Interfacial Engineering

Dr Manigandan S.

Department Chemical Engineering

Indian Institute of Technology, Ropar

Lecture-10

Measurement of contact angle of surfaces at fluid-fluid interfaces

Contact angle; equilibrium position; air-water interface; oil-water interface; dip coating; FESEM

Welcome back.

So in today's video lecture, we will look at the measurement of contact angle of surfaces at fluid-fluid interfaces. So far we looked at various measurement techniques. You know, let's say we have looked at sessile drop method. wherein if you place a drop of liquid on the surface, can we measure the three-phase contact angle using the Young-Duprey equation. So these things we addressed so far.

What if we experience a slightly different situation? Let's say the particle is sitting at the fluid-fluid interfaces. Let us say not on the solid surface, but they are sitting across the fluid fluid interfaces. In such scenario, how one can measure the contact angle? This is important when we deal with the formulations, emulsions, foam and in those applications. The measurement of theta is going to be very important.

We will look at for such case how we can measure the theta, three-phase contact angle. Let's begin our lecture. So in today's lecture, we are going to address the question of how contact angle can be measured. Okay. So there are a few direct methods available.

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Okay, let's say if I consider a scenario where the particle colloidal particle is sitting at the interface, it can be you know fluid-fluid interface like fluid 1 and it can be fluid 2. In such scenario with respect to theta, what is the contact angle of the particle? So Sometimes this theta also is important if you want to know what is the equilibrium position of the particles. So there are various methods available. It could be gel trapping method. One can use the gel trapping to understand the theta but it involves you know the slightly the operation involves works at slightly elevated temperature whereas the freeze fracture shadow casting for this one has to employ cryo scanning electron microscopy.

The other one is the last but not least is the nanoparticle deposition which we are going to discuss in today's lecture. So using this technique one can understand what is the contact angle of the particles. So this may be useful sometime when we are working with let's say various pharmaceutical formulations. wherein you may have to create an emulsion or you may have to create a foam. For these applications, the measurement of contact angle will be very crucial.

So we are going to look at exactly the same thing. So how we are going to do is, we are going to use what is known as the nanoparticle deposition method. For that we have to deposit particle at the interface of your choice. Let's say it can be water air interface, water oil interface. In this schematic we have shown water air interface.

Let's say you have the particle sitting at the interface. We just deposited, we spread these particles at the interface. Now in the subphase if you look at What we will be doing is we will carry out the wet chemical deposition method. In this wet chemical deposition method, what we basically do is we nicely deposit nanoparticle on the surface, which are exposed to the water side, right? So, which means that if you look at here, the particle

exposed to the water side will have deposition, right? This is done by the wet chemical method wherein we carry out the we use the precursor gold precursor which is gold auric chloric acid so and then we also use reducing agent which is sodium borohydrate the principle you know goes like this so you have particle which is amide functionalized particle And you have the sodium gold auric chloric acid, which is also, which bears negative charge, right? Which carries negative charge with it. Since particle is amidine functionalized, it carries positive charge, right? So, there will be electrostatic interaction between the positively charged polystyrene, amidine functionalized polystyrene surface.

Here we have taken polystyrene as a representative system. So, because the auric chloric acid carries negative charge, there will be electrostatic interaction between the positive side and the auric chloric acid. So, there will be a nice binding. This auric chloric acid will nicely sit on the surface of the polystyrene, whereas the sodium borohydrate will help reducing this, you know, gold auric chloric acid. So that the nanoparticle, you know, it nucleates on the surface itself and grows over the surface, right? So this is how you create deposition of nanoparticle on the surface exposed to water side.

Remember, because there is no deposition on the air side, because there is no wet chemical reaction going on on the air side, can say that you can say that there will be no deposition on the side part exposed to air side. So in this way what you can say is you are able to trace the the equatorial plane right the part exposed to water side. In this way you can understand by visualizing these particle using the scanning electron microscopy and then so what we do is we transfer this particle onto the glass substrate using the dip-coater. So, dip-coater is necessary for this method and scanning electron microscopy is also important for this method. So, how do we do? So, once the deposition occurs, you can take an example of let's say hydrophilic particle where theta is less than 90 degree.

In this case, the nanoparticle is used as a tracer material in this case, so you can see that as they nicely deposit on the surface, you can by transferring them onto the glass substrate and imaging them using the scanning electron microscopy, what you can do is from the top You can understand from the morphology, you can understand there is an uncoated region which is denoted using the small d, right, which is denoted using the small d. So this will help us understand what is the theta 1. So in this case, the theta with respect to the interface we can measure using the simple geometric rule. So one has to deduce this small d and capital D is the diameter of the particle itself. So, using the scanning algorithm microscopy, we can very well obtain these data.

So, by using the geometric rule, we can understand this theta, which is three-phase contact angle. Similar way, one can also understand for hydrophobic particle, where theta is going to be greater than 90 degree. In this case, because very small part is exposed to water side and deposition will occur only on that surface, so when we visualize them under scanning electron microscopy, we will not be able to see from the top very easily

because this nanoparticle will be will be depositing on the lower part of the particle surface so when you try to visualize you may not be able to see so what one can do is using the carbon tape one can flip this particle so that the bottom part is now up for the you know visualization. In that way, we can measure the D. In this case, D is not the uncoated region.

D is the coated region for hydrophobic particle, correct? So, we used sodium borohydrate predominantly to show that this measurement can be carried out at room temperature itself. One can use sodium citrate and other reducing agent, but they work at a slightly elevated temperature. So, it is better to use the sodium borohydrate. Okay, so why this theta is important? So, when you work with range of particles, some particles are hydrophilic in nature, some are hydrophobic in nature. When you are working with, you know, food and, especially in the application of food and drug formulation, you may have to know what is the theta and as they may be used as, I mean, as the colloidal particle may be used as a stabilizer in some case, right? Right.

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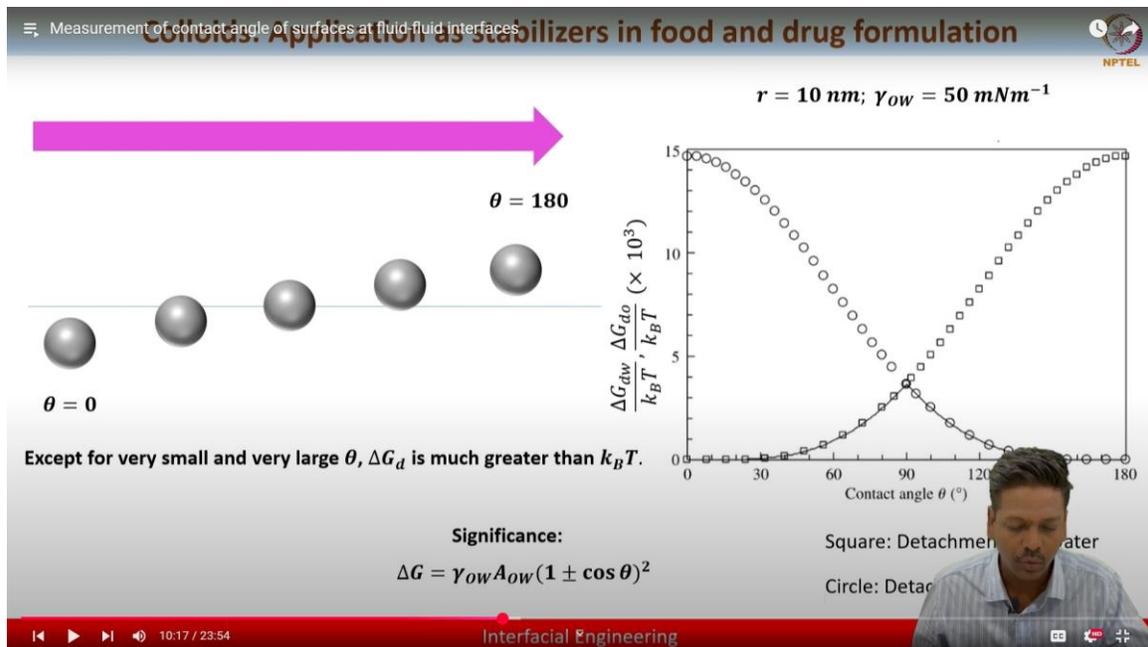
So, one important parameter is delta G detachment energy. So, what delta G detachment energy says is that, let's say the particle is, you know, exposed more into water side, it is more likely that particles can completely detach into water side not on the oil side. Let's say in this case since most of the part is exposed to oil side by while you apply when you apply a gentle force this may be pushed into the oil side right. So it is more favorable to go into the oil side. So depending on the degree of you know immersion into respective fluid whether it will completely detach into oil or water, you know, one can say using the what is known as theta, but there is something called delta G detachment.

One can quantify this using this relation, which is nothing but, you know, you can by knowing the interfacial tension of, you know, given interface, let's say water-air or water-oil, and interfacial area, which is basically a function of the radius of the particle. One can easily calculate that, and by varying θ, one can observe how $\Delta G\_detachment$ varies.

So, $1 \pm \cos\theta$ indicates that:

- For $\Delta G\_detachment$ into water, the equation is:

$$\Delta G_{\text{detachment, water}} = 1 - \cos\theta$$

- For $\Delta G\_detachment$ into oil, the equation is:

$$\Delta G_{\text{detachment, oil}} = 1 + \cos\theta$$

This means that when $\theta = 0°$ (in the case of a hydrophilic particle), $\Delta G\_detachment = 0$. When $\theta = 180°$ (in the case of a hydrophobic particle), $\Delta G\_detachment = 0$.

But what we need to know is whether $\Delta G\_detachment$ has to be large or small. It has to be large if you are working in applications like emulsions and foams, where stability is very important. This means that once a particle is adsorbed at the interface, it should not be easily detachable. In other words, a high energy penalty must be paid to remove the particle from the interface. By calculating $\Delta G\_detachment$ into water or oil, one can determine whether the energy penalty is large or small. The energy penalty should be large to ensure that the particle remains at the interface.

In this plot, $\Delta G\_detachment$ into water is already normalized using thermal energy ($K_B T$) to express the energy required to detach the particle:

$$\frac{\Delta G \text{detachment}}{K_B T}$$

Both detachment into water and detachment into oil are plotted on the y-axis against the contact angle (θ) on the x-axis. Between the range $\theta = 0°$ to $30°$ and $\theta = 150°$ to $180°$, $\Delta G\_detachment$ is zero. One must avoid these ranges of θ when employing particles with a radius of 10 nm. For the rest of the range, $\Delta G\_detachment$ is fairly large, which means a high energy penalty is required to detach the particle, indicating that the particles are very stable. Now, we will see how this measurement is done.

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You can see that for air water interface case, this is how the scanning electron microscopic image look like. You can see that the shiny part is the deposition. I mean it indicates that nanoparticle deposition has been done. Whereas this dark part represents that no such coating has been done. okay because this part is exposed to air side you will not expect to have any sort of deposition on the air side.

So by measuring the two-dimensional projection of this uncoated region which is small d in this case and the diameter of the particle one can deduce this information using the simple geometric rule okay. So in this way you can measure the theta for hydrophilic particle which are you know, for which the theta is less than 90 degree. So, you can also use different reducing agent, but one can prefer sodium boride because this measurement can be done at room temperature. So, we also have compared this method with the gel trapping technique. You can, although there is some fluctuation and there is a good amount of agreement between these, you know, measurements, right, yeah.

This is just an overall view of the particles deposited at the air-water interface. You can see the monolayer of particles are arranged nicely on the interface. This is just a tilted view to show the enlarged view of the particle monolayer. decorated with gold nanoparticles. The shiny part here represents the nanoparticle deposition.

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Contact angle at water-oil interfaces

Octanol oil-water

1 µm

Decane oil-water   111 ± 5°   1 µm   158 ± 1°

$$\theta_1 = 180 - sin^{-1}\left(\frac{d}{D}\right)$$

Interfacial tension of
$\gamma_{D\text{-}W}$ = 52 mN/m
$\gamma_{O\text{-}W}$ = 8 mN/m

Gel trapping technique (GTT)

➤ By changing the liquid-liquid interface, contact angle of particle is changed

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The dark part represents the region where there is no such deposition. So the similar technique can also be carried out using for the oil water case. Here you can see that because the very small part is exposed to water side, you will have deposition at the bottom most of the bottom most part of the particle. When you look at from the top, and using the scanning electron microscopy, one cannot see this easily. So, what one can do is, using the carbon tape, one can flip this particle so that the bottom part is now up for the examination.

In that way, you can measure the small d, which is the coated region in this case. By using the geometric rule, one can measure the theta for hydrophobic particle. Here, we have shown for different case. One is a decane-oil water case. and ethanol oil water case, you can see that the contact angle for these cases are largely, I mean they are significantly different because of the changes in the interfacial tension of decane oil water and the ethanol oil water.

So this is the summary of measurement of contact angle for different particle type. We have used polystyrene and silica. And for different interface type, you can see that for a different interface type, air water, decane water, ethanol water, and how the contact angle, you know, for different cases varies, right? We have also compared them with the direct methods available in the literature. So the shortcomings of the previous method is like, you can only use that technique for positively charged particle, right? The particle that I have shown that we have demonstrated is for the amidine functionalized polystyrene particle, right? So in such case, you would expect particle to have positive charge, right? So the technique that we have demonstrated is only will be applicable or will only work for such particles, right? What if the particle is negatively charged? Can

the technique be used even for negative charged particles? If that is the question, then the answer is no. one can use a different technique you know to quantify I mean to measure the contact angle for both positive charge and negative charge that is what we are talking about in this slide which is a heteroaggregation so if you want to measure the theta for positive charge one can employ the negatively charged nanoparticle in the surface okay if you want to measure the negative charge particle then one can employ the positive charge nanoparticle in the surface.

So in this way, by using the exploiting the heteroaggregation, we can actually measure the theta. So even this plot is to show that even if we employ the nanoparticle, silicon nanoparticle in the surface, even up to 2%, there is no significant variation in the interfacial tension of air-water. So this method can be still used to measure the theta. So even if you use the weight percentage of silicon nanoparticles, even up to 2%, the variation is not very significant.

But one can use 0.51 or 1 also so that the cost of nanoparticle that we employ will be less, which can be minimized. So here we show that for different type of particles, let's say you have positively charged particle which is amidine functionalized and you also have negatively charged particle which is sulfate functionalized and different types of particles, different sizes of particles at different interfaces, water-air interface and water-decane interface. You can see that the contact angle for these cases can also be measured using this technique. This is the summary of the contact angle measurement. You can see that for different, you know, particle with a different charge, right, particle with a different size can be used to, you know, this method can be employed to measure theta for, you know, the range of particles, right? Having different sizes, having different charges, right? So, what we understand from this summary is that the smaller the nanoparticle size, the better the accuracy of the measure contact angle, okay? So, which means that if you measure the ratio, which is Db by D, the nanoparticle diameter in the bulk and the diameter of the particle of our interest.

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interface	colloidal particles at the interface			nanoparticles in the bulk			size ratio, $R = D_B/D$	contact angle (θ)
	type	charge	D (μm)	type	charge	D_B (nm)		
air−water	PS	+ve	0.22	Au	-ve	10	0.045	$51 \pm 2°$
	PS	+ve	0.52	HS30	-ve	14	0.027	$67 \pm 4°$
	PS	+ve	1.07	Au	-ve	10	0.009	$46 \pm 2°$
	PS	+ve	1.07	HS30	-ve	14	0.013	$48 \pm 2°$
	PS	+ve	1.07	TM50	-ve	37	0.034	$54 \pm 4°$
	PS	+ve	2.04	Au	-ve	10	0.004	$39 \pm 1°$
	PS	+ve	2.04	HS30	-ve	14	0.006	$36 \pm 3°$
	PS	+ve	2.04	TM50	-ve	37	0.018	$38 \pm 3°$
	PS	-ve	2.94	CL30	+ve	15	0.005	$46 \pm 3°$
	PS	-ve	8.71	CL30	+ve	15	0.001	$53 \pm 4°$
decane−water	PS	+ve	0.22	Au	-ve	10	0.045	$132 \pm 3°$
	PS	+ve	1.07	HS30	-ve	14	0.013	$110 \pm 2°$
	PS	+ve	2.04	HS30	-ve	14	0.006	$127 \pm 5°$
	PS	-ve	2.94	CL30	+ve	15	0.005	
	PS	-ve	8.71	CL30	+ve	15	0.001	

Sabapathy, M., Md, K. Z., Kumar, H., Ramamirtham, S., Mani, E., & Basavaraj, M. G. (2022), *Langmuir*.

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If you want to measure the contact angle of the 2.2 micron particle, then the nanoparticle that we employ in the bulk, if it is very small, then the accuracy is better. So that's what it comes to say, okay. And this is the comparison of contact angle measured by heteroaggregation, right, yeah. So this says that if the ratio is, you know, very small, then the accuracy will be better.

So in the case of this gold nanoparticle deposition, because the nanoparticle size is compared to the nanoparticles that we employed. silica nanoparticle that we employed. So, these two are commercially available, commercial grade HS30 and TM50. The size of this nanoparticle is different that we what we employed is also different. So, for gold nanoparticle deposition the accuracy is better than the when you compare the accuracy the golden nanoparticle accuracy is better than these two methods.

It comes to say that the lower the nanoparticle size that we employ, better the accuracy of the contact angle measurements. So we stop here. I think this technique, whatever we covered in this lecture would have given enough insight into the measurement of contact angle at various fluid fluid interfaces. We will stop here and we will continue from the next lecture. Thank you.