Nanostructures and Nanomaterials: Characterization and Properties
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Lecture - 33
Non-Wetting

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In this lecture, we learn about non wetting. What is the importance of non wetting? So, to come to that part, we need to see how wetting can deteriorate the properties of a material. So, in case we see like if you are driving a vehicle, and suddenly it starts pouring heavily then, basically it is very difficult to see what is happening outside, or let us take an example of any materials, so any metallic material.

It is lying on a particular ground exposed to environment and if it starts raining and rain is basically wetting the material of it basically goes on chemically combining with the material and deteriorating material. So, that is the reason we see that the importance of non wetting and such engineering applications, so non wetting is also one the very becomes a very important criteria in engineering it.

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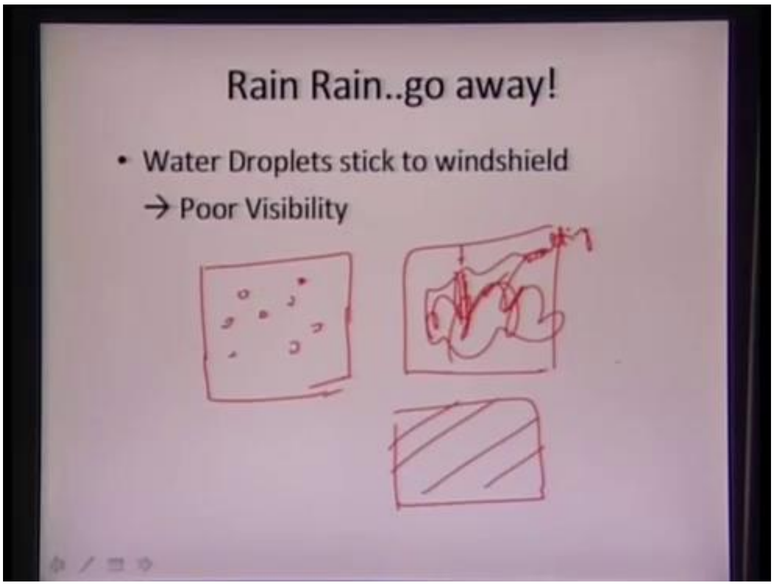

So, let us come back to the first example rain rain go away. So, if you are driving a vehicle and we see that the rain starts drizzling on to the windshield, we see that the droplets of rain they remain on the windshield, unless you start your wipers. But again once you even once you starting with the wipers, and even when the droplets they trickle down, they leave a mark, a mark of what is the edges of the water. This means, that there is some sort of a wetting occurring with the surface of a material, and that leads to the poor visibility and at some times it becomes so difficult that we cannot even see.

So, overall it becomes so shady, we can also see some fogging which can occur on the windshield, and overall it is basically hindering our visibility while we are driving. And, because of that, if we are not able to drive properly, it might lead to even accident. And extended to that like we even certain sometimes we get fogging on the glasses, and we sometimes get corrosion on some metallic interphases, we might get some sticky chemicals on a particular surface and that leads to again much more wetting. So, there are certain things which can basically deteriorate the overall engineering application of a material.

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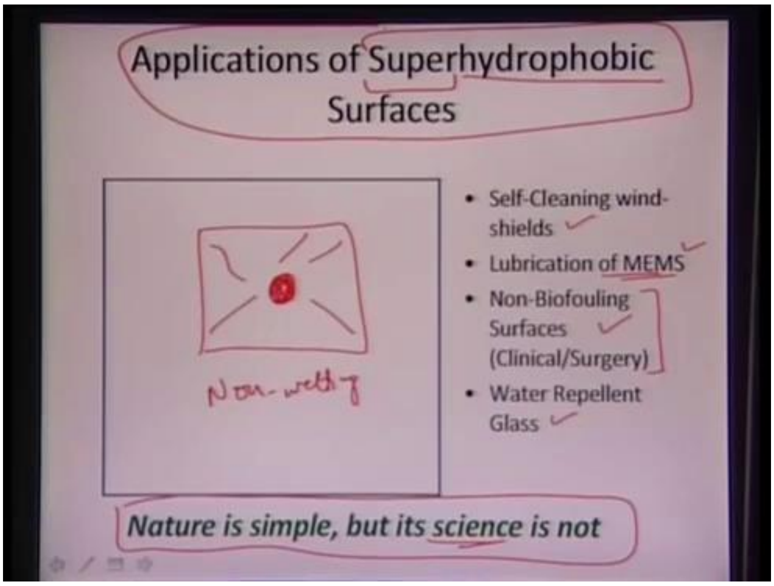

So, we want to go for engineering that what is non wetting. So, coming to the something called hydrophobic surfaces, but here I have mentioned super hydrophobic surfaces. So, basically we have seen that in lotus leaf, if we have a lotus leaf, water will basically come trickling not to every location and it will form a droplet. And this droplet will be totally spherical, and it will not be wetting at all. So, we get a non wetting surface, and that is, that can be basically utilized for say self cleaning windshields, or providing lubrication of micro-electronic mechanical systems. And since, we have water it is, it becomes very friendly surface for contaminants or falling agents.

So, once we have a super hydrophobic, it means it is not reacting with any water to get it, let it wet it surface. We can develop non bio falling surfaces and also ultimately it can also lead to water repellant glass. So, this idea is basically coming from something called lotus leaf, so we can say nature is simple, but it is science is not, because there is some level of complexity which is associated, which is associated with the such structures they are imparting hydrophobicity or non wetting. So, we do not have hydrophobicity, but we have super hydrophobicity, which is associated with the lotus leaf. So, we can say that the science which is dictating this super hydrophobic nature, it is much more complex than what it appears on surface.

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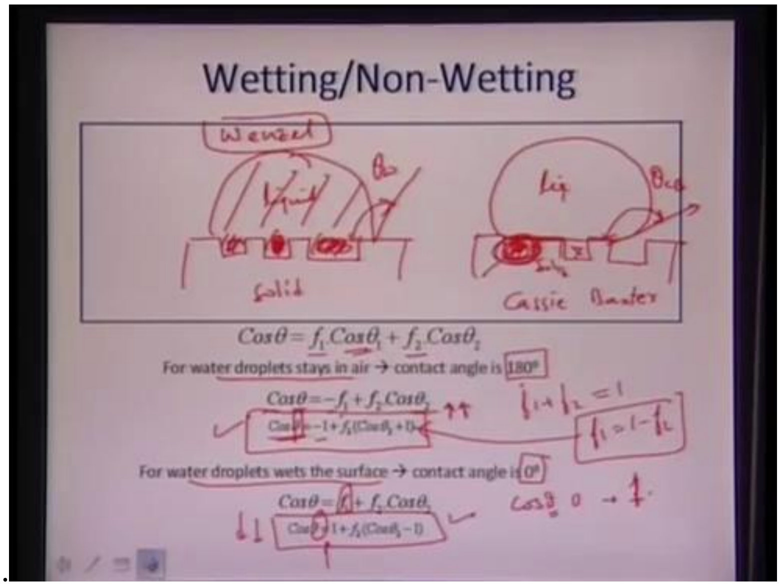

Coming to what is wetting and non wetting, we see if we have a water droplet say, if we have a rough surface, and then, we have certain surface, and we see that a particular droplet once it is sitting on to it, it might assume the shape while filling in those cavities. So, we have a water droplet which is basically, over also taking care of filling the voids or the filling the rough grouse into the material, so we have certain thing like this and that will show certain angle.

So, we have this thing, this particular state, we have liquid, we have solid, and this particular angle is called Wenzel state, this state is called Wenzel, Wenzel state, Wenzel sorry, this is called Wenzel state. And in other case, it might have happened that, a droplet is assuming the similar shape, but in this particular case, it is not filling in those cavities. So, these cavities are not filled, and in this particular case we get certain wetting angle, and this wetting angle is called Cassie Baxter wetting angle, so we have Cassie Baxter.

So, we have two states Cassie Baxter state and Wenzel state. In Wenzel state, we have the droplet also filling in the grouse of the rough surfaces whereas, in Cassie Baxter we had this liquid and we had this solid, but the grouse of the solid they are not being filled by the liquid. So, there is some sort of a non wetting which is occurring already at this particular level, so we have gas entrapped in these two locations. So, considering the overall wetting of this particular droplet, we have fraction which stays in air and we have certain fraction, which is sitting on the surface.

So, while it is in air, the contact angle is 180 degrees, because there is not at all wetting the surfaces. In this particular case, the liquid is not wetting the surface at all, so we have contact angle of around 180 degree out here. So, once we have Cos theta is equal to 180 we get minus sign. So, minus 1, so minus f 1 plus f 2 Cos theta 2. Also we know that f 1 plus f 2, it is a fraction which is sitting on the air bubble and second fraction which is on the solid region, this is also equal to 1. So, we get f 1 is equal to 1 minus f 2, and we can replace that part out here in this particular equation. So, we get the overall theta value or the overall theta or the wetting angle is minus 1 plus f 2 Cos theta 2 plus 1.

So, this is how we are defining the, when the water droplet is staying in air. And when the water droplet is wetting the surface the contact angle is nothing but 0. So, from that particular part, we can say Cos theta is equal to 1, Cos theta when Cos theta is equal to 0, we get this value as 1, that is what we are able to see here plus f 2 Cos 2 theta 2. So, once the water droplet is wetting it, we are getting certain equation, once it is not wetting the surface we are getting a certain equation. And obviously, in this particular case we will have theta much more as compared to the wetting state, because lower theta means, the surface is getting wet, getting wet to a larger extent.

Because, once we have theta equal to 0 it means, the overall water filled or any liquid film is wetting the surface completely, and when we have theta is equal to 180 degree, it means it is not wetting the surface at all. So, once we had a air bubble, the theta was 180 and in case we have complete wetting, we are seeing theta is equal to 0. So, obviously this theta, which is being defined here, it will lead to, this one can easily define what is overall wetting which is occurring in the occurring on the surface of a material.

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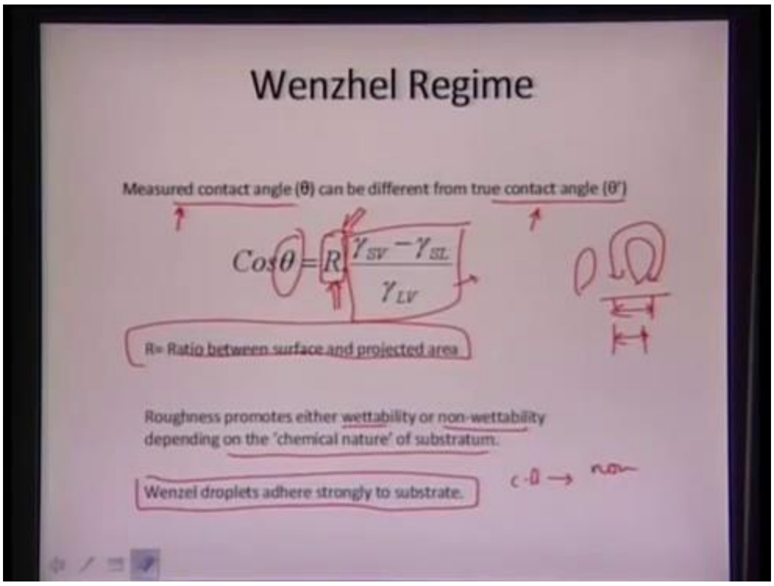

But there is one more aspect to it that the true contact angle. The measure contact angle can be different from the true contact angle, and this measure contact angle is basically given by also a term called roughness, the ratio between the surface and projected area. So, if we have something, some surfaces which has a much more higher surface area, and the projected area is much more like this, we can see that this much area is getting reduced to this much area. So, there is some effect of roughness as well, which is given by this particular term R.

So, if water droplet is interacting with this particular surface, it is interacting with much more surface and the projected area is much lesser. So, we can see, there can be difference between the true contact angle and the measured contact angle and that part is being given by the roughness or the ratio between the surface and the projected area. And this term basically remains the same which defines the overall wetting from the regimes equation. And roughness can promote either wet-ability or non wet-ability, it totally depends on what the original surface is.

The original surface is basically hydrophobic in nature, roughness will induce much more hydrophobicity to it. And if the original surface is hydrophilic in nature it means, it is tending to wet the surface, roughness will have pronounce effect of much more wetting of the surface. So, that is what is defined by the roughness factor, and that basically depends on the chemical nature of the substrate. And we always saw that

Wenzel droplet will adhere stronger to the substrate whereas, Cassie Baxter, it will tend to be non-wetting the surface.

So, we can see those two particular aspects that roughness can have a very drastic effect on what is happening at the surface level, because roughness is a one which will keep effecting the inherent nature of the surface itself. So, non-wetting will be enhanced, if the surface itself was non wetting in nature or if the surface was much more hydrophilic or hydrophobic in nature then, the roughness will lead to super hydrophocity. And again this thing again comes from the lotus leaf, and lotus leaf is a symbol of divine beauty.

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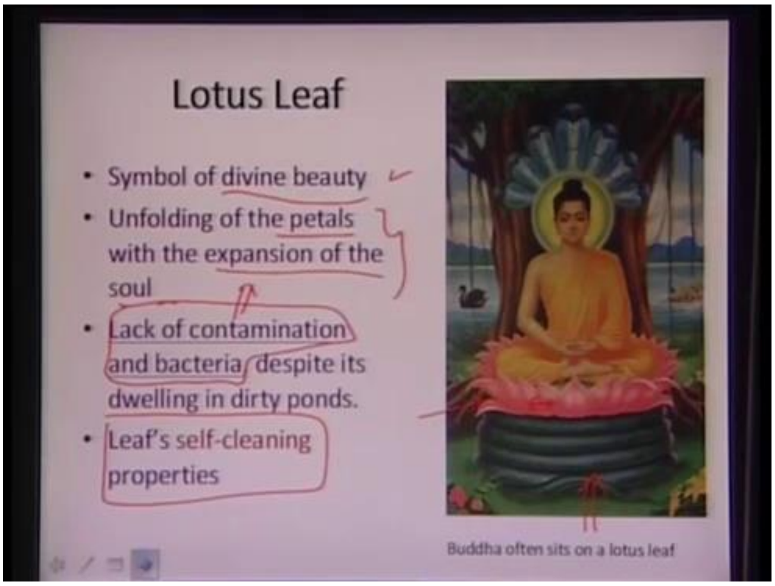

And as we see that, the unfolding of the petals, it basically corresponds to the expansion of soul. So it had much more spiritual meaning as well in the ancient history, that a lotus basically grows in ponds though it is, though it dwells on the dirty pond, it lacks any contamination that is free from bacteria, just, because of its super hydrophobic nature. So, that basically is correlated with the divinity or the divine beauty or the growth, spiritual growth, and it also has self-cleaning properties. So, we have seen Buddha, often sitting on the lotus leaf, this is a lotus leaf and then, it is a lotus around him and that leads to the spiritual growth as well.

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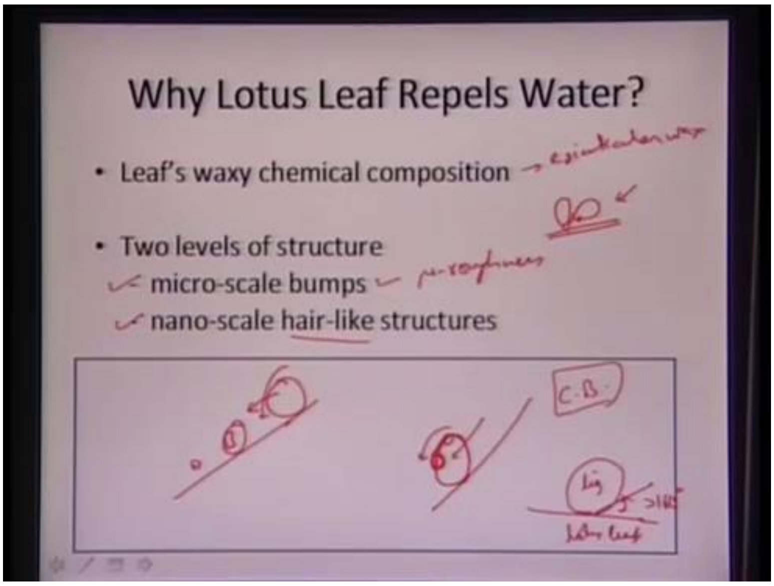

So, that is what out here, and how does this lotus leaf will repel water? First of all, the leaf itself has a some chemical composition which is waxy in nature. So, it is, there is something called epicuticular wax, which is much more waxy in nature and additionally, it is two levels of micro structures. First it is some micro scale bumps, so it is a inducing some sort of micro roughness and as we see as we have seen, that if we have a much more roughness or we have increase in the surface area, the apparent contact angle will be much more higher.

So, the true contact angle may be remain same, the apparent contact angle will be much more high. Additionally, this is the first level of roughness additionally, over those micro protrusions itself, we have something called nano-scale nano hair-like structure. So, we have nano-scale roughness also arising which has a, which is a on addition to that of a micro roughness. So, we have a micro level roughness on the lotus leaf surface over that we have some sort of nano roughness or nano hair-like structure, so we are getting two orders of magnitude two orders two length scales of roughness being induced on the surface of a water.

So, how do, how does this cleaning effect really happen is that, we have say, if we have some impurities on the surface, of a lotus leaf. And if we have a droplet, droplet will be simply roll will keep rolling on the surface of the lotus leaf and eventually it will also capture, sorry it will also capture those particles along with it is surface while rolling. So, it is rolling once it is encountering this particular impurity, it will just tag it along with itself while rolling.

So, we have this water droplet kept which keeps rolling and it overall it keeps taking the impurity along with it. And in this particular case we have Cassie Baxter striate, because the water droplet we can see how easily it can roll on the surface of lotus leaf. So, because of that we can see that there is much very less friction of a water droplet to roll on the lotus leaf surface even an angle of 1, 2, 3 degrees is enough for the water droplet to roll without wetting the surface. And in this process it also carries along the impurities which are existing on the surface of the lotus leaf. So, it is showing a very huge contact angle this is order of more than 160 degrees with the lotus leaf. So, this is the liquid, and this is the lotus leaf, and we see contact angle in excess of 160 degrees with the, which form which are formed with the lotus leaf.

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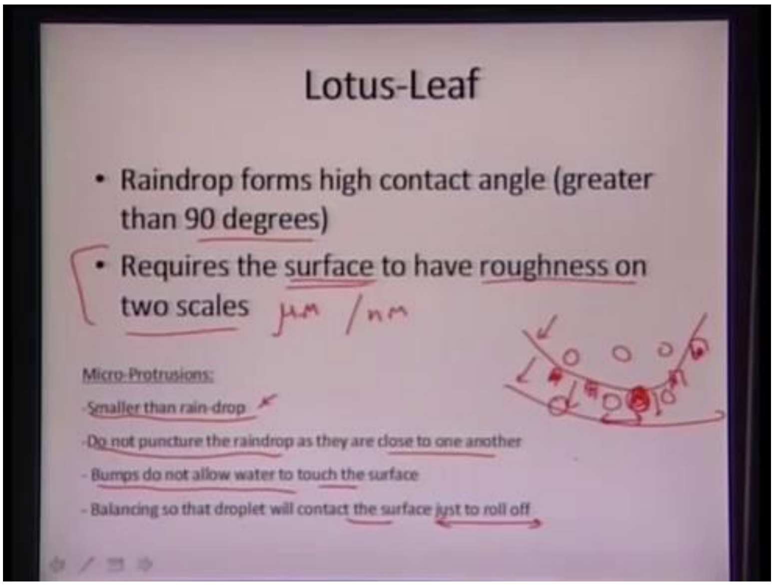

And again the raindrops also form very high contact angle which are which is much greater than 90 degrees and this also requires that the surface of the substrate should have roughness on two length scales. As we saw that lotus leaf has roughness of the order of micro meter, and again some roughness on the nano meter scale as well. And we see that there are some micro protrusions which are dominated on the surface of the lotus leaf and they are much smaller than the rain droplets.

So, they also have to be soft enough that they do not puncture the rain drop, and also they have to be close enough so that they can really let the water droplet sit on it. So, we have certain micro protrusions which are scattered throughout on the surface and once water droplet is sitting, it will get support from many of such micro protrusions. So, this is the water droplet, this is there are certain supports which are spread 5 to 10 micron apart with a diameter of 5 to 10 micron itself and these bumps do not allow water droplet to touch the surface the surface of lotus leaf remains untouched by the water droplet.

And now, this micro protrusions have to be spaced in spaced properly also they have to be balanced properly so that water will contact the surface and will just roll off without wetting the surface. so we can see that the Cassie Baxter state is much more predominant here. We need to induce the Cassie Baxter state, because of the roughness parameter out here that we do not allow the lotus leaf does not allow the water droplet to touch the surface of lotus leaf, and the micro protrusions help to just balance the water droplet and it allows to roll it off very easily.

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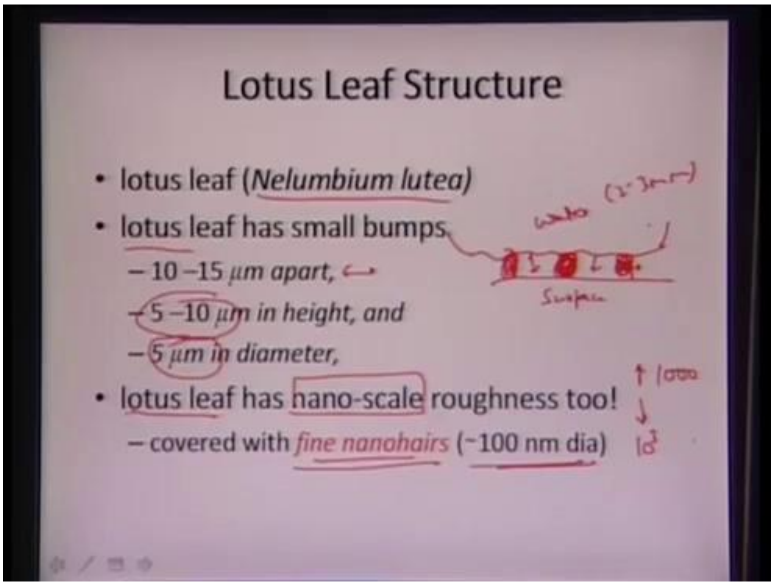

And lotus leaf is also, lotus leaf is also called, lotus is also called Nelumbium lutea and lotus leaf has small bumps, which are around 5 microns in diameter around 5 to 10 micron meters in height and just split it approximately 5 to 10 micro meters apart. So, since they are apart they can easily let the water droplet sit on to it and at the same time not allowing it to puncture or buckle enough that touches the surface. So, with this is surface of lotus leaf and these are the micro bumps out here, and this is the water droplet. Since, these micro protrusions are 5 to 10 micron meters will have a water droplet, which is of the order of 2 to 3 millimeter in diameter.

So, we can see there are many number of micro protrusions which will allow the water droplet to sit on to them, and again over the micro protrusions we also see that lotus leaf has some nano scale roughness, which is basically covered with some very fine nano hair which are around 100 nano meters in diameter. So, we have so it is also observed that micro roughness can induce surface area increase by order of 10000 times. And similarly, going from micro to nano we can again see a factor of 10 to the power 3 increase in the surface area. So, that is being generated, because of the two levels of micro roughnesses micro and then nano roughnesses, which are predominant in the lotus leaf structure.

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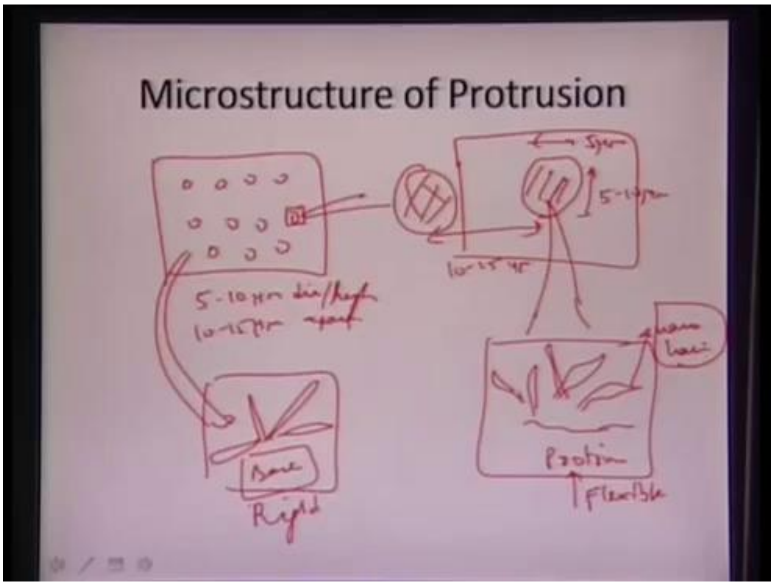

And same coming to the micro structure of the protrusion, we see we have a lotus leaf surface and we start seeing certain micro protrusions on here. And this micro protrusion of 5 to 10 micro meters in diameter has so much their height and they spread about 10 to 15 micro meters apart. And again if we enlarge this particular thing, we will see those particular structures it appears more like a globule which is which will have a diameter of around say 5 to 10 around 5 micro meters height of around say 5 to 10 microns, and it will be spreaded approximately 10 to 15 micro meters from a nearby micro protrusion.

And if we again zoom this particular part, this particular micro protrusion part we will see that all these micro protrusions will have very fine nano hairs, just spreaded throughout the surface of the material of the protrusion. As well we see that the base the base part of it, the base of the lotus leaf also has some nano hairs on to the base hairs as well. So, in the base as well as in the protrusion we see some nano hairs, but there is one catch to it that the overall nature of these hairs at protrusions, micro protrusions and at the base they are little different in nature and so how they are different? We will see them as we go along, but there is a little bit difference in the protrusion and the base hairs.

Base hair tend to be much more they tend to be more rigid as compared to the protrusion hairs much more they are much more flexible also, because they are sitting the protrusion hairs are sitting on a particular micro protrusion. So, what is happening we are seeing dual level of flexibility, because nano on the protrusion hair they much more finer, they are much longer, so their diameter is much finer, the lengths are little longer, so they easily undergo buckling. And over that they are sitting on the micro protrusions whereas, base hairs they are much more they are thicker in diameter and little shorter in the length. So, they are much more rigid as compared to the protrusion hairs and the same time there is no second level of protrusion on which they are sitting, so they tend to be much more rigid than the protrusion hairs.

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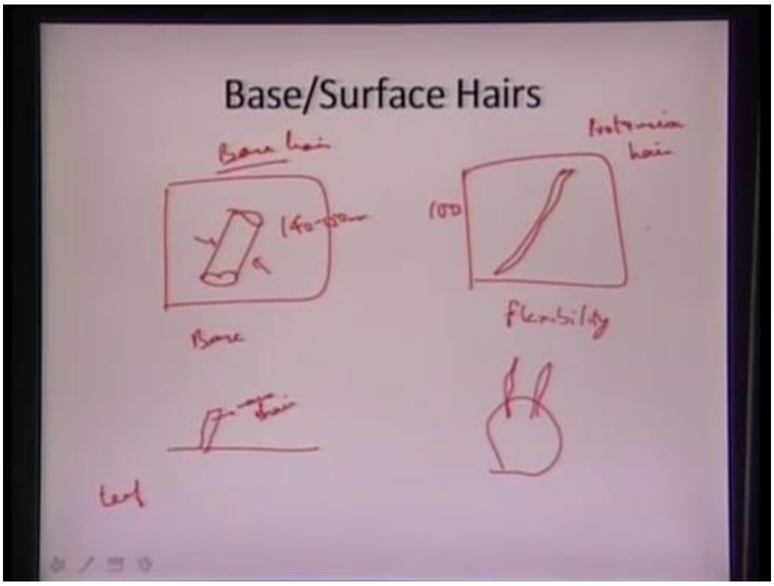

So, we can see that the base hairs they tend to be much more much more thicker and much more shorter whereas, surface hair they tend to be much more longer and much more thinner. So, that is what is basically providing much more flexibility to the surface hairs which are sitting on the protrusions whereas, base hairs they are they tend to be much more thicker.

There might be a minor difference in their diameter if this is around 100 nano meter this can go up to around 140, 150 nano meter and so on, but again there is some difference, because again there is dual level of flexibility which arises from the that we have micro protrusions over that there is some nano hairs and in this case we have a flat leaf surface and over that we have a nano hair.

So that basically brings out the difference in terms of the morphology of nano hairs which are sitting at the protrusions. They are little different than the hairs which are present on the base. So, we have base hairs and then we have hairs which are sitting on the protrusions, so this is how they are little different than morphology.

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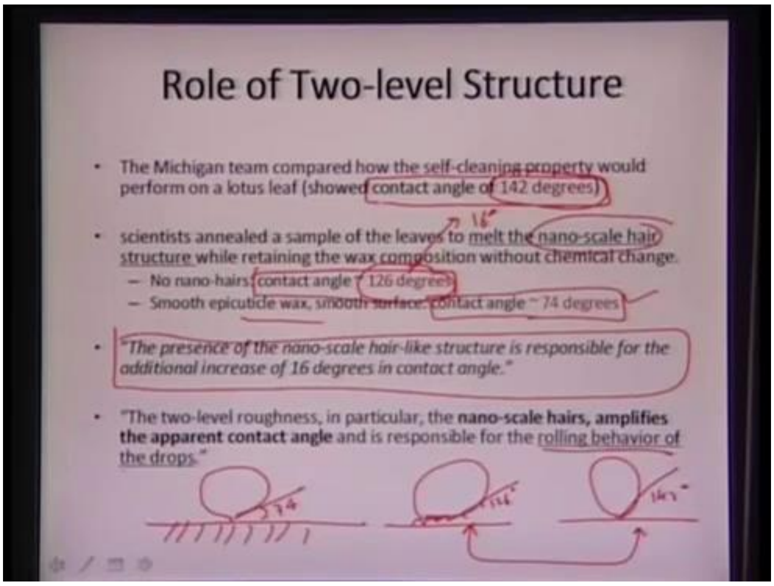

And again to differentiate what is happening, because of the two level of the roughness, Michigan team they had found out that the self-cleaning property that is being performed on the lotus leaf while removing the nano hairs. So, what they have done they have taken the same lotus leaf surface and then from that they have removed the nano hairs.

So, we have lotus leaf surface by some surface treatment they removed the nano hairs and they are just remaining with the micro roughness on to the particular lotus leaf surface. And in third case they have taken out the both levels of roughnesses, so they are keeping the same material, but now nano hairs and micro protrusions they both are gone from the surface. And from that they have realized that if we if they just have the epicuticular wax on the surface, the contact angle is to the order of 74 degrees only. Whereas, if they go only for the nano hairs only for the micro protrusions which are sitting on the surface, the contact angle is of the order of 126 degrees, and with the nano hairs the contact angle has increased to 142 degrees.

So we had one process one surface with epicuticular wax as the similar chemistry of that of a lotus leaf, they are seeing as a certain contact angle of around 74. Once we have certain micro protrusion on the surface, the contact angle basically increases to the contact angle basically increases to 126 degrees. And once they also have some nano hairs on to it the contact angle has gone to 142 degrees.

So, it just means that the nano hairs are responsible for the additional 16 degrees of wetting that the surface is imparting. So, we have this epicuticular wax it is imparting 74 degrees and once the nano scale hair they are being melted away and while returning the wax composition and without any chemical change while returning the micron roughness, we are getting a contact angle of 126 degrees and the initial contact angle of the lotus leaf was around 142 degrees.

So, that tells the overall role of dual level micro structure in terms of imparting hydrophobicity to the lotus leaf. And again as I stated earlier that the additional 16 degrees is coming out totally from the nano hairs which is predominant on the lotus leaf surface. And again this is itself is responsible for the rolling behavior of the drops, because now the water droplet is undergoing Cassie Baxter state. And now, it becomes very easy for the droplet to de-stick itself from the surface, because there are all the cavities which are to the order of nano or micro roughness what is not getting entrapped in those particular cavities.

So, it is very easy for the water droplet to roll rather than de-stick itself, so rolling becomes much more easier, because the lotus leaf is predominant in predominant as a

Cassie Baxter state so the wetting is mostly the in the Cassie Baxter state and rolling becomes much more easier, because of the dual level micro structure.

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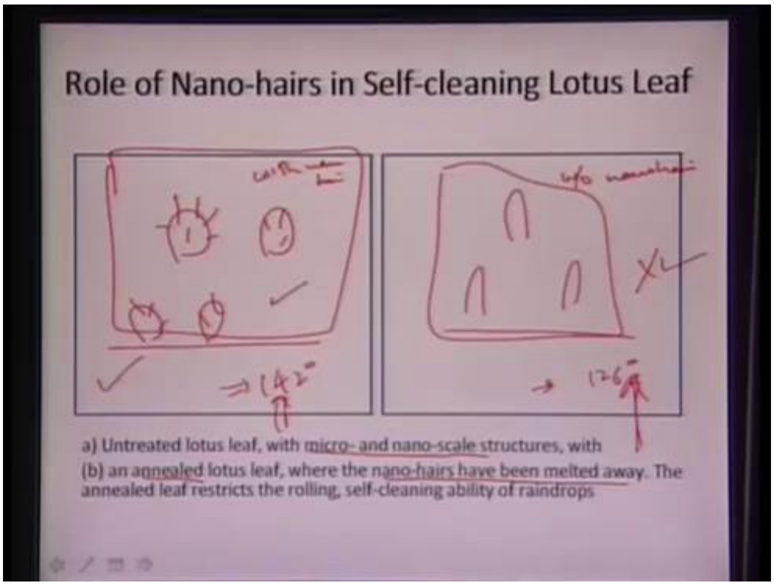

So, this particular part was more like this, that in once case they had all the micro protrusions with nano hairs intact on them. So, that was the surface which was appearing in one, and in second case they had all the micro protrusions, but without any nano hairs. And this one is with nano hairs, so in this particular case they saw a contact angle of 142 degrees and in this case they saw a contact angle of 126 degrees. So, that is how the surface chemistry or the surface morphology of, because of nano hair can alter the overall contact angle of the lotus leaf.

So, untreated lotus leaf with while retaining the micro nano structure it is showing 142 degrees whereas, if the lotus leaf is being annealed, so that nano hairs are being melted away we are seeing the contact angle of around 126 degrees. So, that is basically essentially telling us that the rolling tendency of the water droplet is it gets damaged in this particular case while it is being retained in this particular case.

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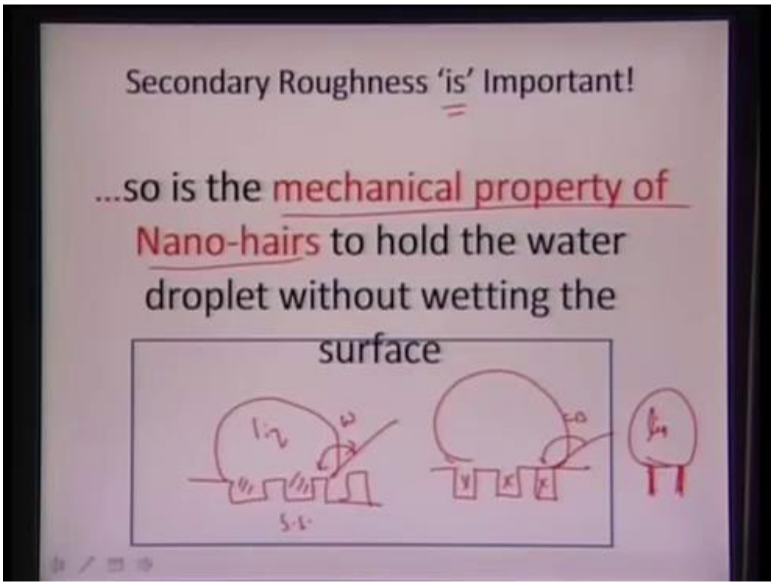

And again therefore, the secondary roughness is important in this particular case and, so is the mechanical property of the nano hairs to hold the water droplet without wetting the surface. So apart from the roughness part we also want to see the mechanically how strong the nano hairs are. Because, if the nano hair start to buckle then again it will lead to the water droplet touching the surface and it will eventually lead to wetting. So, the nano hairs which are sitting on the surface they also have to be equally strong enough so that they do not buckle and they continue supporting the water droplet on the surface without wetting the surface. So, we have this particular state Wenzel state and then the Cassie Baxter state so we have water droplet sitting out here without wetting the surface without wetting the pours out here.

In second case we have water droplet which is being again considering which is again wetting the wetting out surface, so we had certain contact angle of around Wenzel state and then again we had something on Cassie Baxter strait. So, this is what is being attained out here this is a liquid solid surface and again the nano hairs which are sitting on the surface they also should be able to balance the water droplet without bending.

So, this is a nano hair they do not have to buckle enough and at the same time they have to support the liquid droplet which is being supported onto them, because if you have protrusion. If we have a particular rain droplet, which is falling on the lotus leaf surface it comes in contact with the nano hairs of protrusions first. And hairs which are lying on the protrusion they tend to they start buckling then there is no way that rain droplet will remain hanging on the surface without wetting the surface. So, the at the nano hairs they have to be strong enough to be able to support the water droplet.

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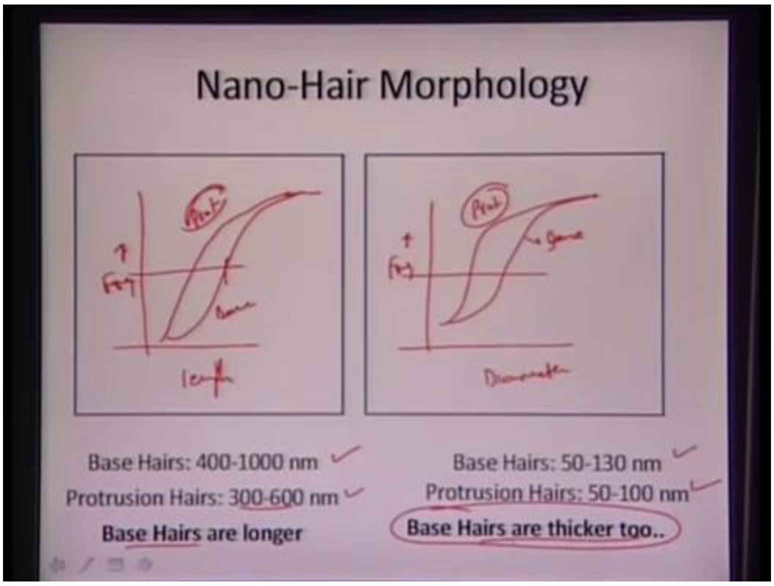

And coming to the overall morphology, the say, if we have the length part, so we did see that the length of the protrusions it was a little longer, whereas the base hairs the length overall. Let us see again this part that if you have a protrusion and then we have base hair the overall diameter was a little longer. And again the base hair also had they are little longer, but the overall aspect ratio for this is for the base and this is for the protrusions this again for the protrusion and this for the base.

So, we do see that the this is kind of frequency, so we are seeing that the protrusions hairs they are little shorter in length as well they are shorter in diameter, but the overall aspect ratio is little different for both of them, base hairs the length is around 400 to 1000 nano meters. Protrusion hair they are around 300 to 600 nano meter whereas, protrusion hairs are a little slender, their diameter is around 50 to 100 nano meter whereas, base hairs have a diameter of 50 to 130 nano meter. So, base hairs are longer and base hairs are thicker as well the overall thickness part basically dominates in the base hair that makes them much more stiffer.

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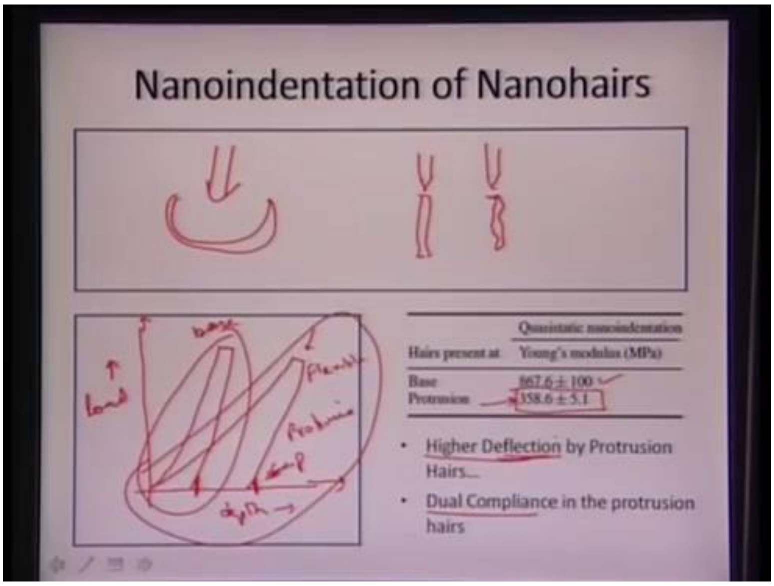

And coming to the nano indentation of nano hairs, if we indent a particular surface all these nano hair will form will buckle. So, if we had this particular nano hair and if we tend to indent it using a nano indenter, this one will basically buckle and from the low, from the low depth curve, we can say which one has a higher ((Refer Time: 28:47)) modulus.

So, if we see particular low depth response for a base hair, so the protrusion hair will go something like this. As I said earlier it is much more flexible the protrusion hair. So, we have load and then we have depth and if this is being done via nano indentation, then we will see that the protrusion hair will undergo too much of deflection while the indentation is being going on. So, this happens, because of the dual level of flexibility which is associated with the protrusion nano hairs.

What is happening? We have a micro protrusions which is much more again organic in nature, over that we have a nano hair. So, once the indent tape is touching the nano hair, nano hair itself will buckle the same time the micro protrusion which is holding the nano hair that also will buckle. So, we will get two levels of buckling in case of a nano hair which is sitting on the protrusion micro protrusions whereas, if we have a base hair, base hair has a very solid leaf surface and we have a very thicker or much more stiffer nano hair on to it.

So, if the base hair is being indented it will resist to a very large extent, because we have a very stiffer leaf surface and a very stiffer nano hair with much larger diameter so that one can resist load deflection to a large extent. So we see that the base hair undergoes a very low depth whereas, our protrusion hair goes undergoes very larger depth. So, we see a ph curve or the load depth curve it is much more steeper for the base hair plus it is very compliant for the protrusion hair. And from this data we realize that the overall young's modulus of a base hair is around 867 mega Pascal plus minus 100 and protrusion hair it is very low, it is even half as compared to that of a base hair.

So, it is doubly flexible and therefore, it can get deflected by it can get deflected easily by the indenter tip. So, it is highly compliant and it undergoes very high deflection once it is been undergoes by a nano indenter. And consequently fluid dynamics modeling has also been done, so we see that the smoother surface without any roughness will tend to have the say this is the extension of a fluid one quarter of a surface this is the water droplet, this is a water droplet one quarter of the water droplet. We can see that the front the front of the water droplet, which is flowing it keeps going without breakage without breaking in case of a smooth surface.

Whereas, if we start increasing the roughness, we see that this particular part starts spreading out or may be starts agglomerating and starts splitting up in this particular rough surface. It means that there is much better wetting in smooth surface good wetting whereas, as we have increased roughness it basically leads to good non wetting. So, we had this water droplet which is flowing in this direction starting from here, so we have only one quarter of the water droplet and we see the water front starts splitting up as we have much more as the time progresses, so with a same kind of roughness as that as available on the lotus leaf surface.

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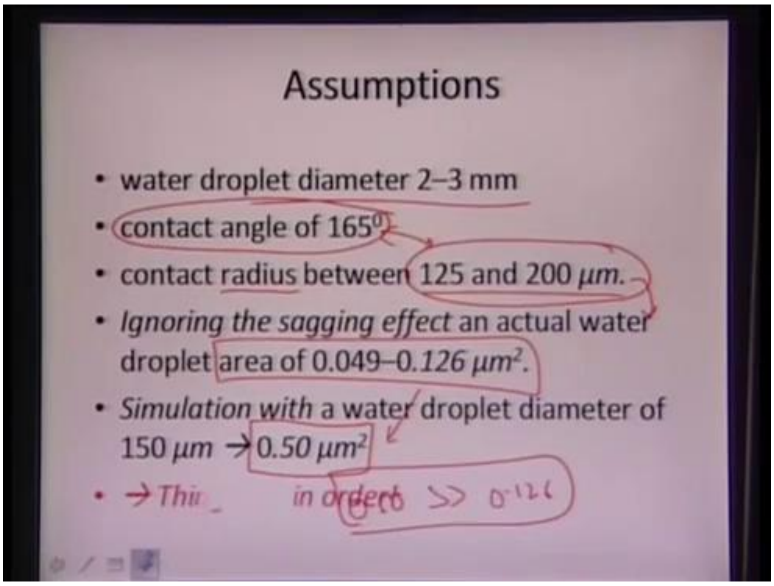

So, assumptions, there are certain assumptions been made for this particular type of modeling that water droplet diameter is around 2 to 3 nano meter, and the contact angle is around 165 is being made with the lotus leaf surface that brings out that the contact radius which is basically supporting the water droplet is around 125 to 200 micro meters. The contact radius at the lotus leaf surface with this typed of wetting it is 125 to 200 micro meter and ignoring that the water droplet will sack, this particular radius will lead to an area of 0.049 to 0.126 micrometer square.

And then the solution has been carried out using a overall wetting area of around 0.5 micro meter square. Since, this one is huger than the actual what will happen so we can say that the assumptions are valid for this type of simulation. So, we had an area of 0.50 which is much greater than 0.126. So this one can take care of the wetting effects which are being rendered by the water droplet, so things are in order for this particular assumption.

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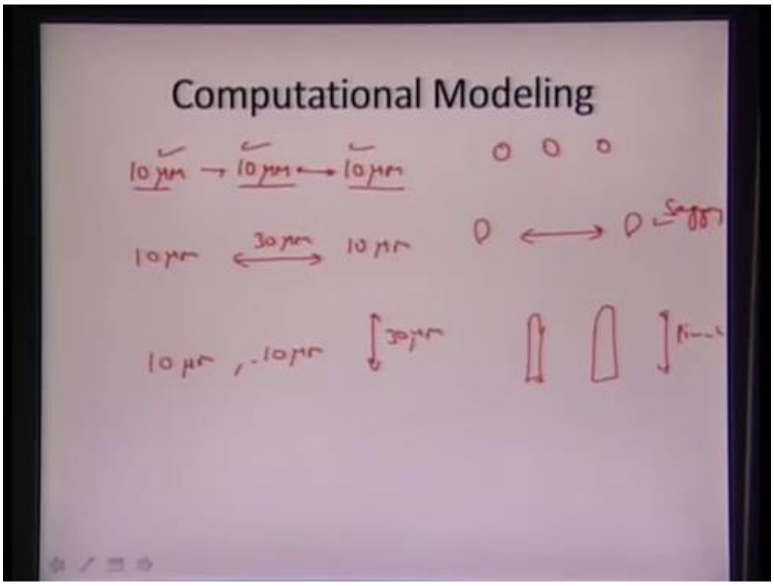

And we see that we have maintained three kind of roughness, in one case we utilized 10 micro meter diameter which is being separated by 10 micro meter of distance and all these pillars are something like 10 micro meter in height. So, we have 10 micron, 10 micron, 10 micron out here, droplet size of around 10 microns again 10 microns of pillars 10 microns meters apart.

And second case what we have tried, we tried to have a distance between a two protrusions separated by 30 micro meter. So, in second case we have 10 micron size 30 microns apart again 10 micro meter of height and in third case what we have tried we utilized the 10 micro meter while remaining the 10 micro meter of distance, but increasing the height by 30 microns.

So, in this case we have the protrusions far are apart, in this case we have the normal distance between the protrusions and this case we have height of protrusions to the order of 30 microns. So, in this particular case once we have a protrusion far apart we can see some sort of a sagging effect, in this case we can see something called a pinching effect and this case we called something called sagging effect we can see.

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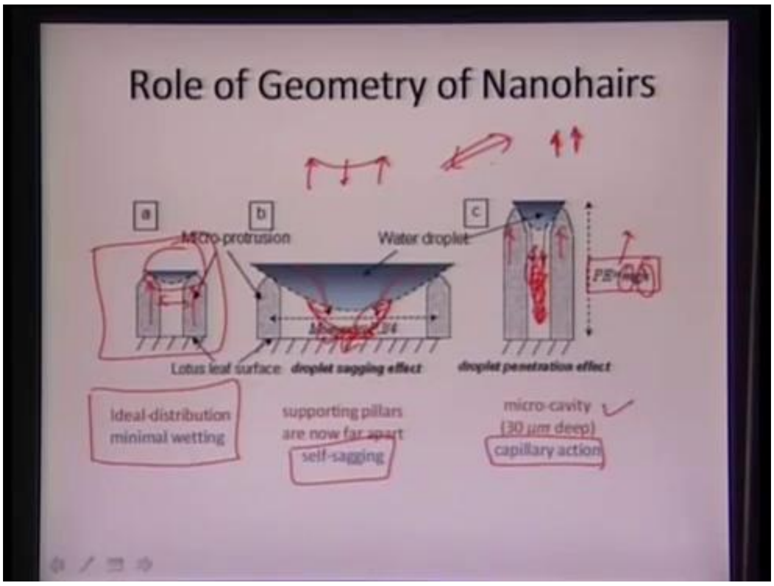

So, how do they really govern the overall wetting? In this case, we see a particular lotus leaf surface these are all the protrusions micro protrusions and once they are certain distance apart around 10 microns, it shows a regular support of the water droplet. And this is the ideal distribution leading to the wetting, but once we start separating the pillars by a distance, we start seeing that the water droplet will tend to sag, and the sagging effect will lead to the wetting of the surface.

So, it might eventually happen that this sagging effect becomes so predominant that it starts facing the surface and eventually it is wetting the surface. And secondly, if we increase the heights of those pillars, it might lead to some pinching effect, because there is some additional term. Because of the potential, the mass also comes into picture, so the mass which is being separated by a height of h.

So, overall potential energy of the water droplet is very high that can lead to a pinching effect and much more water droplet can also basically creep into out here. And this micro cavity which is around 30 microns deep can also induce some sort of a capillary action. So, we see that, once the micro pillars are very, they are very increased height, it leads to capillary action and it can leads to pinching effect. Once the protrusions are very farther from one another, it can lead to sagging effect, and once the there is some ideal distribution, you can see that the both these wax are basically being balance. So, there is no pinching and no self-sagging of the water droplet in terms of retaining the water at the surface.

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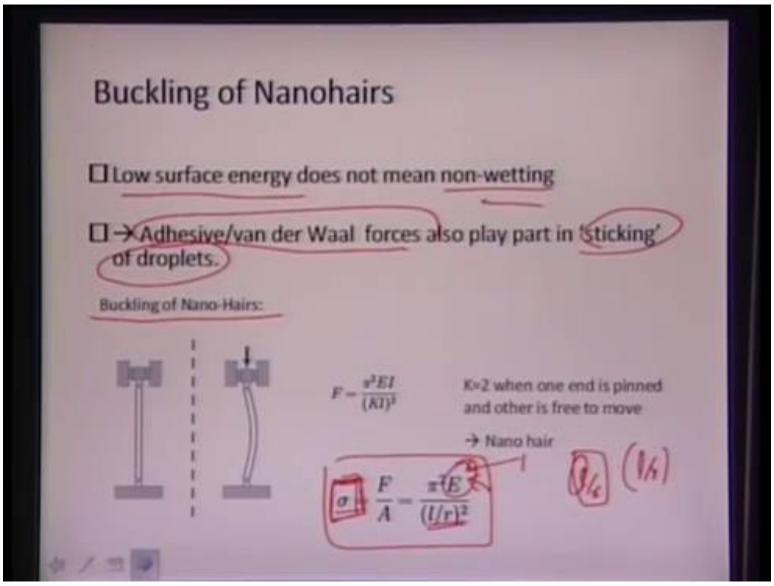

And again the energy which is being utilized by the hairs before buckling it is being rendered like this, we have the overall stress which is being generated it can be related to the young's modulus of the material, so we require certain force to buckle the particular material. So, we have stress which is which a particular hair can take depending on its l by r ratio and the young's modulus which is the property of the particular material. And again the low surface energy does not mean non wetting, again the adhesive or the van der Waal forces which are acting at such a scale they also take part in sticking of the droplet. So, apart from a low energy we also need to have minimize the adhesive or the van der Waal forces which are dominant at nano scale.

And the same time it has to be balanced, so that it as a high enough and l by r low enough so that, we have a minimum stress which is acting on the particular surface to result non buckling to result non buckling of the nano hair. So, basically I will stop here, so we also see that the effect of l by r ratio, so if we have very high lengths then overall stress will basically keep reducing. So, the flexing style which can be taken by the hair will reduce as we start increasing length or the particular material will start undergoing much more buckling. So, need to have the proper ratio of l by r should be low enough so that it can support the support and it should not really buckle.

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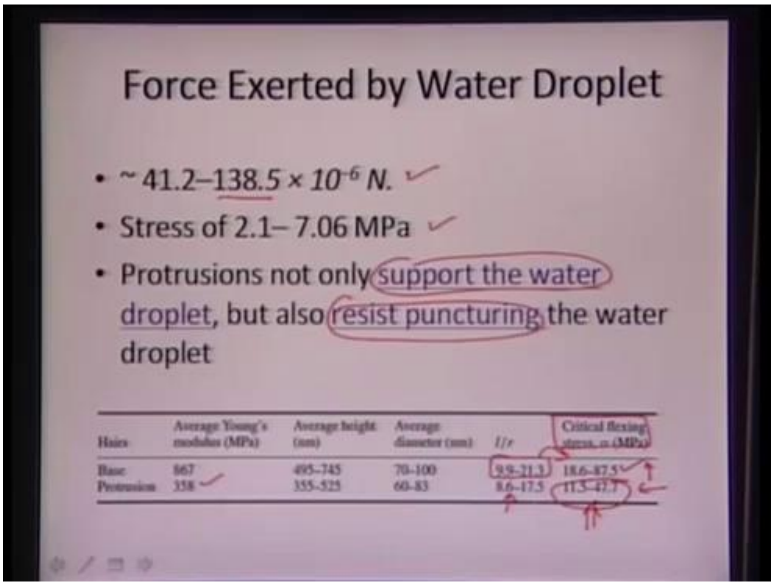

And the force exerted by the water droplet it comes out to be around 41.2 to 138.5 into 10 power minus 6 Newton, which corresponds to a stress of around 2.1 to 7.06. And there are two very key features out here that protrusions are not only supporting the water droplet, but they are also resisting the puncturing of the water droplet.

If water droplets get punctured then basically there is it will basically flow out as a capillary and it will wet the surface. So, as we saw earlier the protrusion hair have a young's modulus of around 358 that corresponds to overall flexing stress of 11.5 to 47.7 with a certain l by r ratio. And as we know that the l by r ratio of the base here is very high, so it will lead to a much more critical flexing stress and this is this one will be very difficult to achieve.

If you are able to maintain that protrusion hair are not getting wet obviously the base hair will also not get wet, because the flexing stress is very high at the same time they are the secondary hair which on which the water droplet will eventually come on to. So, we see that protrusion hair have a certain flexing stress, so this is the critical part and this should not be exceeded in order the in order for the water droplet to remain on the surface of the lotus leaf without wetting it,, so this sort of a getting critical flexing stress.

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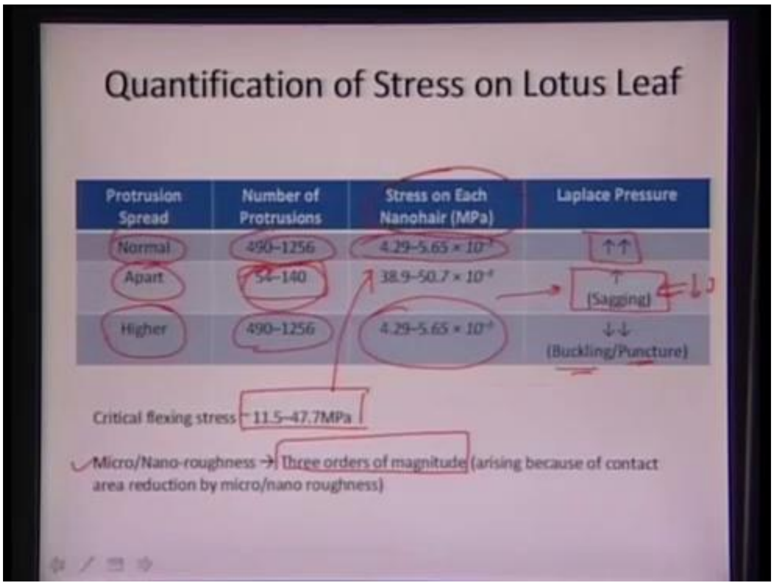

And as we see, if we have a normal protrusion spread this 10 microns, 10 microns, 10 microns, it corresponds to a number of protrusions 490 to 1256 and then stress on each nano hair is to the order of 4.29 to 5.65 and again coming to the Laplace pressure will be very high. Laplace pressure is nothing but the kind of pressure which is required to go through the go through those two protrusion hairs and be able to wet the surface and since they are only 10 micro meters apart it will need a very high datum of water to be able to able to wet the surface.

We can see when the particular protrusions are far apart they create the number of protrusions basically reduce to 54 to 140. And therefore, because of sagging effect the Laplace pressure is very it is little higher, but again it is it will lead to some sagging of the water droplet and it might even wet the surface. But when the protrusion spreads are much higher though there are similar number of protrusions stress on each nano hair will also remain the same. But the Laplace pressure will be little lower why, because there will be some datum effect which will also come into picture and that can also lead to the buckling or the puncture.

So, puncturing effect might be much more predominant in case of a higher, but once they are sagging obviously the number of protrusions are very less and thus the sagging effect will have a very low kind of Laplace pressure. And the critical flexing stress is around 11.5 to 47.7 and as we see these values are much more lower than those. So, what is happening is that the micro or the nano roughness it is inducing around three orders of magnitude reduction in the orders of reduction. And as we see that, the critical stress is around 10 power minus 3 lesser and still it is been able to hold the particular droplet. So, that is the reason we are seeing the effect of roughness, which is being imparted on here in terms of being able to hold the water droplet.

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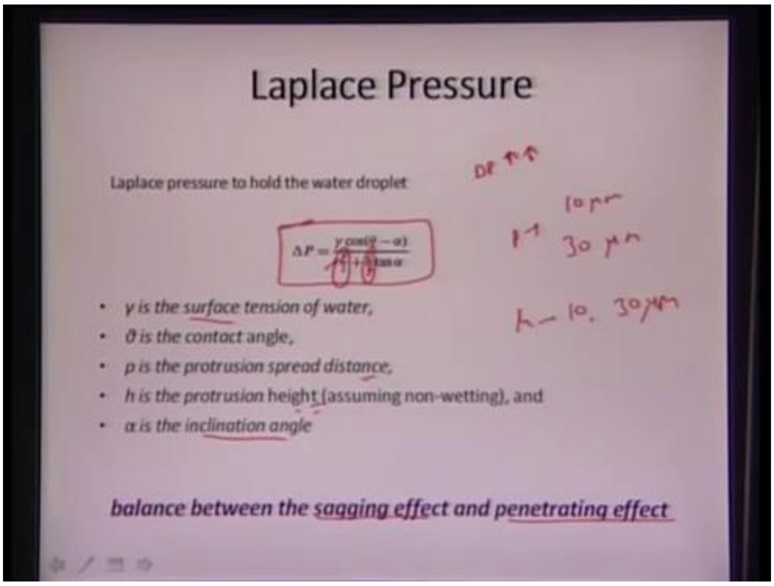

And Laplace pressure is basically given by which is dependent on the surface tension on water, minus the inclination angle and it again depends on the protrusion spread and the distance which is out here the protrusion height and the protrusion distance. So, we have kept a protrusion distance of around 10 microns in one case and with a spread it becomes 30 microns. Similarly, with the height we have a height of 10 microns in each and in one case we have taken the height of around 30 microns to see the pinching effect and using this particular equation we see a balance between the sagging effect and the penetration effect.

So, if we see this part out here we need to keep the maximum of protrusions minimum of protrusion distance and minimum of the spread height, so the overall delta p goes higher and higher it means the higher datum can be supported by the particular for the particular thing for holding the water droplet. So, we need to have both high p as well as the h or the protrusion spread should be spread distance should be will be minimal and protrusion height also should be minimal, so that we have the overall delta p to be very high.

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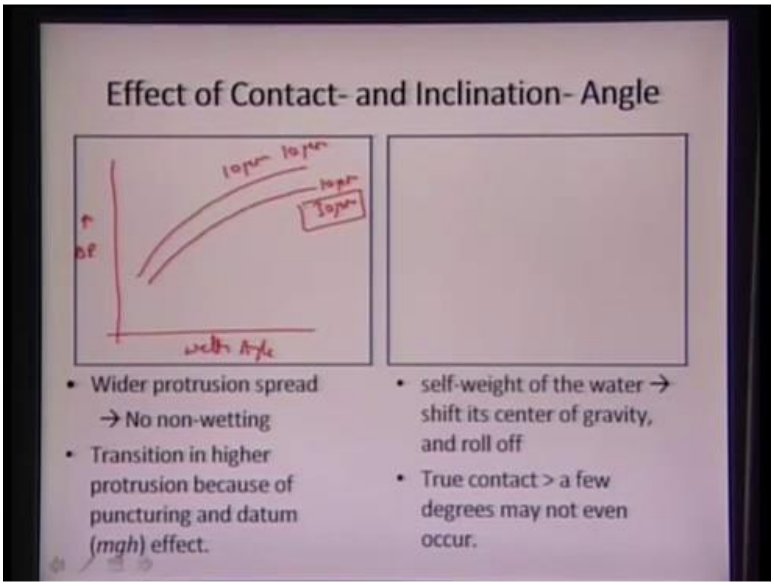

So, coming on to the effect of contact and the inclination angle we can see the overall Laplace pressure how it basically delta p how it changes with the wetting angle. So, we see that for the for our ideal case if we have something like this, like we have 10 microns of protrusion spread with 10 micro meters of the protrusion height. We see that the wetting basically wetting angle remains approximately similar with once we have very given much more height, so we have 10 micro meters of spread, but 30 micro meter of height.

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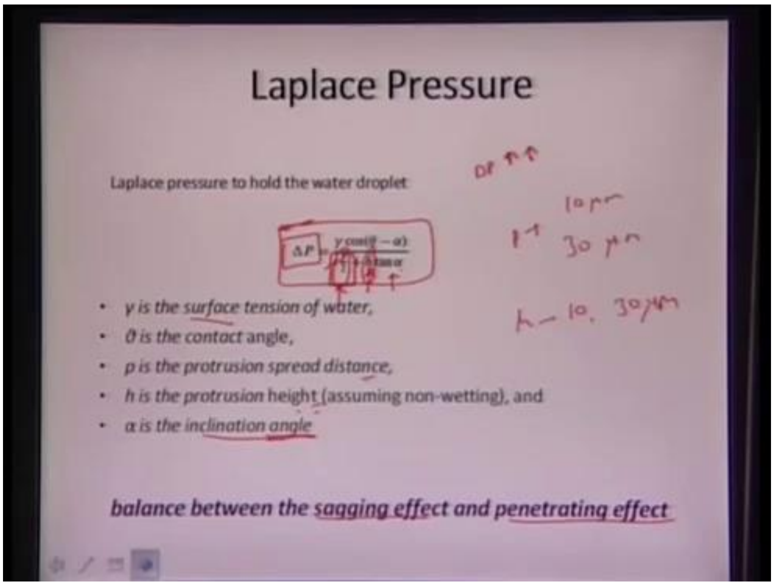

So, height is not playing that important role in terms of being able to wet it, because we see there is also some dependence on the alpha where alpha is the inclination angle. So, depending on the inclination angle as well the h will keep affecting in certain manner, but protrusion spread distance it is only half of it which is basically affecting it. So, we see that once the once we have very in this case we have the spread distance the spread distance is increasing it is affecting the delta p in a large extent. So, if you are increasing this p by say three times we are getting around 1.5 times decrease in the delta p.

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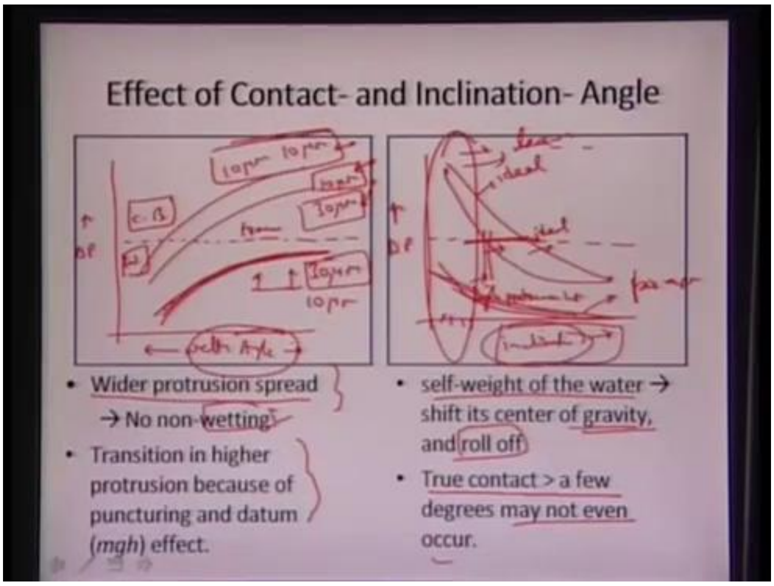

And that is what we are seeing out here, we are seeing a certain transition from Cassie Baxter to Wenzel strait. Cassie Baxter is not wetting state, Wenzel it means more of a wetting state where the cavities are also being captured by the water droplet. So, we have seen Cassie Baxter state which is basically incorporating the height of the particular protrusion hairs that we have both the cases of ideal nano hair and something with the increased height as well.

So, we have increased height and ideal protrusion and thus showing that the particular surface will remain hydrophobic in nature whereas, for the once we have increasing the protrusion spread to 30 micron. So, we have a height as 10 microns, but spread as 30 microns there are not enough protrusions to support the water droplet and that is basically making it lie below the transition layer the transition between the Cassie Baxter and Wenzel and this particular state remains in the Wenzel state and this basically keeps below the non-wetting line and it basically is wetting the surface.

So, that is the effect of the wetting angle and the spread of the nano hair spread of the micro protrusions. And coming to the inclination angle Cassie Baxter state remains obviously Cassie Baxter state is again the same transition out here. So, we see the ideal always remains above the Cassie Baxter once the wetting inclination angle is a couple of degrees, but as we start increasing the protrusion height, we see very minor deviation from the same, but it will wet before the ideal case is achieved so this is for the ideal.

So, wetting will, and in this case once we have the wetting, the wetting will be, will initiate earlier for the, for the higher protrusion, for the higher protrusion height whereas, for the, once the protrusion, once the protrusions are spread far apart, we see wetting at much lower inclination angles. So, this was the inclination angle, this is the Laplace pressure, we see the wetting will occur very easily for the, when the protrusions are far apart.

So, this are, this is the overall observation of this one, but once we have wider protrusion spread, there is no non wetting or there is easily wetting of the surface. And again transition is occurring in the protrusion, because of the puncturing in the datum, because once we start having a wetting angle of, wetting angle of lower and lower. This basically means, that water is being able to get trapped into the surface, because of the overall geometry, and the overall inclination of the particular water droplet, and wetting angle is basically getting decreased.

And secondly, the weight of water droplet itself can also play a part, because while we are shifting its gravity, centre of gravity. It means, we are changing the, changing the inclination angle then, water will roll off and the true contact basically will be a few degrees, greater than a few degrees may not even occur. So we are seeing that true contact will occur in this particular region, and water droplet will simply roll off.

So, this inclination angles, they do not make much importance in practical applications, why, because with certain role of say, couple of degrees will make the water droplet to go and leave the surface. So, at higher inclination angles, we do not see that effect of inclination which might be dominant in inducing the wetting of the lotus leaf surface. And this is what the overall thing is all about that, once we, that first of all the lotus leaf surface will have effect of super hydrophobicity rising from two levels of micro structure, one is the micro protrusions which is dominant on the surface.

And over that, they have some sort of nano hairs, and again the geometry of nano hairs is different which is lying on the protrusion surface, and which are lying on the surface of the base hair. Because base hair surface leaves base hair, nano hairs which are lying on the surface of the base hair, they are much more rigid, they are much little larger diameter and much more height as well, but they are much more rigid, because of their higher diameter. And again this leads to effect of what will be the effect of protrusion spread and height on the non wetting of lotus leaf.

So, a modeling has been done and which basically tells that, if we have protrusions spread ideally of ideal height then, it can support water droplet very easily. But if we have protrusions, which are much higher in height, it can sustain, it can sustain very high Laplace pressure, but of course, lesser than that of an ideal case. And later on the pinching effect starts creeping in, because of once we have some very high datum then, it can lead to much more, much more puncturing of the water droplet itself, and it can wet the surface much earlier as compared to that of an ideal case.

But the worse case, if we have the supporting pillars of this micro protrusions much farther apart, then it can basically cannot support the whole water droplet, because the number of protrusions will decrease by around 4 times and, because instead we have 2 or 3 protrusions in certain distance.

Now, there will be 2 or 3 protrusions in more than 3 times the distance, so that will basically reduce the overall holding capacity of the protrusions and then, that will lead to easy wetting of the surface. And sagging effect may come into play as when the protrusions are very apart, and that leads to the easy wetting of the surface, both in terms of either wetting angle or the inclination angle. So we did see that, the inclination angle is also plays a part in wetting the surface and it may not allow the water droplet to roll of, so easily and it will, the gravity effect will also come into picture once we have some inclination angle.

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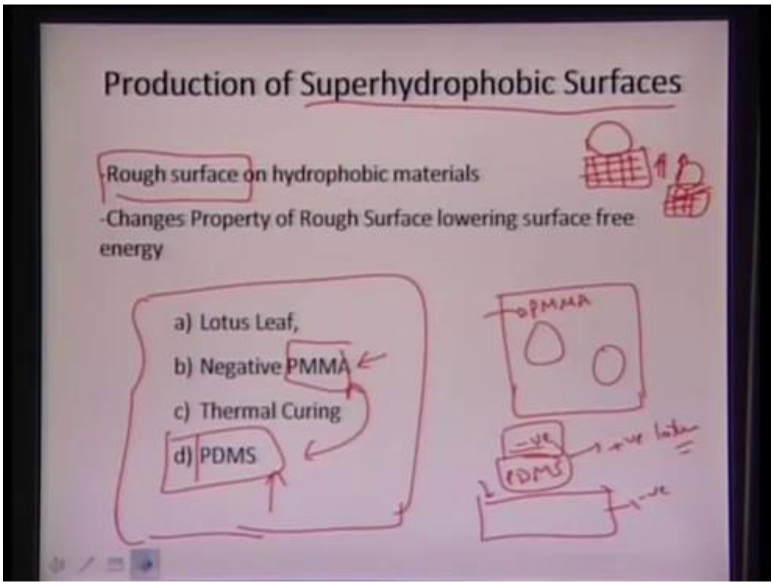

And that is the basically the effect of the super hydrophobicity. And there also have been certain ways in which a super hydrophobic surface has been engineered or has been produced synthetically. So, what they have, one group has basically done that they, that they take lotus leaf surface and then, a negative poly methyl methacrylate has been deposited on the lotus leaf surface. So, basically it is mimicking the negative replica of the lotus leaf surface. So, once it has ((Refer Time: 50:44)) negative of the negative replica then, this particular material has been cured. And over this particular material which is the negative replica on onto it we have spread polydimethyl siloxane.

And now, PDMS takes the shape of the negative of negative and it becomes again positive lotus leaf surface. So, this PDMS mimics what is happening at the lotus leaf surface, but again there are two transitions, one PMMS flowing into the cavities of the lotus leaf, and again PDMS is going onto the cured PMMA. And again tracing its topography, so becomes very difficult to fill in the profiles which are to the order of nano meters in length and diameter.

So, it becomes really hard to make each and every contour of the surface. So, these particular coatings are super hydrophobic, but they can be made even more super hydrophobic depending on if you are able to trace those particular thing. But we able to achieve a surface which is really super hydrophobic in nature. And, so this negative to negative mimicking also leads to formation of a super hydrophobic surface. Again inducing some sort of a surface roughness can also make surface highly super hydrophobic.

So, if we start inducing some sort of roughness, inducing some sort of micro pillars, or nano pillars on a surface, we can really make water droplet go from hydrophilic to super hydrophobic in nature, just by altering the overall roughness of the particular surface. And in this case, one group has already achieved developing negative PMMA and over that they are able to deposit the PDMS and able to mimic the, what is happening at the lotus leaf surface. So, this is what I will end my lecture with.

Thank you.