Concepts of capillarity and surface tension (ST) and measurement of ST and contact angle

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Lecture-4

## Surface tension (ST) and contact angle

Welcome back. So, from now onwards, we will move on to module 2. Under module 2, we will cover topics such as capillary surface tension. We will look at various measurement techniques that are available to determine surface tension if we know contact angle or contact angle if we know surface tension. Apart from that, we will also try to understand some of the fundamental equations like, you know, Young-Dupré, Young Laplace equation. And after that we will look at the application of Young-Dupré and application of Young Laplace equation. But in this lecture we will look at the, you know ,the capillarity and surface tension, we look, at the, you know ,we will see what is surface tension and ,you know, how it is defined ,okay, and after that we will see from thermodynamics perspective, how we can define surface tension, right ,and then after that we will look at we have some 12 session also, so we try to solve this small problem exercise and after that we look at, you know ,the types of ,various types of contact angle measurement techniques, we will not describe them in detail but we try to list them in today's lecture okay, right, let's begin our lecture right

(Time: 2:00)

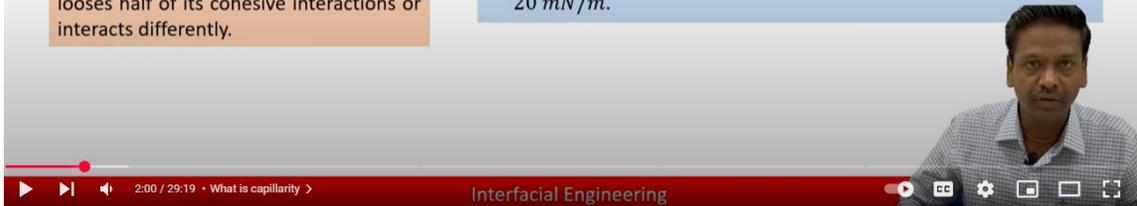## Capillarity and surface tension

Capillarity is regarded as a consequence of surface tension in the liquid at the solid-liquid interface, and the usual expression for the capillary rise is derived from this idea.
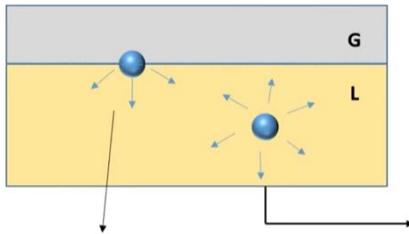
Molecules that approach the interface looses half of its cohesive interactions or interacts differently.

➤ If cohesion energy per molecule is U in the bulk, then a molecule sitting at the surface finds itself short of roughly U/2.

➤ The ST is a measure of the shortfall of energy per unit surface area.

➤ Water involves hydrogen bonds, hence its ST is larger ($72 \frac{mN}{m}$ at 25°C).

➤ Oil involves van der Waals type interactions and its ST is $\approx$ $20\ mN/m$.

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Interfacial Engineering

So, first of all, let us first understand what capillarity is. So, capillarity is regarded as a consequence of surface tension. We are going to look at the capillary rise. So, capillary rise is due to the upward movement of the liquid through the narrow space.

The process by which liquid climbs up the surface through a narrowed, I mean, a narrow space or the porous channel. It is due to manifestation of forces of cohesion, adhesion and surface tension. Surface tension and capillarity both go hand in hand because capillarity is regarded as a consequence of surface tension. In this lecture we are going to look at first what is known as surface tension. And I am going to briefly touch upon from the thermodynamic perspective how we can understand surface tension. And we are going to look at combined first and second law of thermodynamics.

So, from combined first and second law of thermodynamics how we can define surface tension. right and after that we'll solve with a small exercise, we'll see small exercise and we'll try to ,you know ,calculate specific surface area from given, you know, image, right, yeah ,so first let us understand what is surface tension, so it is basically nothing but cohesive energy per molecule Let's say, Let's assume that ,molecules in the bulk, there are molecules in the bulk. These molecules are, if you look at in the bulk, the molecules are surrounded by each neighboring molecule. So, there will be interaction from all the neighboring molecules from all directions, 360 degree.

And since all the neighboring molecules interact and there will be a pairwise interaction between all the molecules, we can understand that, the interaction of that, I mean, the cohesive energy per molecule in bulk, let's say, we denote it as U. Now it is a similar case if we take a molecule and assume that the molecule is at the interface. Now at the

interface, there is a shortfall of energy. It's because there are two adjoining phases here, one is the the sub phase which is nothing but ,you know, let's say we talk about water air in this case, you create a water air interface in this case because your sub phase is water okay we're talking about water air in this case, right, now so since part of the molecule is exposed to water side and the remaining part is exposed to air side So, the part exposed to air side, loses contact with its neighboring molecules. So, the interaction in this case is expected to be less than the interaction in the bulk.

So, this shortfall of energy, leads to, you know, the changes in the net, so there will be net imbalance in the force, okay, which cause the molecules to minimize their contact area within the adjoining bulk phase, right, which is air in this case ,so that there will be a downward force okay and that is nothing but the force will be acting downward in this case because they want to maximize their contact area, within the, you know, the the sub phase okay so that they will get more contact with their own molecules okay In such case, you would expect there will be a net imbalance in the force. So, eventually force will be acting downward which is nothing but surface tension in this case. So, you can understand in this way also the cohesion energy per molecule. Let's say, if molecules are confined in the bulb, the cohesive energy of molecules, I mean energy per molecule is U. If you denote that as U, then we can say that the cohesive energy of molecules at the interface is U/2. This is because of the shortfall of energy. in the absence of neighboring molecules, the molecule experiences net imbalance in the form and that is acting downward because they want to maximize their contact with their own neighboring molecules.
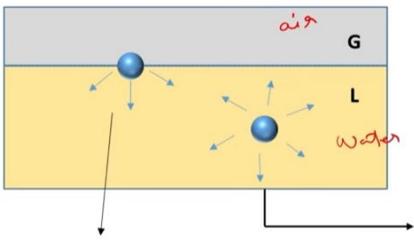
So, this is nothing but surface tension. So in a nutshell, you will have at the surface, at the interface, there will be a force, line of tension, okay along the length of the surface okay because of the shortfall of energy okay so that's why it is often expressed in terms of Newton per meter, unlike, you know, pressure unit, this is always expressed in force per unit length, right, length of the surface, right, So because this is acting at the surface. The shortfall of energy is due to the molecules because some of the molecules are confined at the interface. So, we can also get more insight into the surface tension. So now, let's ask a question. So, is this going to be the same in all the, you know, in different kinds of, I mean, in different types of interfaces as well? For example, let's say in this case, you have taken an example of an air-water interface. What if I replace this air with some other fluid, okay? or you know some other liquid say, for example, i replace air with oil like a substance so you will have a two immiscible mixture one is water and the another one will be oil ,in this case, what will be the surface tension okay so the surface tension in this case will be drastically different it is because of the interaction between the molecule, at the interphase so they are experiencing they are exposed to two different adjoining phases ,so the neighboring molecules are entirely different , So, in the case of water air, the surface tension is, you know, little larger than any alkane water system.

Okay. So, here it is 72 milliNewton per meter. At same temperature, if you measure for oil water, it is 20 milliNewton per meter. The difference is due to the different types of interaction. In the case of air-water interface, there is significant increase in surface tension. In the cas e of air-water interface, it is because of the hydrogen bond , you know, hydrogen interaction, right? Hydrogen bond interaction. Whereas in the case of oil, water- oil interface system, it is because of the Van der Waals type interactions. So, because the, as the types of, as the molecules type changes, the interactions, you know, that come along with the molecules also change because of which the surface tension value also goes down. I mean, it changes drastically.

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So, this is nothing but surface tension.

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Surface energy and capillary force

It is a known fact that supplying energy is needed to create surfaces.

$$\delta W = \gamma \cdot dA$$

Work required to increase the surface area by an amount dA

Work required is proportional to the no. of surface molecules.

$$G = f(T, P, n, A)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n,A} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n,A} dP + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,P,A,n_j} dn_i + \left(\frac{\partial G}{\partial A}\right)_{T,P,n} dA$$

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,P,n}$$

Molecules that approach the interface looses half of its cohesive interactions or interacts differently.

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10:53 / 29:19 • Surface tension and work

Interfacial Engineering

Now we look at, So, we can also relate surface tension with respect to work done. Let's imagine, we have, okay let's imagine that we have, filled, you know, in a container, we pour water and fill the container like this ,okay, right ,now at the interface right between water and the air i place a very thin wire okay very thin wire and interface, maybe, i can draw something like this, right, very thin wire okay it is very light in weight so it floats it doesn't sink and it doesn't settle, i mean, it doesn't sink in the water so it just floats at the surface, now this wire is very, you know, tiny and light in weight so you know that there is surface tension acting along this thin wire at the interface so eventually what happens because this water molecule tries to maximize that contact area so there will be a net imbalance in the force, there will be force in the downward direction so this surface tension will pull this wire you know ,downward, right, in this way, right, so if we assume that at time, t=0, this thin wire is placed at the interface maybe after some time if you look at this thin wire would have been displaced to, displaced a bit from the surface, okay, in the z direction There will be small displacement. okay at the surface because of the surface tension now this is at any, t ,right, so ,so ,that the thin wire would have moved, uh, in the z direction downward okay so small displacement would have happened because the surface tension pushed the thin wire downward, right ,so now, uh, we know that some work is uh being done by the system in this case now we can relate this work with respect to I mean with surface tension, so one can say that if I apply equal amount of work ,okay, and then I can bring this wire back to its original position. That means the work done in this case is nothing but γ into d. Because we know γ, γ is surface tension. Now the surface tension, you know, you know, and the I mean the product of surface tension and the change in area should give as the work done ,right, by the system

in this case or you can impose equal amount of work so that you bring this wire back to its original position so in this case we can delete the work done with surface tension in this way so

$$\delta W = \gamma dA$$

Now, we can also define γ from the thermodynamic perspective. Let's say we know that G, which is Gibbs free energy,

$$G = f(T, P, n, A)$$

By employing the total derivative approach, one can get the equation in this differential form. In this differential form
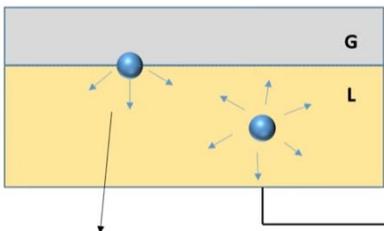
$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n,A} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n,A} dP + \left(\frac{\partial G}{\partial ni}\right)_{T,P,n} dni + \left(\frac{\partial G}{\partial A}\right)_{T,P,n} dA$$

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{T,P,n}$$

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So now we can even look at from the Combined first and second law of thermodynamics, how we can get the definition for surface tension? We know the first law of thermodynamics and we know the second law of thermodynamics. Now by using combined first and second law of thermodynamics, can we get the relationship for surface

tension? okay with Gibbs free energy, the same partial ,you know, that the same relation that we get when we try to derive using combined first and second law of thermodynamics right yeah, now we will look at how we can define γ okay,

So we know from the first law of thermodynamics we know what is,

$$du = \delta q + \delta W$$

So this is our first law of thermodynamics, for a closed system, now if I expand this I know for reversible system

$$du = TdS + \delta W$$

Now here because so this comes from the second law of thermodynamics. So, the relationship for ∂q comes from the second law of thermodynamics. Now we can call this equation as combined first and second law of thermodynamics. Okay right now

$$\delta W_{total} = \delta W_{pv} + \delta W_{non-pv}$$

$$du = TdS + \delta W_{pv} + \delta W_{non-pv}$$

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For reversible system,

$$du = TdS - \text{pdv} + \delta W_{non-pv} \qquad \ldots (1)$$

Okay this minus takes care of the suitable sine convention that means if work is done by the system it should be, negative, then on the system, should be positive so this minus takes care of that sine convention ,

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We also know our Gibbs free energy equation which is nothing but

$$g = \text{h} - \text{TS}$$

Now if I differentiate this I would simply get

$$dg = d(U + PV) - SdT - TdS$$

$$dg = \left(TdS - PdV + \delta W_{non-pv}\right) + PdV + VdP - SdT - TdS \qquad \ldots (2)$$

If we impose a condition that at constant temperature, okay, at constant temperature and pressure. So,

$$dg = \delta W_{non-pv} \qquad \rightarrow \gamma dA$$

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We can even say γ is nothing but $\partial G/\partial A$ at constant temperature and pressure.

$$\gamma = \left(\frac{\partial g}{\partial A}\right)_{T,P}$$

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Alright, so, we know, the relation from both way, we can relate, we can find γ as, γ is nothing but $\partial G/\partial A$ at constant temperature and pressure.

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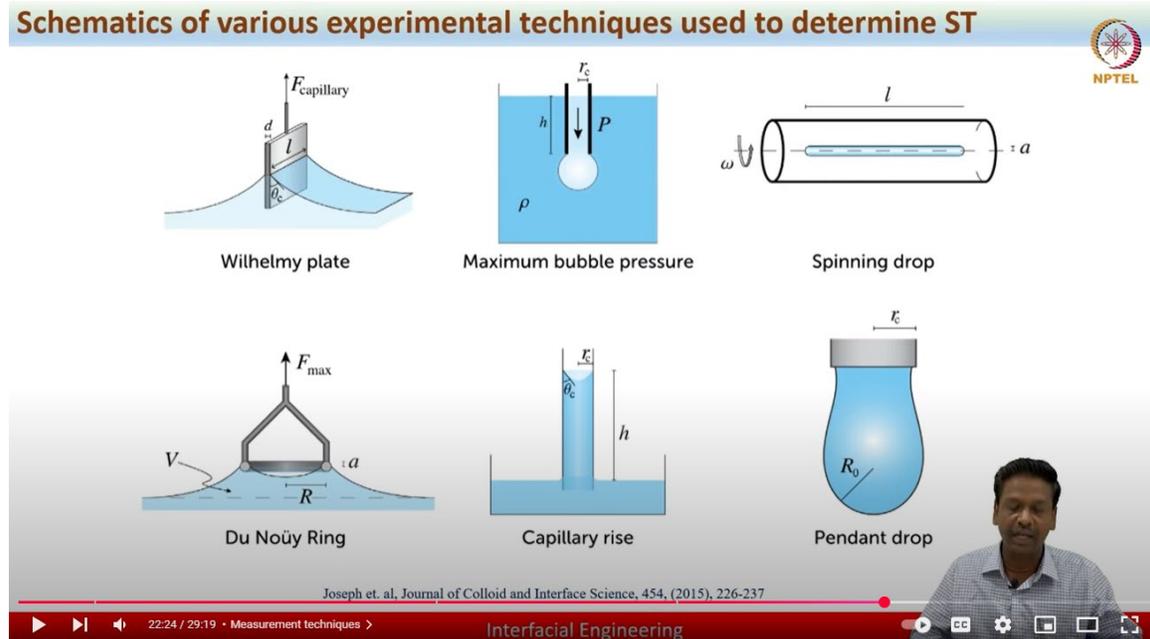
Now, we will look at different types of measurement techniques that are available to determine surface tension. So, we are going to, there are, I mean, at least there are, I mean, a couple of them is quite often used, but many have been proposed by, you know, at different i mean from time to time so we can you know list i mean we can name some of them here we have what is known as Wilhelmy plate and maximum bubble pressure, spinning drop, Du Noüy ring, capital rise pendant drop method and so on Although there are many more techniques available, we are only listing few of them which are quite familiar.

So, among these, we will discuss the Wilhelmy plate and capillary rise in detail. and Wilhelmy plate and Du Noüy ring, both works on a similar principle only the geometry are different okay geometry is different so we will see the principle of Wilhelmy plate and capillary rise in next video lecture but at least we should know there are different techniques available to measure surface tension if we know what is contact angle or contact angle if we know surface tension, so contact angle is the angle established by liquid on the solid surface we are talking about solid surface, a simple solid and on top of which you have a liquid drop if I place a liquid drop or if I spread a liquid on top of the solid surface where the liquid will completely wet okay ,or not depends on the contact angle established by the liquid with the solid surface ,okay, say for example so liquid may be partially wetting which means that they may be spreading to some extent

although they are not completely spreading in such case you would expect theta to be less than 90° okay whereas on the other hand so the drop may not spread they may want to detach from the surface they may want to detach from the surface in such case it will establish theta, which may be greater than 90° so so something like this okay So in such case theta may be greater than 90°.

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There are many macroscopic applications where the macroscopic properties are governed by microscopic properties like surface tension, theta which we will see in detail later.
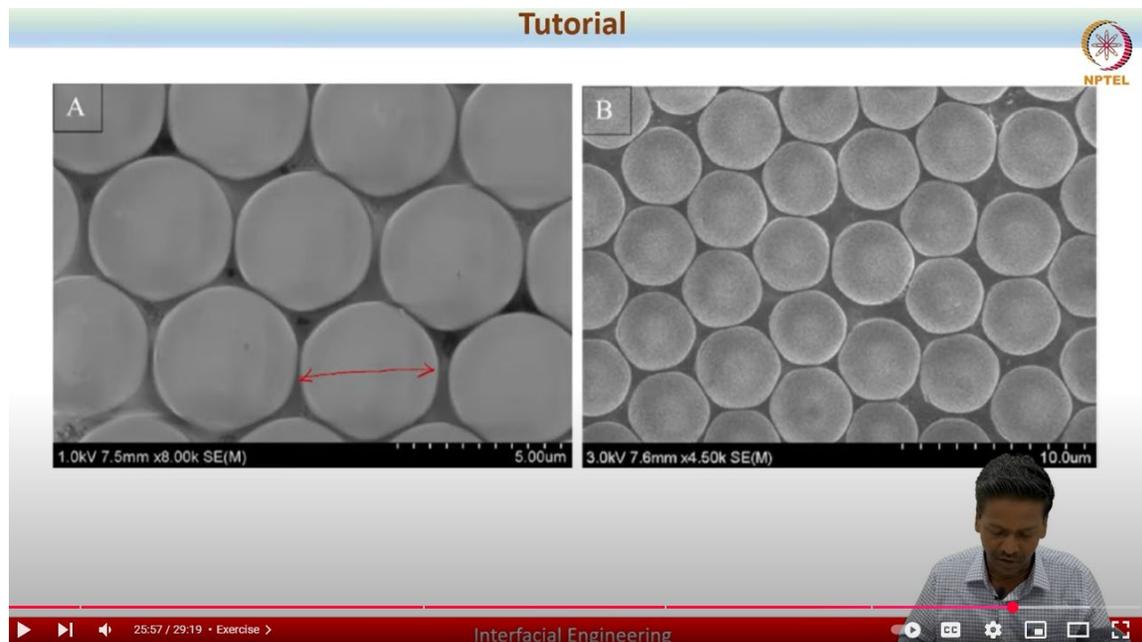
So, now we will move on to the small exercise. We will try to do some small exercise. In this tutorial, let's say we have scanning electron microscopic images and what you see here is the silica particles. So, there are number of silica particles. and you can see the scale bar at the bottom of this image which is which says that the scale bar of this length is 5 μm ,okay, so if i press this scale bar and try to fit in this particle i can actually calculate or reduce diameter size of the particle so in this way one can do ,you know, reduce diameter for you know you know for large number of particles and try to take the average out of that okay so if one does for a large number of particles and get the average that will be you know i mean that we have i mean we can even report along with the error also, right, in such case so let's say in this case the average size of the silica particle is let's say 4 μm the diameter the radius of this will be 2 μm okay ,So we know for a spherical particle the specific surface area

$$A_{SP} = \frac{3}{\rho R_s}$$

$$\text{SSA} = \frac{3}{\left(2000 \frac{kg}{m^3} \times 2 \times 10^{-6} m\right)}$$

$$= \frac{3}{4000 \times 10^{-6}}$$

$$= \frac{3}{4} \times 10^3$$

$$= 0.75 \times 10^3 \text{ m}^2/\text{kg}$$

$$= 0.75 \text{ m}^2/\text{g}$$

So, in this way also you can calculate the specific surface area of a given particle. So, this couple of we have done a similar problem in module 1. Okay, for different geometry, right? So, this will be based on scanning electron microscopic images. So, can we calculate?

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So here we ask the question like, can we calculate what is the specific surface area in this case? So, we'll stop here and we'll continue from the next lecture. Thank you.