Soft Nano Technology

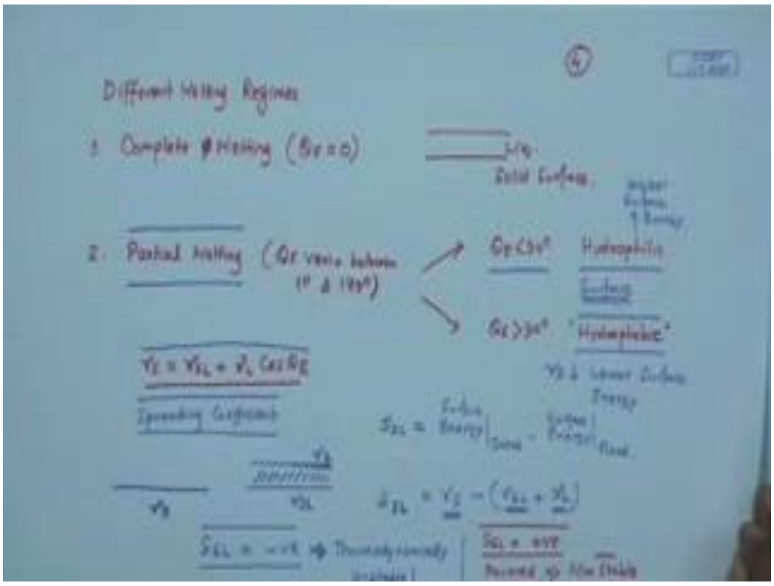
Prof. Rabibrata Mukherjee
Department of Chemical Engineering
Indian Institute of Technology, Kharagpur

Lecture - 06
Fundamental Concepts Related to Surface Tension – 3

Welcome back. Now we will continue our discussion with concepts related to surface tension, which we have been doing now. We have in a very slow but in a narrative fashion, learned quite a few things. We now understand; what is the difference between surface tension and interfacial tension or surface energy an interfacial energy. Then we went on to define or understand what can be the configurations - possible configurations if you dispense a liquid on a solid surface a flat solid surface.

And we understand that depending on the relative values of the surface energies of the liquid and the solid, in principle have 2 primary configurations and the configurations are either complete wetting or partial wetting.

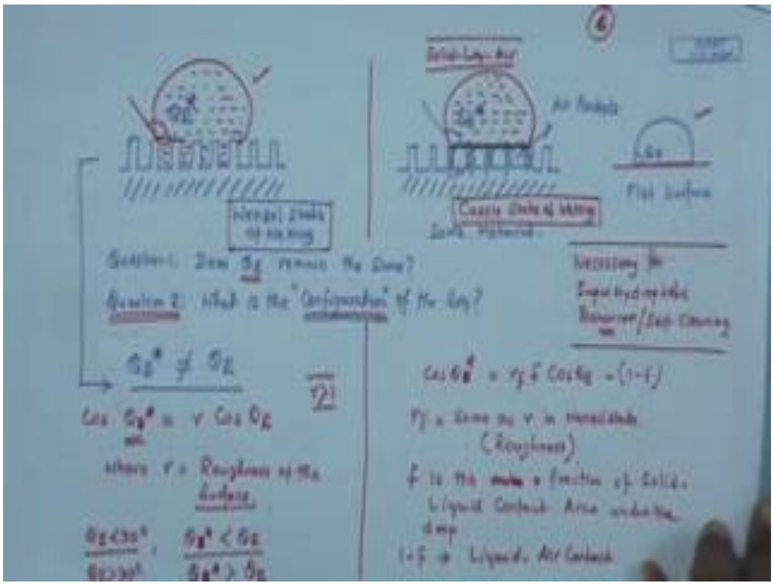
(Refer Slide Time: 01:21)



Then within these regimes of partial wetting if the liquid is water then it is possible either to have an equilibrium contact angle lower than 90 degree or higher than 90 degree. And depending on the magnitude the surface is conventionally termed as hydrophilic and hydrophobic. So, hydrophilic if it is less than 90 degree hydrophobic if it is more than 90 degree. Subsequently we also understood what the definition of spreading coefficient is.

In fact, spreading coefficient gives us a qualitative idea about the stability of a film straightaway because a negative value of spreading coefficient implies that by creating a film on its surface one has in fact added more energy to the system and anything that has high energy is on stable. Whereas, a positive spreading coefficient shows that a film formation is favor.

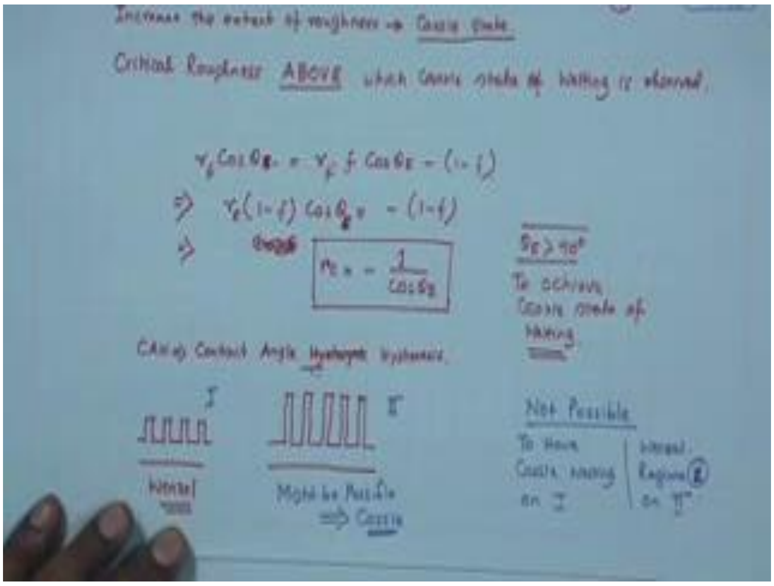
(Refer Slide Time: 02:26)



After that we moved onto another interesting area and that is wetting on a structure surface. And we understood that on a structure surface to different configurations are possible. This I am sure is new to some of you 2 different configurations are possible, and those configurations can be either Wenzel state of wetting, where the liquid flats, the protrusions of the liquid confirmedly adheres to the boundary of the structure substrate. Or one can under certain special conditions particularly when the roughness is very, very high one can have a different type of wetting which is known as the Cassie state of wetting where the air pockets there are air pockets interact within the substrate protrusions which the liquid fails to dislaunch.

And therefore the composite they the contact line is now a composite liquid solid air contact line. Of course, Cassie state of wetting sought of leads to maximum contact angle effective contact angle as well as the addition is sort of least. And therefore, this is a sought of a necessary condition for super hydrophobicity behavior of course, I have not yet defined what is a super hydrophobic surface super hydrophobic behavior are to achieve self cleaning property. We also look from a very simple equation that there is a critical roughness only above which Cassie state of wetting is possible

(Refer Slide Time: 04:17)



Increase the extent of roughness → Cassie state

Critical Roughness ABOVE which Cassie state of wetting is observed.

$r_c \cos\theta_E = r_f f \cos\theta_E - (1-f)$

$\Rightarrow r_c(1-f)\cos\theta_E = -(1-f)$

$\Rightarrow \boxed{r_c = -\frac{1}{\cos\theta_E}}$

$\theta_E > 90°$
To achieve Cassie state of wetting

CAH ⇒ Contact Angle Hysteresis.

Wenzel

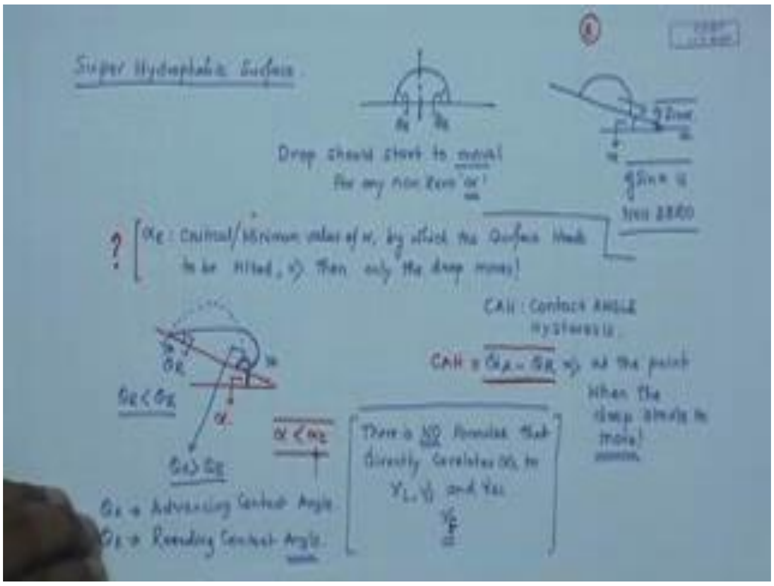
Might be Possible ⇒ Cassie

Not Possible
To have Cassie wetting on I | Wenzel Regime ② on II

If 1 asks you that you have let us say different type of structures on the same material like these structures we will do a lot of these structuring, so what type of structure this and that we will not a big deal at this moment. So, qualitatively if one expects are tells you to comment on the wetting regimes that you are likely to have. Well, without knowing the relative values of gamma s gamma l and theta E nothing should be commented, but if one ask you to make a back of the envelop comment, you may say where it looks like on this a more likely to get Wenzel regime and it might be possible to get a Cassie state of wetting. It is also possible that even this roughness is not adequate and you end of getting a Wenzel wetting.

But if at all one can achieve a Cassie state of wetting it has to be on this one. Other way of looking at it is if somehow the wetting regimes are Cassie on this particular case it has to be Cassie on this particular case. It is not possible; this is something that you can surely say if the material remains same the periodic remain same to have Cassie regime on 1 and Wenzel regime on 2 that is not possible.

(Refer Slide Time: 06:19)



Super Hydrophobic Surface

Drop should start to move! for any non zero α!

CAH : Contact ANGLE Hysteresis

There is NO formula that directly correlates

θa → Advancing Contact Angle

θr → Receding Contact Angle

Now, I have used a term a several times you might have also heard it at different places and that is a super hydrophobic surface. So, let us try to find out what this is. So, you now know that if a surface on which the water contact angle is more than 90 degree is a hydrophobic surface installment pedagogically or conventionally as a hydrophobic surface. Now, what is super hydrophobic surface? Before I can define super hydrophobic surface accurately to you let me I need to highlight another critical aspect, and what is known as the contact angle hysteresis.

Suppose, you have a drop of a liquid, which can be water resting on a flat horizontal surface, important into notice all the drawings we have all the sketches we have made so far actually talk about a horizontal surface. Now, suppose I tilt this surface by n angle let say alpha what we expect. The moment you tilt the surface there is in fact a component g sin alpha - component of gravity g sin alpha that is acting on this drop. And if you just way recall of what is the definition of the fluid, the definition fluid it is that it deforms under shears stress; however, small the amount may be.

Even if alpha is very small that corresponds to sin alpha to be very, very small, but g sin alpha is nonzero. In principle, the drop should start to move. I will write down there a certain very interesting aspect. In reality, something different happens. Often when one sees that you really have to tilt the surface by some value of alpha, some significant value of alpha only above of which the drop starts to move. If so there is sort of a critical value of alpha or I would say a minimum alpha by which the surface needs to be tilted then only the drop moves.

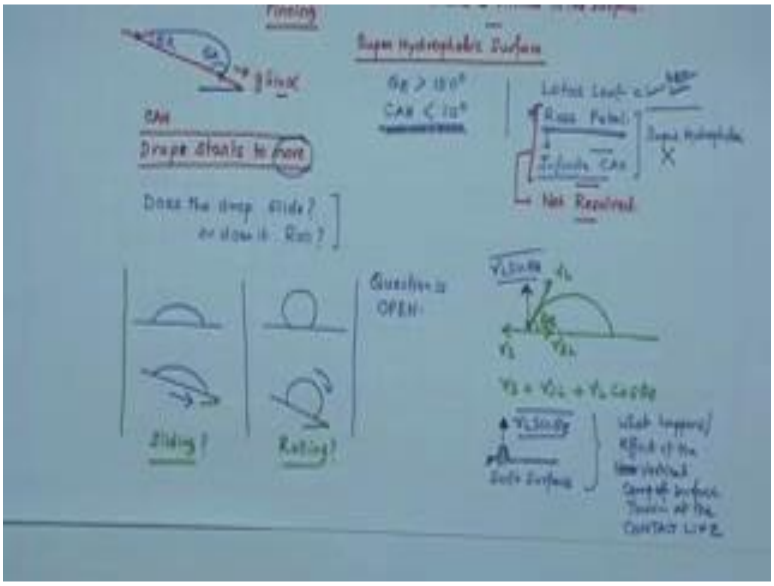
Let us think term of a situation that for this is how is it possible, because you have nonzero force acting on the liquid and somehow it is not flowing. So, what really happens, this is the very simple observation I am sure you have seen rain water sticking to vertical windows and that is exactly the situation. There several issues that needs to be highlighted this is something I very, very active area of researching micro fluids and things like that you will not going to all the detail, but I will highlight to you the key features of what happens.

1 of the important things or interesting thing is suppose you have tilted the surface by a value alpha, and this alpha is less than alpha c. Unfortunately unlike Young's equation, there is no clear formula that can correlate alpha c yet. That directly correlates alpha c to what gamma l, gamma s and gamma s l, and may be also roughness on a structure surface it is not there. I am coming to several important things now. This is a very practical observation. So, you have tilted it that the degree of the tilt is not adequate, so that the drop starts to move. So, what to do you expect the first thing that you will expect that on a flat surface you have been drawing a hemispherical drop, which is in fact axis symmetry.

If you consider an axis about the midpoint to center is axis symmetry. The first thing that will happen in fact, what I did not highlight it was so obvious that this is theta E and both the sides. The moment you tilt it and the drop is still stationary what happens is it sort of loses its axis symmetry shape, and that 2 angles on the left and the right, left and right is not the right thing to discuss, because to tilt it in this direction it is going to be the geometry is going to be the different on the other one. They are going to be different.

If you now superpose the equilibrium shape, you can see this angle which is marked as theta R, why R, I am coming is less than theta E. On the other hand, this angle, this is marked as theta A is actually greater than theta E. Now what are these reason why one is using A and R; theta A is termed as the advancing contact angle, and this is known as the receding contact angle. Simply because once the drop starts to move, the drop will be advancing in this direction and it will be receding in this direction. So, one typically, so let me now formally define what is contact angle hysteresis. It is the difference between theta A and theta R at the point when the drop starts to move. So, this is a very, very important parameter, the contact angle hysteresis. While we are happy to learn the concept of contact angle hysteresis, we need to also understand 2 more critical aspects associated with this.

(Refer Slide Time: 14:48)



I will redraw the shape of a tilted drop. So, this now all of you understand thus surface over which it was resting is tilted, it has a finite angle with the horizontal, therefore, there is a net force g sin alpha. Question to ask is why the drop still does not move. So, what is holding it back? Well, there are very many contradicting conjectures, but this phenomena of there is a driving force, but the drop still remains stock to its original or stock along the contours of its original three phase contact line is briefly refer to as pinning. We will talk about evaporative drying of a drop, where you will see that pinning can happen even in case of a horizontal in case of a retracting drop on a horizontal surface, you may not have to always tilt, but it is tamed as pinning.

As if the contact line is pinned to the surface. So, this is a very, very interesting observation. So, in order to achieve a self cleaning surface lets a where you would like your liquid to roll off, you need to have very low strength of pinning. And a low strength of pinning necessitates that the contact angle hysteresis has to be low. So, this is the appropriate time to define what a super hydrophobic surface is. Again it is partly based on convention; there is no genuine reason why the numbers have to be followed as these.

A super hydrophobic surface is a surface where the equilibrium contact angle is greater than 150 degree and the contact angle hysteresis is less than 10 degree. Only then it falls into the category of a super hydrophobic surface.

I will give a very exciting example again from nature, it turns out that lotus leaf and rose petal both exhibit if it water contact angle roughly of 155 degree it is 150 degree plus. However, so the super hydrophobic surface lotus leaf is much more famous and popular than a rose petal, is it because people did not know is not that. It turns out rose petal has almost infinite contact angle hysteresis. So, you tilt it and drop simply does not move. What is the reason again research is going on probability is related to the structures the difference in the nature of the structure.

In fact, this is also very interesting example that you have very high equilibrium contact angle, but the contact angle hysteresis is very, very high. And now all of you understand what it means that the strength of the pinning force is very high on rose petal. Therefore, rose petal is does not qualify to be a super hydrophobic surface, does not qualify to be a super hydrophobic surface, while lotus leaf is a very, very widely used super hydrophobic surface.

Coming back to so while we agree to this clear definition of what is a super hydrophobic surface we understand theta E has to be moved that 150 degree the contact angle hysteresis has to be low. It is also logical to expect that why Cassie state of wetting, so popular from the stand point of a super hydrophobic surface. It is simply because of the fact that since the drop of liquid or water is almost floating on the substrate protrusions when you tilt it, it is very lightly that it will start to move or roll very easily.

As compared to here where the liquid is actually gone in and it stuck up within the substitute groups and it is very lightly that the pinning in Wenzel state of wetting might exceed that on the flat surface very likely. So that is why from the stand point of super hydrophobic and self cleaning surfaces the Cassie state of wetting is decided. It is lightly that the pinning is going to be lower and that is going to lead to lower value of contact angle hysteresis.

But there is a more to that I mean in fact, research is still going on it, one does not really have a very convincing answer. Probably rose petal also exhibits Cassie state of wetting, but it exhibits very high contact angle hysteresis. Probably as I told that in the initial slides, this is course that is very open ended research is still going on, this is not clear not at answered. There is another very interesting issue that is associated to what we have discussed so far and that is we have been mentioning that once the drop sought of exceeds the magnitude of the contact angle hysteresis or sort of. So, what happens I mean as you tilt I mean there is in fact and imbalance along the horizontal imbalance in surface energy along the horizontal component of surface tension. And when the magnitude of this imbalance exceeds the strength of the pinning force in fact, the drop starts to move, this is the what I have deliberately used be honest.

Another very important question at this point of time is what is the nature of the movement does the drop slide or does it roll. Back of the envelop expectation is higher is the level of hydrophobicity. This is sort of an intuitive answer that may be for a hydrophilic drop the motion is sliding for hydrophobic surface probably the motion is rolling, but it is difficult to say. This is again a question that is still open the question is clearly open.

You might now add your concept of Cassie and Wenzel states of wetting to the discussion. And you may argue that it is very logical that if the wetting state is Cassie, probably you would see rolling. And probably here it is very difficult say whether it is sliding, because one thing and one hand the pinning sort of increases and I have no option back to put these question marks because it is not yet known. So, see such a simple systems such a simple thing that is a drop moving on a tilted surface, which we encounter every now and then every now and then we encounter this has so many very interesting scientific aspects associated with that. And some of them are associated with the surface tension, some of them are related to pinning which everybody now sort of agric based on experimental observations that pinning exist because there is an instrument contact angle goniometer, which we will discussed partly as a part of this course. Where you can clearly tilt the platform on which a flat surface is resting and you can see to the droplet does not move.

There is pinning, but what exactly causes the pinning, whether it is a deformation of the contact line due to its vertical components something as just a need to highlight which I need did not talk about yet or the some other effects like a local molecular interaction or some differencing pressure, it is not fully known. Just the way, it is also not fully known when the drop actually starts to move on a tilted surface whether the nature of the motion is sliding or rolling under what condition or to put if very specifically what exactly is the transition probably both the things happen, but where exactly the transition takes place from a sliding to rolling is something that is yet to be fully resolved.

1 more thing, I need to highlight before I end this particular lecture is we have in order to obtained the Young's equation made the balance of the horizontal components of forces, but what happens to the vertical component there is in fact, the vertical component of the liquid surface tension, and which is gamma l sin theta E. This is again a very, very interesting area of research because this tries to pullout the surface right this is acting outward.

For a rigid surface, in fact, if the substrate is rigid, this is 2 lays to cause any deformation, but there are lot of work that is going on and which suggest that if you look into the wetting on a soft surface or a surface that is not very stiff, it is likely that this might cause some very mine or deformation this horizontal component might cause some very minor or deformation that is sort of again a counter a sort of an intuitive expectation on a soft surface like that of a gel may be; but a lot of research is actually going on and I should not comment on that, because this again a very open area.

I will put the question, what happens or what is the effect of the vertical component of surface tension at the contact line. These are things that you need to think and you can search in the literature what is the latest state of art and find out yourself.

Thank you very much.