting. What is the advantage? It is obvious that, if you now tilt the surface, the additions since there are air pockets is going to be less and therefore, the drop is going to get dislodged easily if the wetting step is Cassie and that is one of the requirements of a super hydrophobic surface or whatever.

In the next lecture I will spent some time on defining what is super hydrophobic surface and it is not only the equilibrium contact angle that determines, whether a surface is super hydrophobic or not, but there is another parameter which is known as the contact

angle hysteresis CAH, which is also an important parameter that determines, whether a surface is super hydrophobic or not and we will start our discussion from this point.

Thank you.