

Soft Nano Technology
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Lecture - 04
Fundamental Concepts Related to Surface Tension – 1

Welcome back to the lecture number 4 of this course on Soft Nano Technology. We had a sort of extended introduction and now I am sure you are convinced about certain utilities of nano patterns and also some aspects of the nano skill how things are slightly different in terms of the interaction forces at the nano skill, particularly due to pre dominance of van der Waals forces. And how that might lead to some bit of influence stability of thick films.

Now, 1 of the things that is very important again at the nano and meso skill is surface tension. And one of the classes earlier, we talked about the difference between a surface and interface. You may recall that in your school days probably in your high school, you sort of started to talk about surface tension and viscosity, roughly at the same time, but as we have learn fluid mechanics and stuff like that, we have seen a very significant role of viscosity there. How viscosity affects flows and how fluid becomes slower or faster depending on the viscosity of the system, we have all seen that.

Even simple example like you take two bottles of identical volumes of liquid let say you have honey one of them and you have water in the other one, you sort of top down both of them so that liquid flows down. And you will see that the honey is flowing slowly that is because honey has higher viscosity. But we rarely talk particularly in the context of flow about surface tension.

However, we will soon realize that at the nano skills, surface effects become very, very important and the reason for that is pretty obvious because as size becomes smaller the surface to volume ratio sort of start to a increase and therefore, a we need to look into surface tension in rather greater detail. So, what we will do in this course - this particular class is that we will understand build our concepts on some of the fundamental issues related to surface tension.

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Surface and Interface

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

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

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

Diagram 1 (Left): A vertical stack of three layers. The top layer is labeled 'Air or Vacuum', the middle layer is 'Liquid', and the bottom layer is 'Solid'. A red bracket labeled 'S' spans the top 'Air or Vacuum' and 'Liquid' layers. A red bracket labeled 'I' spans the 'Liquid' and 'Solid' layers.

Diagram 2 (Right): A vertical stack of three layers. The top layer is 'Air or Vacuum', the middle layer is 'Liquid', and the bottom layer is 'Air or Vacuum'. A red bracket labeled 'S' spans the top 'Air or Vacuum' and 'Liquid' layers. A red bracket labeled 'I' spans the 'Liquid' and bottom 'Air or Vacuum' layers.

We have already defined you can follow this particular slide again we have defined what is the difference between the surface and an interface. So, some amount of material, so important thing to note down is every object we will have ultimately a surface or interface irrespective of whether it is a thin film or a huge chunk of material. Now, whether that surface if that surface that particular block of material is making is with the non-condensed phase that is either with air or vacuum where essentially what it means is the number density of molecules in the non condense phase is much less as compared to that in the material itself it is termed as a surface. In contrast, if it is actually in contact with another condensed phase, it is termed as an interface, this is more of a pedagogic discretion, but this is very important for our understand.

Surface is a boundary between a condensed material and a condensed phase with rarified gas or vacuum. An interface is boundary between condensed phases with another condensed phase. So, this picture this is in fact, this is here it say self standing, self supported film which as surface in both sides, and this is a coated film or a coating which has one surface. So, this is an interface and this is a surface. I have also given you example of the film where it can be bound by within two medium to let us say two blocks and then it has interface on both the sides.

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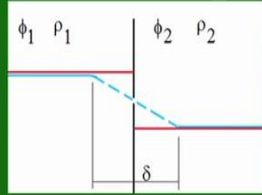
Surface and Interface

Air or Vacuum
Liquid
Solid

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

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

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



A surface or an interface is ideally not a zero thickness mathematical entity that is extremely important to understand. Like a properties of the two phases do not really drastically change at the interface of the surface as one typically draws or would expect. But often what happens is there is in fact, an interfacial region over which the surface is change slowly. There are issues related to this I mean there are can be situations where this interface eventually broadens with time, but for the time being, we will not discuss about those cases. Of course, in case the two phases are completely miscible, then eventually miscibility you can sort of re look from a new prospective now, miscibility is a situation where the interface ceases to exist. And certain other implications of miscibility are we will also talk as we look into certain other issues related to surface tension.

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Surface Tension / Energy
Amount of energy necessary to create a surface.

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

Coordination number at surface is low!

This is a term that all of you are very, very familiar with surface tension; it is often also called surface energy. So, what exactly is this so called surface energy. If you remember at this point, I would tell you to remember the first law of thermodynamics, which states that the energy is constant. Suppose, you have a block of butter and you take a knife, you cut it into two half. Now, as you cut it into two half, you are spending some amount of your own metabolic energy, but once you cut it you if you notice that no amount of butter is sticking to your knife then essentially before and after cutting mass is conserved.

Why did you in fact, spend this much of amount energy and reality is that you have. In fact, spend this amount of energy in creating the two additional surfaces corresponding to the two smaller blocks, so that is I am in sort of a very simple, but practically manifestation of surface energy yes you. In fact, need to spend energy to create a new surface. So, what it is a like? So, here you have a material a bulk material let say and you are cutting it let us into half two materials. So, in order to cut it into these two half you are actually crating surface here and here what you are actually doing you are.

In fact, removing or over coming by spending this energy from outside you are overcoming the interaction between these molecules. Please understand these are not chemical bonds, because you are not breaking individual components of a molecule, but you are essentially dislodging molecules or removing the molecules of the same material.

What are you essentially overcoming, you are overcoming the interaction forces between them; irrespective of the material we have already learned that one of the type of interaction can be the van der Waals forces.

Of course, if your material has polarity then that can be polar interactions like hydrogen bond etcetera, which also you are overcome. So, the first definition that comes, so the first things allow one of the immediate things that you may start understanding that surface energy higher will be the earth. If there is polar interaction then the surface energy of the material is going to be higher than a material whether no polar interaction is, and we will see the proof of this soon.

Simple definition of surface tension or surface energy is the amount of energy necessary to create a surface typically per unit area or whatever you write. From a molecules (Refer Time: 08:13), what happens is, what is also important is from if the standpoint of the single molecule what is the fundamental difference now between these two molecules. Please understand that this molecule was earlier resting over here or this is the same molecule, and therefore it had no difference with this particular molecule.

But once you have created the surface, now these molecules have different properties. And can you identify, what is the difference in property? The difference in property is you say this molecule is surrounded by 6 numbers of molecules. According to this particular sketch there can be other types of arrangements also and this is a brief sketch. And you see roughly you pick up any molecule in the bulk, you find the ways I have drawn all of them are surrounded by 6 numbers of molecules. So, what is this called this is called the coordination number.


Even if you consider simple van der Waals interaction between all the molecules. So, it is sought of has identical interaction in all directions. So, the net force acting on this molecule is sort of zero, because you have similar molecules the interaction is same across in all directions, so net force is 0.

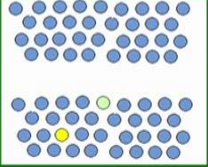
However, now you see any molecule that resting on the on the surface. It has a similar interaction with these molecules, which are all identical molecules of the same material, but there is nothing on this side, there is nothing on this side. So, one immediate thing that you see that not only this one, but let say any surface molecule is sort of surrounded by lesser number of molecules or the coordination number at surface is low. What is the

consequence, consequences is the net force acting on this molecule is none of zero, and this is the energy that you actually need to supply. You just multiply the net energy that is required for one molecule net unbalanced energy for one molecule multiplied by the number of surface molecules that is the energy you actually need to supply to create a surface and this is the manifested as surface tension.

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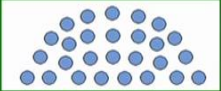
Surface Tension





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

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




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

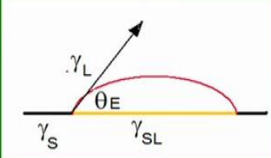
I will revisit this somewhat later.

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Young's Equation



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



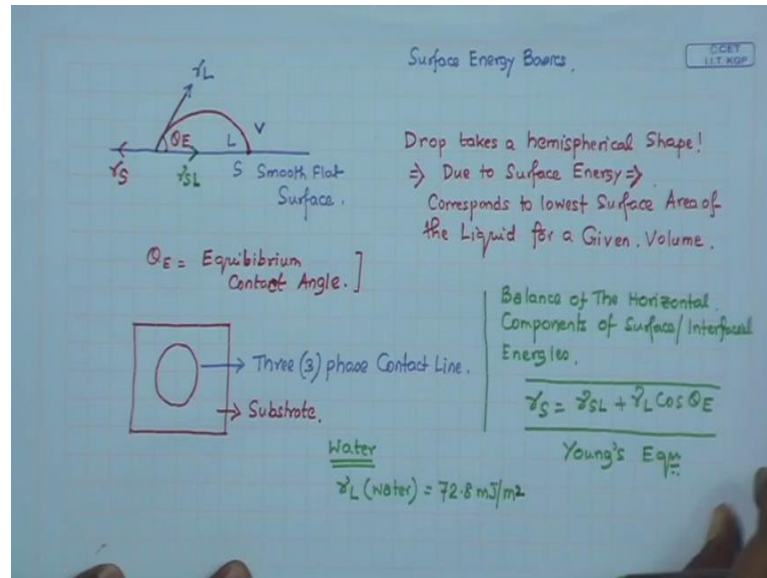
$$\gamma_S = \gamma_{SL} + \gamma_L \cos \theta_E.$$

θ_E is the Equilibrium Contact Angle

What happens to the vertical component of the forces

Before that let me pick up a simpler example that involves surface energy. And this is a very important concept where a very simple concept also. So, what you have is this is something that you have to visit again and again and again.

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Suppose, we have a smooth flat surface, and you put a drop of water onto it. You all know that in most cases that drop takes a hemispherical shape; most of you also know that this hemispherical shape is due to surface tension energy. (Refer Time: 12:14) one-step higher we can go and identify. In fact, this hemispherical shape corresponds to the lowest possible surface area for a given volume or a given mass given volume, let say. So, there can be different other configurations also this, in fact corresponds to area of the liquid for a given volume.

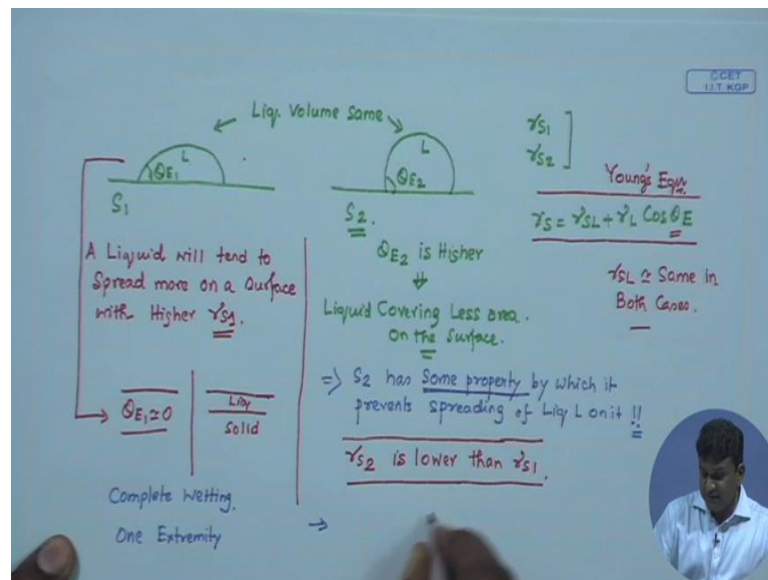
Now once the drop is at rest, so you can identify certain things; and one of the critical things that is identified is theta E, which is known as the equilibrium contact angle. Why it is so called, because this is the shape of the drop at equilibrium. Now, we have already talked about surface tension and interfacial tension. So, this particular solid as a surface tension the liquid also has a surface tension where are they acting. So, over here the solid surface tension acts, which we will term as gamma s, along if you draw tangent at the point of contact.

Just for your knowledge if you see the drops from the top this is the thing we will get this part of this figure. So, this is the substrate this particular line is called the three phase

contact. Why three phase is a contact line, because you have solid, you have liquid and you have vapor, all the three are coming in contact simultaneously along this line. So, if you do try to draw a free body diagram or try to do a force balance, if you draw a tangent to the liquid meniscus at this point along this line, the liquid surface tension acts. And what is the energy component along this line. See, over this area now the solid is covered under liquid. So, the solid is condense phase, the liquid is a condense phase so in fact over this area the γ_s is no longer acting it is γ_{sL} , it is actually an interface liquid solid interface.

If you do a balance of the horizontal components of surface and interfacial energies, what you will get is $\gamma_s \cos \theta = \gamma_{sL} + \gamma_L \cos \theta$. This is a very, very important equation and this is known as young's equation. What does it give you, it gives you many things, and though the equation is very simple the consequences are not simple. Suppose, you would like to put the same drop let us assume the drop is of water, which is the most commonly encounter liquid, and this is one number you may want to note down γ_L for water is 72.8 milli joule per meter square.

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Now, suppose I dispense I take two surfaces two solid surfaces S_1 and S_2 ; and I put water to the same liquid and this is what I get. This is very, very logical and common because the two solid surfaces are likely to have two difference surfaces. But based on the equations what we have already written can you comment anything. Well, the first

thing that you can comment is θ_E is higher. What it means is the same volume of course the liquid volume in both the cases, liquid is actually covering less area on the surface.

In other words, the surface has some property. So, this can also be look for a different prospective that the surface is two has some property by which it prevents spreading of liquid 1 on it. So, what is that property? This is important, what is the property. If you now look into this equation carefully, and for the time being, you assume both cases you will find that in fact if you now plug in to different values higher value of θ_E and versus lower value of θ_E , γ_L remaining same, you will find actually γ_{S2} is lower than γ_{S1} .

This is in fact a very important finding that what will be the shape of the drop, if you put a drop on a solid surface is going to be governed by a balance between the surface and interfacial energies of the solid and the liquid, this is one. We say if the same liquid is dispensed on different surfaces, surfaces with higher surface energy the liquid will tend to spread more. So, a liquid will tend to spread more on a surface with higher γ_S and how at you get that it is not that you have to believe because I am telling it you get it straight away from Young's equation.

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Young's Equation

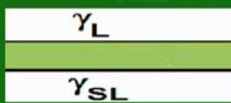
Based on the value of θ_E it is possible to have two distinct wetting regimes

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

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

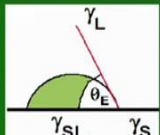
2. Partial wetting, when θ_E is finite

When
 $0 < \theta_E < 90$: the surface is lyophilic
If the liquid is water, then hydrophilic



γ_L

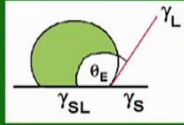
γ_{SL}



γ_L

θ_E


γ_{SL} γ_S



γ_L

θ_E

γ_{SL} γ_S

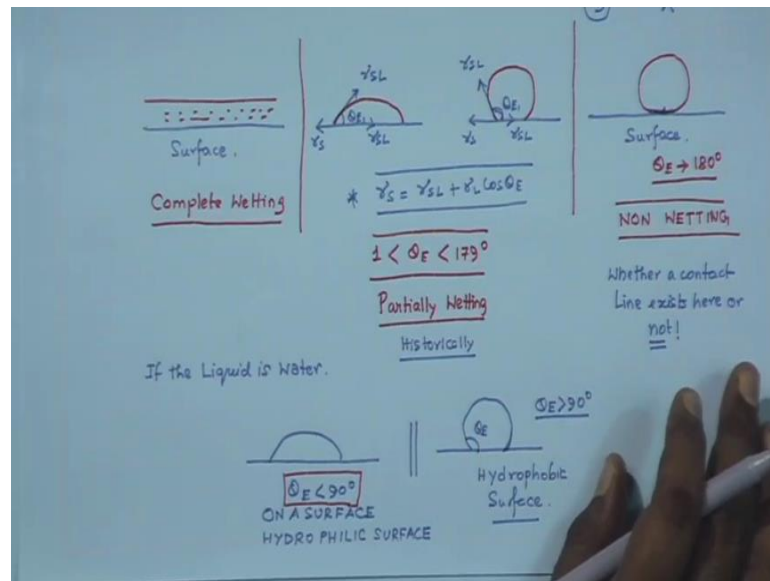


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Now, as we talk about a liquid is spreading more or spreading less then the next obvious question that comes up is what the limits of spreading are. Well, if you now look

carefully you can look into this transparency, I will redraw it of course, the limits are this is in fact one of the limits. And what do you see you actually see the liquid is spreading fully on the solid. And how can this picture be transformed into this particular picture. So, this is the liquid, this is the solid you in fact, consider theta E 1 equal to 0, and you get this type of a configuration. This is what is known as complete wetting versus what is the other extremity. So, the other extremity is so on one hand we have complete wetting, I take another slide.

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All these scribbles I will also upload, so that you can refer to them and correlate to the notes. So, you have a surface and you have a film that is fully wetting. So, what is the other possible limit, what is the minimum liquid can spread, where a liquid spreading will be least if theta E tends to 180 degree. Now, this does not happen, but well surface is with contacts angle close to 165 or 170 has been achieved. In between you can have all different values of theta pairing let say from 1 degree to 179 degree. So, theoretically for the time being you transmitted this does not happen this is non-wetting. And in between any contact angle it is actually partially wetting.

If you look very carefully and a sort of do a bit of thinking, it is say debatable question on whether a contact line exists here by contact line I mean a three phase contact line. A contact line exists here or not. For the time being, let us not bother too much about this particular situation, because this is still a theoretical conjuncture I mean compete 180

degree wetting while a drop is in contact is slightly difficult to perceive. A people have started to use methods like cavitations and things like that where the drop is not in contact then one can achieve a completely spherical drop, but whether you have a solid liquid contact line or not that is a bit debatable.

We worry more about this setting which is which you have actually see in most of the cases. So, here you can identify the equilibrium contact angle. See, irrespective of the contact angle in fact your equation remains, the Young's equation a remains fully valid. And you can always claim that the setting is roughly same, whether your equilibrium contact angle is 5 degree or 160 degree because both are cases of partial wetting. But periodically or historically if the liquid is water, and it makes an equilibrium contact angle of less than 90 degree on a surface, the surface is termed as a hydrophilic surface. The limit is θ_E is less than 90 degree.

On the other hand, if the equilibrium contact angle with a water drop is greater than 90 degree then and the drop is water of course, then the surface is termed as a hydrophobic surface. Please do not forget that for a completely wetting surface, a surface on which let say water exhibits complete wetting is also a hydrophilic surface. And this discretion around 90 degree is more of the pedagogic. And in one can always ask that we what is the great difference in the property of the surface between two surfaces let say over which one in one the water contact angle is 88 degree and in the other the water contact angle is 93 degree.

Well, they are very close, but there are certain cases where difference manifests and there is something that we will learn in the next lecture. And this becomes a very, very prominent where we start talking about structural hydrophobicity or structural super hydrophobicity. Or in other words, instead of looking the wetting an flat surface we now start looking wetting on a structured surface or a pattern surface. These patterns are something that you are going to learn in course of this particular course how to make these structures.

Thank you.