Colloids and Surfaces
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Lecture - 45
Characterization of Particles

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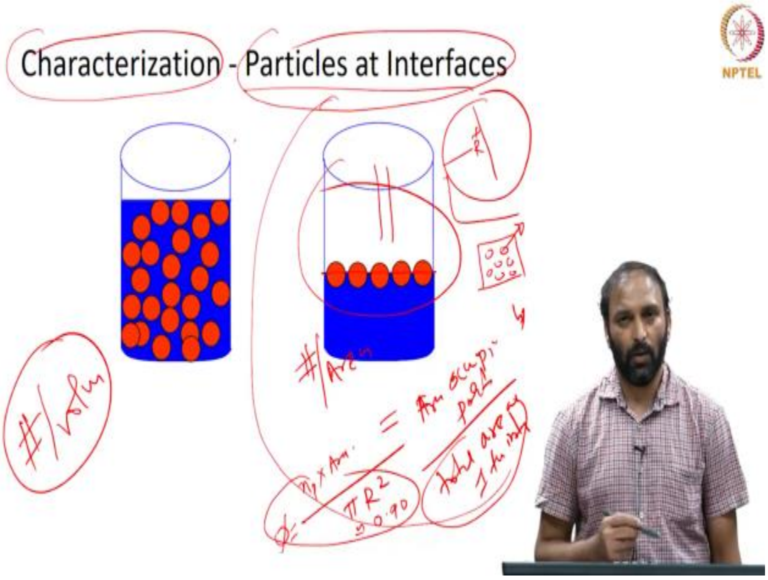

Characterization - Particles at Interfaces

So that is so that brings us to concluding the fact that there is a lot of interest in looking at particles at interfaces concept, because there are a large number of applications in the materials, which have been prepared by exploiting this concept. So now, what we will do is we will talk a little bit about characterization of particles at interfaces. So, if you look at in the bulk, we have talked about several techniques and several parameters one need to characterize the particles.

For example, size, surface charge density, grafting density, you know, several parameters. Now, when it comes to particles at interfaces, of course, the characterization of all these parameters is also equally important. And while in the bulk one of the important parameter which is used to characterize particles in a fluid is what is called as a volume fraction which is the volume of particles divided by the total volume of the dispersion.

And analogous parameter for colloids at interfaces would be what is called as a surface fraction that is fraction of the surface that the particles occupy at the interface that is the area occupied by particles divided by total area of the interface. For example, if one is using a

Petri dish for example, and whose size is like say whose radius is capital R then what one could do is the total area that of the interface is going to be pi R square.

And now, the area that the particles occupy at the interface depends on what is the concentration of particles at the interface. And typically, when one works with particles at interfaces, if the particles that are micron in size are used, you can actually do an optical microscopy and obtain an image which contains particles. Now, if you know the number of particles at the interface.

And if you know what is the total area that or the area that the particle occupies the interface that means, the number of particles at the interface multiplied by the area that it occupies, and that gives you what is called as surface fraction or the fractional area that the particles occupy at the interface and the typical value of phi could vary from say 0 to about 0.74 if you work with spherical particles and that 0.74 is when all the particles pack in the form of a crystal and if the particles are randomly distributed in the fluid you can go to a value as high as 0.64.

However, if you look at spherical particles if they are sitting at the interface and if you assume that you know they are sitting exactly with half of the surface in the two phases then one could do a simple calculation and show that if they are arranged in the form of a hexagon or a HCP or HCP close packing you can just consider a triangular area and then you can calculate that this phi can be as high as about 0.90 roughly.

So therefore, while the volume fraction when you work with dispersion as a bulk can go from about phi to 0.74 for spherical particles, the surface fraction can go all the way from about 0 to about 0.90. And the other parameter that one could also use is in the case of you know, the particles in the bulk, we can talk about number density of particles that is number of particles per unit volume.

Similarly, in this case one could talk about surface density, which again would be the number of particles interface divided by the area of the interface. So, these are some additional, you know, characterization that one has to talk about when one is dealing with particles at interfaces.

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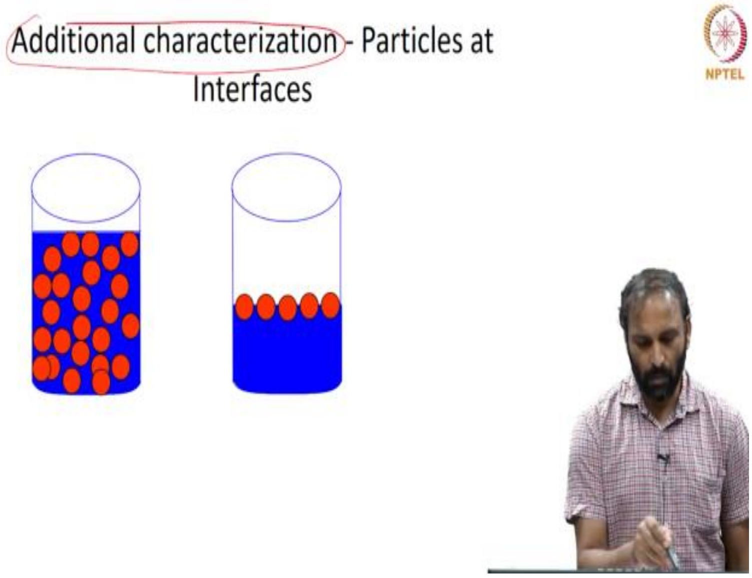

Additional characterization - Particles at Interfaces

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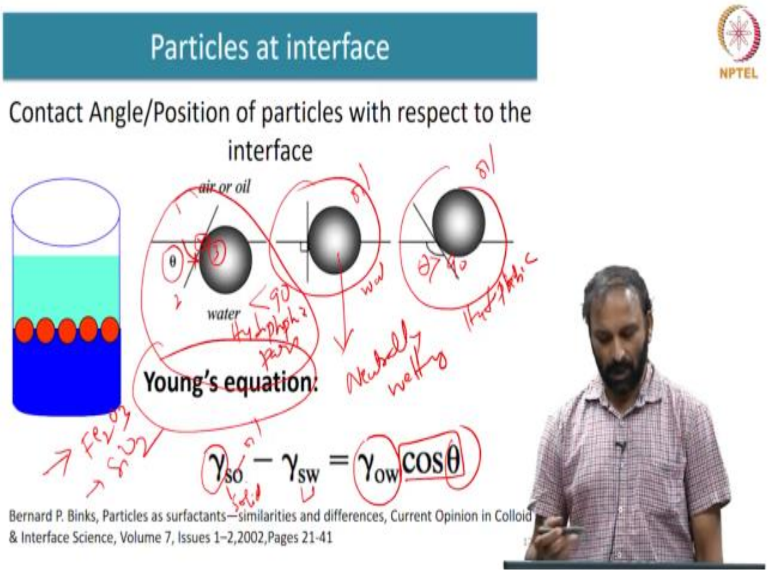

Particles at interface

Contact Angle/Position of particles with respect to the interface

Young's equation:

$$\gamma_{SO} - \gamma_{SW} = \gamma_{OW}\cos\theta$$

Bernard P. Binks, Particles as surfactants—similarities and differences, Current Opinion in Colloid & Interface Science, Volume 7, Issues 1–2,2002,Pages 21-41

And another additional characterization that would also be important which is not so much when you have particles sitting in the bulk is what is called as the position of the particles with respect to the interface or the contact angle of the particles at the interface. And this is defined by what is called the Young's equation, which relates the interfacial tension of the solid.

In this case, the particle that we are dealing with, that is oil that is the interfacial tension of the solid-oil interface and the solid-water interface and they are related to the interfacial tension between the oil and water and cos theta and this theta is what is called as contact angle and that is determined by drawing a tangent that to the particle surface at what is called as a three phase contact point.

So, what is shown here is a location where the fluid 1 and fluid 2 and the solid particle that is the three phases that come into contact, and at that location, you draw a tangent to the particle surface and the angle that the tangent makes with the interface gives you what is called as a contact angle and this contact angle could be less than 90 degree and that is when the particle is more in contact with the aqueous phase and such particles are termed as what are called as hydrophilic particles.

And you could have a case where the contact angle theta is greater than 90 when the particle would like to maximize its contact with the oil phase and such particles are referred to as hydrophobic particles, and you can have a case where the particle would like to be in equal contact with both the oil phase and the aqueous phase and such particles are termed as neutrally wetting.

Therefore, depending upon the type of particles, either the particles could be wanting to be more in contact with aqueous fluid example of such particles could be several metal oxide particles for example, hematite particles or SiO_2 particles for example, and the examples of particles which are more prone to being in contact with oil could be several types of polymeric particles for example.

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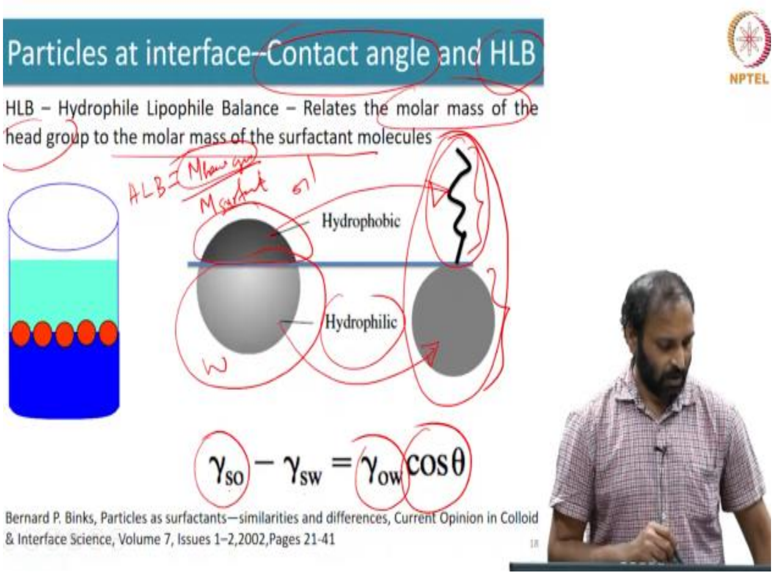

Particles at interface--Contact angle and HLB

HLB – Hydrophile Lipophile Balance – Relates the molar mass of the head group to the molar mass of the surfactant molecules

$$\gamma_{so} - \gamma_{sw} = \gamma_{ow} \cos\theta$$

Bernard P. Binks, Particles as surfactants—similarities and differences, Current Opinion in Colloid & Interface Science, Volume 7, Issues 1–2,2002,Pages 21-41

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And this concept of contact angle is very similar to what is called is a concept of HLB or the hydrophile lipophile balance, which is defined for a surfactant molecule. So, in the case of surfactant molecules HLB is defined as it relates the molar mass of the head group to the total molar mass of the surfactant molecule and that is defined as the molar mass of the head group divided by molar mass of the surfactant.

And, if the molar mass of the head group is large, that means, the out of the total molecular weight there is a lot of contribution that comes from the head group and such surfactants are known to be water liking or they have a affinity for being in contact with water. So, and if the molar mass of the head group is very, very small, that means, the because of the fact that the surfactant has a tail group.

And a head group in the case where the molar mass of the head group is small, what really dominates the behavior is the molar mass of the tail group and such surfactants are more oil soluble in a similar sense, when the particle is sitting at the interface, you could have the part of the surface that is in contact with oil for example, you can think about analogy with the tail group of the surfactant and the portion of the particle that is in contact with the water.

And which is a hydrophilic part, you can think about that as an analogy with the head group of the surfactant molecule and the relative magnitude of the interfacial tension between the solid and oil, solid-water and the oil-water interfacial tension determined how much of the surface is in contact with each of the fluids and that is quantified by the contact angle.

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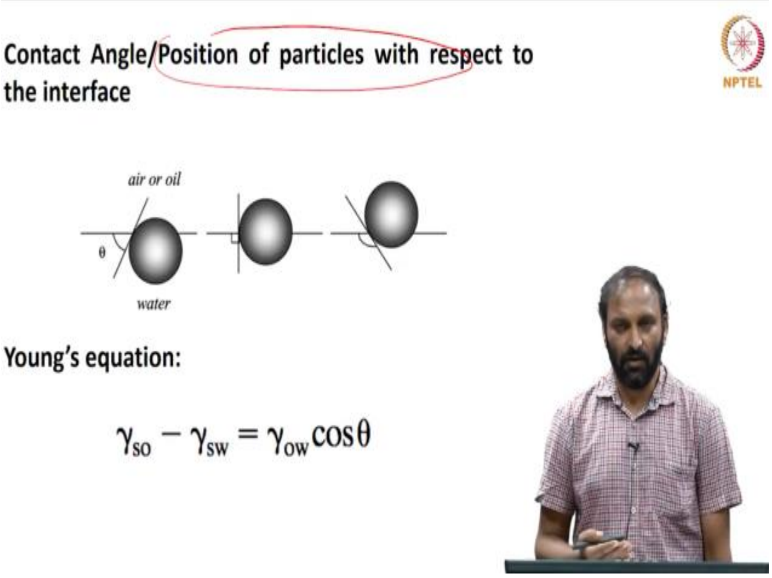

Contact Angle/Position of particles with respect to the interface

Young's equation:

$$\gamma_{so} - \gamma_{sw} = \gamma_{ow}\cos\theta$$

And measurement of the contact angle or the position of the particle with respect the interface is one of the additional characterization that you know one has to deal with.

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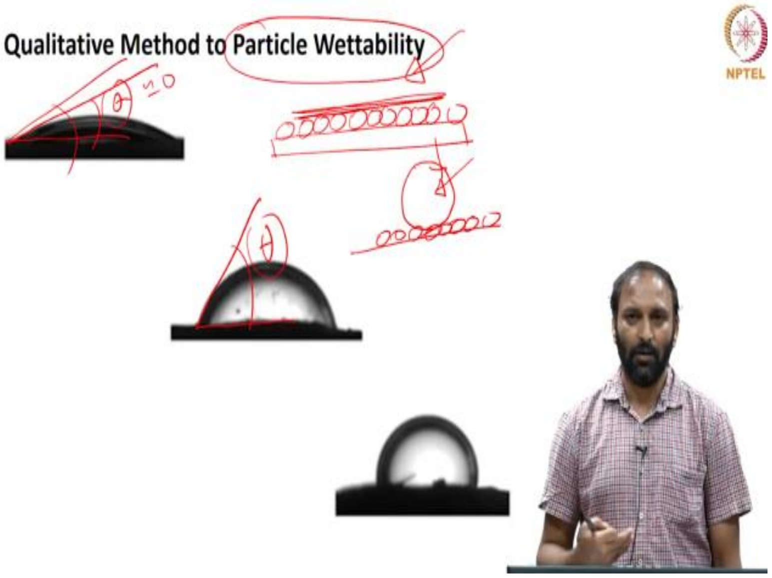

Qualitative Method to Particle Wettability

And there are qualitative methods to talk about particle wettability or the preference of the fluid particle to one of the fluids and that is simply done by basically creating taking a substrate and you deposit the particles of interest you know whose wettability you want to measure and then you deposit a layer of the fluid for example, an oil or water and look at what is the contact angle that is again you measure you just draw a tangent at the three phase contact you know point.

For example, something like this and you measure what is this angle with respect to the horizontal and you calculate and you find out what this theta value is. So, if the theta value is close to 0 that means, the fluid that is put on a surface coated with particles it spreads completely. And therefore, the particles have more preference to that fluid. On the other hand, if you have a case, where the particles the fluid that is deposited.

If it takes a shape like a perfect sphere, the particles do not have any preference whatsoever to the fluid and the concentration therefore, depending upon this contact angle, one could come up with a qualitative way of inferring what is the particle wettability or whether the particle prefers to be in contact with either oil or water or is it neutrally wetting to both the fluids.

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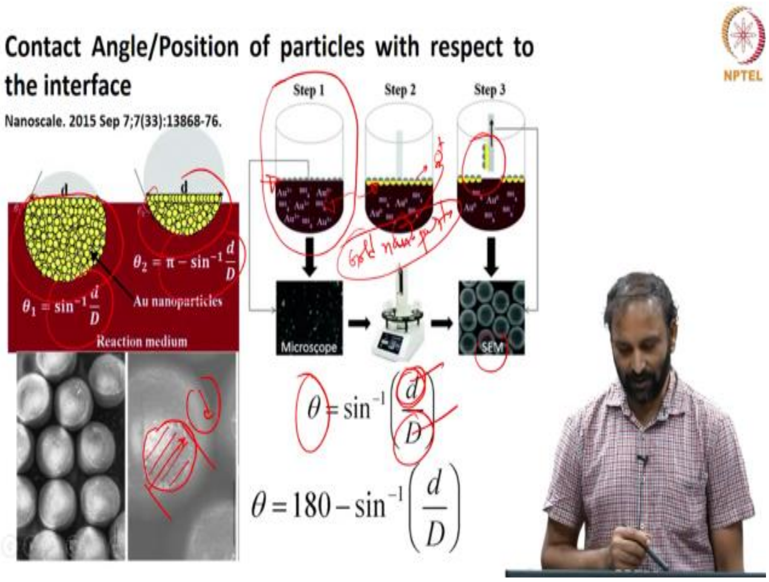

Contact Angle/Position of particles with respect to the interface

Nanoscale. 2015 Sep 7;7(33):13868-76.

$\theta_1 = \sin^{-1}\frac{d}{D}$

$\theta_2 = \pi - \sin^{-1}\frac{d}{D}$

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

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

One could do a quantitative estimation of contact angle. Again, we will go back to the method that we discussed in the context of making new particles wherein, a portion of the particle surface was coated with gold. So, the experimental setup looks something like this. So, you create a monolayer that means you deposit particles at the interface and into the aqueous solution, you add reagents that lead to the formation of gold nanoparticles.

Now, the gold nanoparticles that are there, they can preferentially go and deposit onto the surface that has in contact with the reaction solution. And that occurs because of the electrostatic attraction between the particles that are produced as a result of this reaction and the particles that are sitting at the interface and the fact that the gold nanoparticles are produced and the particles that are sitting at the interface, they are oppositely charged in this case, the gold particles are produced.

They are negatively charged and the particles are deposited at the interface they have positive charge and because of the electrostatic attraction, there is a deposition of gold and once the gold the reaction is complete, you can transfer these particles onto a substrate and you can observe these particles under SEM you can calculate what is d that is the area over which the deposition has occurred.

So, if you look at this, so, if I can fit a circle and I can calculate what is the diameter of the patch that has been produced? So, I can I have a direct way of measuring d and if we know what is the diameter of the particle that we started with that is the diameter of the particles that were deposited at the interface calculation and measurement of the small d and capital D enables the calculation of D.

So, depending upon whether the particle is more in contact with water or less in contact with water, you know, you can use a different expression which you can actually derive from simple geometry as well.

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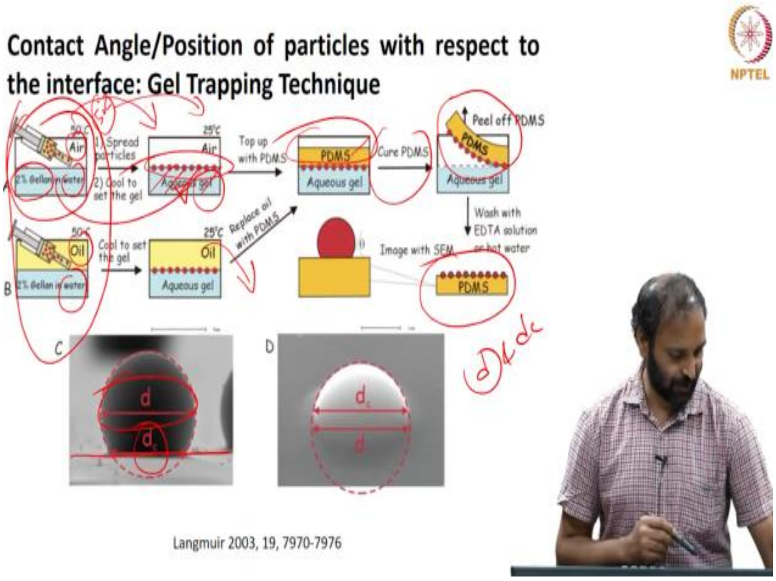

Contact Angle/Position of particles with respect to the interface: Gel Trapping Technique

Langmuir 2003, 19, 7970-7976

So, therefore, this is a simple and a direct method for measuring the contact angle of the particle at the interface there are other methods in which what is typically done is that you deposit particles at an interface between air and aqueous solution or oil and aqueous solution instead of taking pure water what is done is a small amount of a hydrocolloid is dissolved in the aqueous phase and the spreading of the particles at the interface is done at a high temperature.

For example, 50 degrees centigrade in this case and what is done is once you spread the particles you allow them to reach equilibrium position, you can change the temperature from 25 to from 50 to 25. And when that happens, the aqueous sub phase it solidifies there is a conversion of a liquid like sub phase into a gel like sub phase and once the gel like sub phase is formed, the particles are trapped at the interface and they become immobile.

And what you could do is you can pour out the oil because gel is of sufficient strength, I can pour out the oil and I can replace the top phase with PDMS and along with the PDMS there will be some cross linking agent which will help the linking of this PDMS molecules to the surface and after a certain curing time, you can peel off PDMS and because of the cross linking reaction, the particles get embedded in the PDMS.

And that could be observed on an SEM and I can get a micrographs again of what is the contact diameter that corresponds to the location of the particles with respect to interface and what is the diameter of the particle and again knowing d and dc one could estimate what is the contact angle of particles with respect to the interface.