Young-Dupre equation; Tutorial

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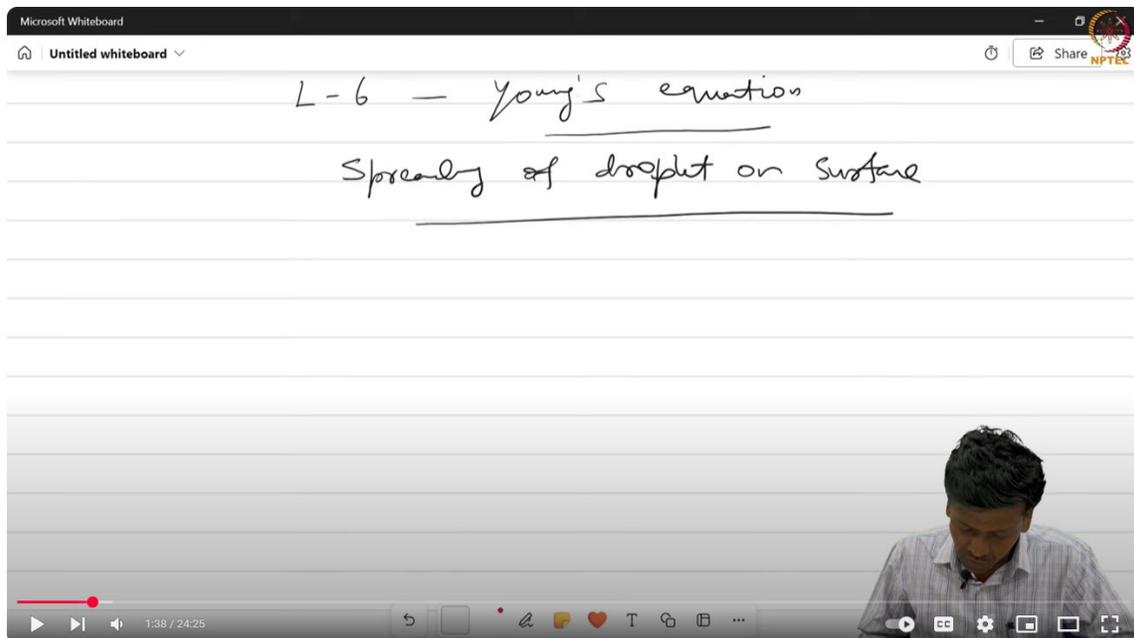**Department Chemical Engineering**

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Lecture-6

Contact angle and wetting behavior

Welcome back. So, in today's video lecture, we will look at the derivation of Young's equation, right? So, in the last class, we looked at various measurement techniques, okay? We looked at it like, you know, using the capillary method as well as the Wilhelmy plate method and maximum bubble pressure method. we have shown that how you can measure surface tension if theta is known, right? So in today's lecture we will look at it was spreading of droplet on surface so this is important when you want to understand you know the surface property okay whether a droplet, a little droplet will spread nicely on the surface or not can be easily assessed using what is known as by knowing the conduct angle, but we can also use the relation, I mean, the relation proposed by, the equation proposed by Young's, right? So, we'll see that part in today's lecture, okay? Right, we move, let's begin our lecture, right? Yeah.

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So, in today's lecture, we will look at How spreading a droplet on surface, right? You know, or how the surface will influence the spreading of a droplet, right? So, let's say we have surface. And we want to understand whether a liquid droplet, if I place it on the surface, will it have a tendency to spread or will it have a tendency to retract, right? So wetting or de-wetting characteristics of surface can be easily quantified or assessed using what is known as Young's equation. So, we are going to look at. The importance of this equation in various applications. For example, in this equation, we are going to look at the competitive forces, surface energy, various surface energy, that exist.

when we spread liquid on the surface. For example, γ_{SG}, which is associated with surface and gas phase, which is exposed to, and γ_{SL} and γ_{LG}. So, these three competitive surface energies will decide or will dictate what is going to be the contact angle of a given liquid. Now, what is the importance of this, you know, study is, let's say, whenever you want to understand, let's say for the application of, you know, the, you know, farming and pesticide where you use pesticide to promote plant growth. there we want to know whether the pesticide which we will spray on the leaves or branches of tree will spread nicely or not because here the spreading is very important right so in this case you want the surface to be more hydrophilic in nature, okay ,based on which you will design your the formulation so the liquid will spread on the surface ,right, on the other hand You want to make, let's say, you want to make, you know, waterproof fabric.

In this case, you want the surface to have more water repellent property, right? Usually, you should exhibit the contact angle with, you know, the water. above 150 or 160 degree in this case you would expect the surface to behave like a super hydrophobic right so in these applications one would want to quantify the surface like whether it is naturally hydrophilic or hydrophobic or not, if not one would want to modify the surface so that it can be used for the given application right so so in this case we will look at a one important equation proposed by Young himself. So, before we begin, let's understand the assumptions proposed by Young, which is nothing but this equation can be used, right, only when equilibrium condition is, you know, considered, right? For example, in this case, when we place a droplet, okay, we are not interested in measuring the theta instantaneously, rather we are interested in measuring the equilibrium contact angle. So which means that equilibrium condition the, you know, the shoot code, right? So equilibrium conditions are attained. So, we assume that the droplet does attain equilibrium condition, right? Okay? The second important assumption is the surface should be smooth. So, it must be smooth and homogeneous.

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So, which comes to say, this equation is not valid for surface where it has roughness, right? The surface with roughness and chemically heterogeneous surface. So, in these cases, this equation is not applied, right? Or applicable. And third one is no imbibing or surface should not absorb any liquid. Okay. Should not absorb any liquid or no imbibing conditions. Okay, so this should imbibe. Only then can we say that this equation can be used, right, you know, with all these conditions made.

Okay, so let's begin by how we can calculate or understand the contact angle which is three-phase contact angle. Let's look at the sessile drop for this case.

Let's say we place a droplet on the surface. The theta that we define is nothing, but the theta established on the liquid or solid is nothing but theta. which is also nothing but three-phase contact angle because at this point junction, at this junction all three phases exist for example solid liquid gas all three phases exist that's why we call it as a three phase contact angle okay so what is there are three governing forces which dictate the contact angle which decides what is going to be the theta on the surface for example when you spread low energy liquid on high energy surface it will spread whereas When you spread high energy liquid over low energy surface, it will not. This is actually dictated by the surface energy.

As I explained already, there are three competitive forces which exist in this case. They are nothing but γ_{SG}, which is because of association with solid and gas. and γ_{SL}, so this γ_{SL} is this part, this part is nothing but γ_{SL} whereas this is nothing but γ_{SG} and this is nothing but γ_{LG}.

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So, if you look at this equation Let's say when we spread droplet, the components, you know, that the components of γ_{SL} plus γ_{LG}, okay, cos theta. This ensures that the droplet is spreading. On the other hand γ_{SG} which will try to opposed spreading because this want expose maximum exposure with the gas but when you try to spread liquid this particular force will try to oppose it that's why there are two competitive forces in this case there will be two counteracting forces one will be some total of γ_{SL} and γ_{LG} cos theta the other one will be γ_{SG}, right So why this cos theta coming into picture is because LG is the γ liquid which is associated with the gas because it establishes a surface with some angle that is called theta. There will be, you know, the component of the resulting component will be γ_{LG} cos theta, which you can obtain through a simple geometric relation, right? So, this is nothing but, so this will yield, because there are two competitive forces, so this will yield an equation at equilibrium. What will happen is both these contracting forces balance each other, so it will you will get an equation in this way which is nothing but

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG}\cos\theta$$

because this force is acting in the positive x direction whereas γ_{SL} and LG acts in the negative x direction so at equilibrium both should be equal So, in this way you can calculate what theta is. Okay

$$\cos\theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}$$

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so, this Young equation can be used to quantify working with the theta on a given surface, right, yeah so one can derive this equation alternatively also using the Gibbs change in Gibbs free energy equation which is nothing but energy after droplet attend the equilibrium and energy from the initial configuration. So, if droplet has to spread, then the energy associated with the final configuration should be minimum compared to the initial. So in this way, you can say that the process is spontaneous.

So what we can try to show is, let's say initially we have droplet When you place a droplet, the droplet sits on the surface at time t equal to zero. But after it reaches the contact point, it will try to spread. And then at equilibrium, it will spread until it reaches the equilibrium. This is what we know. So, let's understand that this. Initial and final configuration we look like this okay so okay yeah, so this is actually initial, and this part is final after spreading right

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$$\cos\theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}$$

$$dG = Final - Initial$$

$$\frac{dG}{w} = \left(\gamma_{SL} \times \delta L + \gamma_{LG} \times \delta L \cos\theta\right) - \gamma_{SG} \times \delta L$$

after it attains equilibrium So let's say if we assume that this process is spontaneous, now how we arrive at this equation is what we are going to look at, this alternative way of obtaining this equation, right? So, if you look at this, this surface, right, is now covered by γ_{SL}, which means that Previously this was occupied by γ_{SG}. Now that surface energy is launched because that is replaced by γ_{SL}. So, γ_{SG} no longer exists. Right. So, we know this γ_{SL} and at the same time this the area associated with the γ_{LG} has also increased because of the spreading. So if you want to understand this increase in area, one can calculate using the geometric relation which is nothing but in this case it is nothing but δ, if I say this is nothing but δL, if I say this part, this length change in length nothing but δL then the increase in area due to the spreading of droplet is nothing but $x = \delta L \cos\theta$. Okay, so we know this part also. So, because of the spreading, you know, some of the γ_{SG} parts are replaced by γ_{SL}, so that γ_{SG} is lost. At the same time, because new energy is created, new surface is created as the droplet spreads, you will also have change in area with respect to due to droplet spreading associated with γ_{LG}. So, you will have a component there, γ_{LG}, the entire cost data. So, we will now write these things in detail in the form of equation.

$$dG = Final - Initial$$

Nothing but, you know, I know γ_{SL} because γ_{SG} is replaced by γ_{SL}. So, this part is γ_{SL}. So, γ_{SG} no longer exists. So, it is nothing but γ_{SL} into δL. So, if you look at this, γ_{SL} into δL is nothing but the force, simply nothing but the force, because it will be Newton ultimately. So, to make this equation consistent, we will divide this change into Gibbs free energy with respect to unit of weight, so that the equation is consistent throughout.

Because of the spreading, because it establishes some angles with solid surface, and you can obtain using the geometric rule. So, based on which you will get

$$dG = (\gamma_{SL} \cdot \delta L + \gamma_{LG} cos\theta \cdot \delta L)\text{-}\gamma_{SG}\delta L$$

And my initial configuration, I mean, when I split droplet, when it just touches the surface, hits the surface, at that time, what was existing before splitting was γ_{SG} itself. That is what I am going to write in this case, right? which is again multiplied by delta L. That portion, γ_{SG} into delta L, is going to be replaced by γ_{SL}. δL, right? After, you know, spiriting, right? Yeah. So, now we know at equilibrium,

$$\frac{dG}{w} = (\gamma_{SL} \cdot \delta L + \gamma_{LG} cos\theta \cdot \delta L) - \gamma_{SG}.\delta L$$

$$(\gamma_{SL} \cdot \delta L + \gamma_{LG} cos\theta \cdot \delta L) = \gamma_{SG}.\delta L$$

$$\gamma_{SG} = (\gamma_{SL} + \gamma_{LG} \, cos\theta)$$

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$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG}\cos\theta$$

$$\cos\theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}$$

So, based on this equation we will also try to solve the tutorial exercise and exercise in this lecture itself.

Now we will move on to the tutorial part. So, the tutorial part So we have got a couple of equations. One is based on the capillary method that we saw in the previous lecture. Capillary method used in the previous lecture and the other one is based on the Young equation. Sometimes it is also known as Young-Duprey equation. You will find in many textbooks it is called as Young equation, but it is also sometimes known as Young-Duprey equation. So, in this exercise, we are going to calculate the rise of ethanol, okay? Basically, nothing but the height of the liquid column is what we are going to measure. We know the relation, right, that we obtained using the capillary method, which is nothing but

$$\Delta P = \frac{2\gamma\cos\theta}{R_c}$$

$$\rho g h = \frac{2\gamma\cos\theta}{R_c}$$

$$h = \frac{2\gamma\cos\theta}{\rho g R_c}$$

Rc is the capillary radius, right, so we know the So you can check that, right, yeah

$$h = \frac{2 * 0.224}{0.1 * 10^{-3} * 790 * 9.81}$$

$$h \approx 57mm$$

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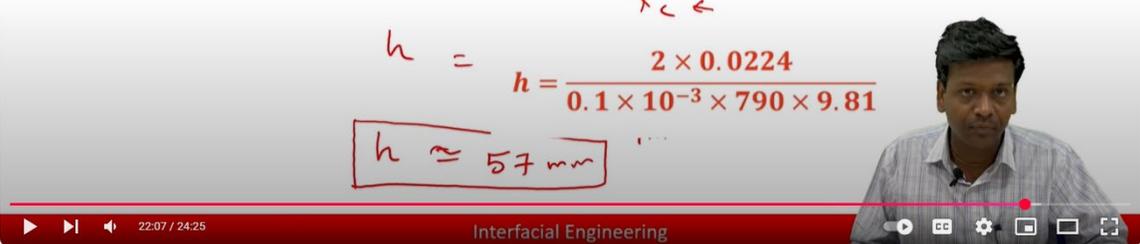So the next exercise is going to be using the Young Dupre equation or Young equation can we calculate what is the wetting angle of alumina by a nickel based liquid, so some of the data is given already, so we know γ aluminum gas, so

$$\gamma_{SG} = 0.9 \text{ N/m}$$

$$\gamma_{LG} = 1.72 \text{ N/m}$$

$$\gamma_{SL} = 2.3 \text{ N/m}$$

So, we know what is

$$\cos\theta = = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}$$

So if I simply substitute all these values here,

$$\cos\theta = \frac{0.9 - 2.3}{1.72}$$

$$\theta = \cos - 1(\frac{0.9 - 2.3}{1.72})$$

$$\theta = 144°$$

So, it is highly hydrophobic. The surface is highly hydrophobic. So, comment on the wetting of the liquid. So, you can say that because theta is greater than 90 degree. Since it is hydrophobic, in fact, this is almost, I mean, it is, you can say that theta is very high. So it is almost like a super hydrophobic surface.

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So you can comment saying that the liquid will not wet the surface so easily, right? So we can stop here. We can continue from the next lecture. Thank you.