Colloids and Surfaces

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Lecture – 46
Experimental Observations: Concept of Electrostatic Interactions and Stability at Interfaces

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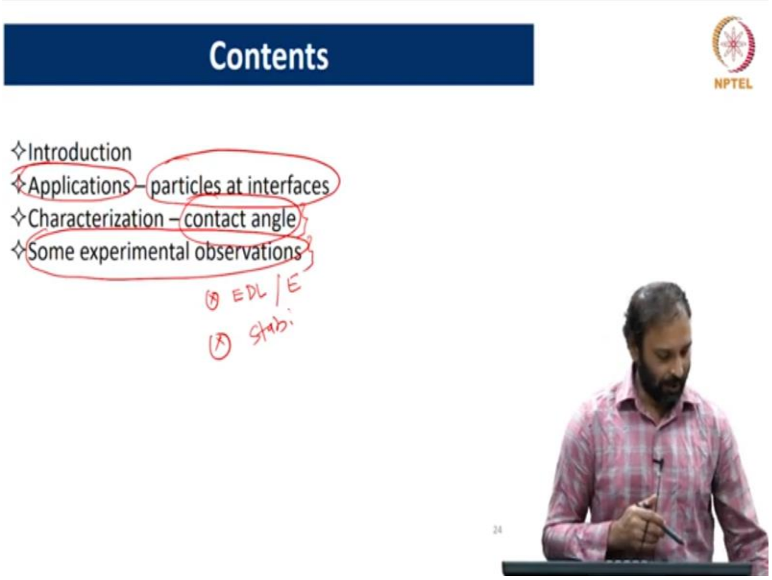

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- ✧Applications – particles at interfaces
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- ✧Some experimental observations

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In this module so far what we have done is we have introduced the concept of particles at interfaces. And we have looked at several applications, where this concept can be exploited. And we discussed characterization of particles in the context of when they are at the interface. And we mentioned that an additional characterization one has to worry about and we discussed about a contact angle measurements, which is a method of finding out what is the equilibrium position of particles with respect to the interface.

What we will do in this lecture is that we will look at some important experimental observations and these experimental observations enable us to make two interesting points. One is that electrical double layer interactions or the electrostatic interactions are modified when the particles are at interfaces. And number two is that some of the experimental observations can be used to discuss what is called as stability of colloids at interfaces. We will discuss some of these observations and we will think about mathematically deriving some equations which enable us to make these statements.

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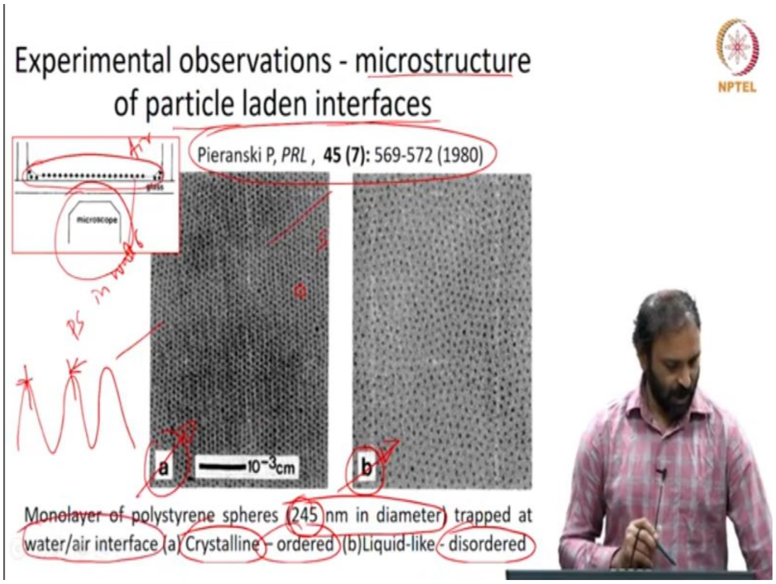

Experimental observations - microstructure of particle laden interfaces

Pieranski P, *PRL* , **45 (7):** 569-572 (1980)

Monolayer of polystyrene spheres 245 nm in diameter trapped at water/air interface (a) Crystalline - ordered (b)Liquid-like - disordered

And the first result that I am going to show is the seminal work of Pieranski we are looking at the microstructure of particle laden interfaces. In these experiments, what was done is there is a small container and that container is filled with a colloidal dispersion what is highlighted now, and in this container, a very dilute dispersion of particles was placed and this is a dispersion of polystyrene particles in water and the size of the particle is 245 nanometer in diameter.

And naturally, when you do not have anything at the top as you will have here, therefore, does not interface between water and air. And what you see here is a schematic of a microscope objective and you know, you can move this objective up and down. So, that you can focus at the interface and look at the microstructure of the interface containing these particles. And there are 2 distinct micro structures that can be seen here.

So, if you look at the image, you see these small dots, and these are the, the particles of 245 nanometer diameter. And if you take a closer look, you will see that every particle has its neighbor, for example, if I look at, let us say a particle here, there is 1 neighbor there 1, 2, 3, 4, 5, 6 right. So, therefore, every particle has 6 neighbors, and it appears that the distance between if I were to draw a line, you will see that you will see peaks and valleys.

And this, the distance between the peaks corresponds to the, the particle position and looks like they are periodically spaced in figure a and therefore, this microstructure resembles a crystalline arrangement or an ordered arrangement of particles, on the right, figure b is obtained by doing a similar experiments, the only difference is that the concentration of the particles at the interfaces lower.

So, in the context of surface fraction or the fraction of the area that is occupied by the particle, it is higher in the case of a and it is likely lower for the case of b, and if you look at image b You know the particles are not as ordered as what you see in a and so, this corresponds to a liquid like you know microstructure or in this case the particles are disordered. So, these are the experiments with very tiny particles that are 245 nanometer particles and these are the microstructure at water air interface.

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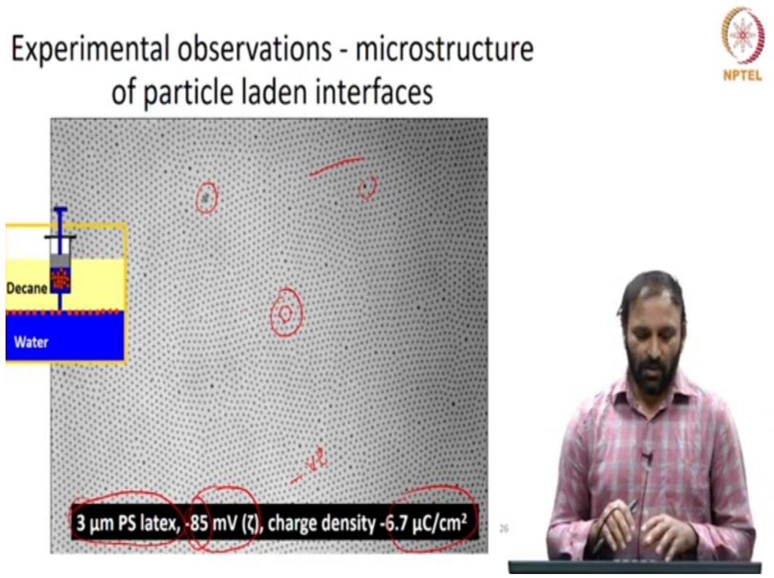

Experimental observations - microstructure of particle laden interfaces

3 µm PS latex, -85 mV (ζ), charge density -6.7 µC/cm²

And what you are seeing now is microstructure which is obtained by depositing 3 micrometre polystyrene particles, and they have a zeta potential of minus 85 millivolts they are highly charged and the fact that zeta potential is minus 85 that means, they are negatively charged particles and the charge density that is corresponding to this zeta potential is 6.7 micro coulombs per centimeter square.

And these are deposited at Water-Decane interface, again similar features can be seen the monolayer is crystalline that means, if I were to draw a line like this, he will see that you know, the inter particle spacing between the particles is very similar and every particle has except for some small dirt, you know, you see that every particle has 6 neighbors, for example, if I look at this, so, I can beautifully draw a nice hexagon right. So, therefore, there is a non-closed packed hexagonal arrangement of particles at the interface.

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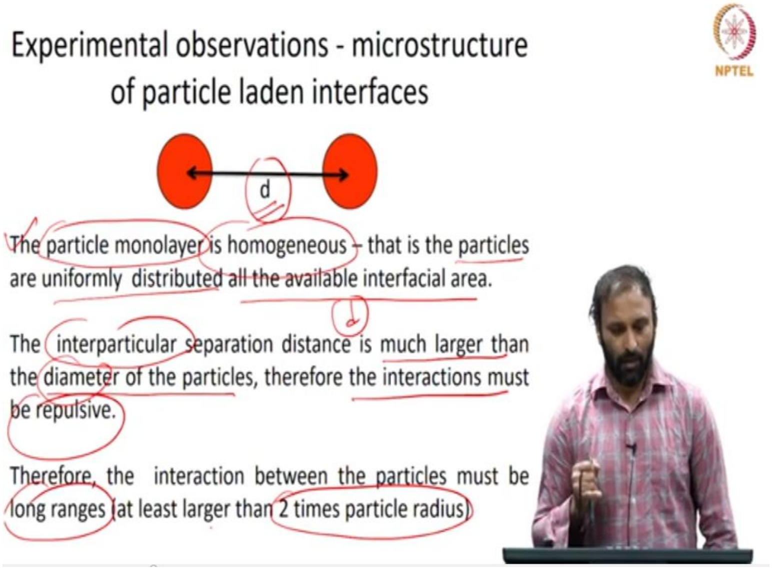

Experimental observations - microstructure of particle laden interfaces

The particle monolayer is homogeneous - that is the particles are uniformly distributed all the available interfacial area.

The interparticular separation distance is much larger than the diameter of the particles, therefore the interactions must be repulsive.

Therefore, the interaction between the particles must be long ranges (at least larger than 2 times particle radius)

Now, the these 2 experiments, the conclusions that can draw that one can draw from these two, the microstructure that we have discussed So, far is that, so, you have two particles and you can designate the inter particle separation by this d, the separation distance d what is evident is that the particle monolayer is homogeneous, what I mean by that is, if I look at any region of the monolayer whether you are in one corner or in the other.

Or you know, anywhere across the monolayer, the monolayer looks homogeneous that means, the particles are uniformly distributed all through the available interfacial area. The second conclusion that one could draw is that inter particle separation distance that is d is much larger than the diameter of the particles that means, if I look at so, these particles are 3 micrometer in diameter.

Now, if I look at the inter particle separation distance between the 2 particles, it appears that the inter particle separation is at least about two times the particle diameter or more depending upon you know the concentration the particles that one works with and, and the fact that the inter particle separation is much larger than the diameter of the particle, it suggests that the interactions must be repulsive and that the interactions are a long ranged because of the fact that the separation distance are at least 2 times the particle radius or larger that suggests that the interaction between the colloidal particles are repulsive and they are more long range.

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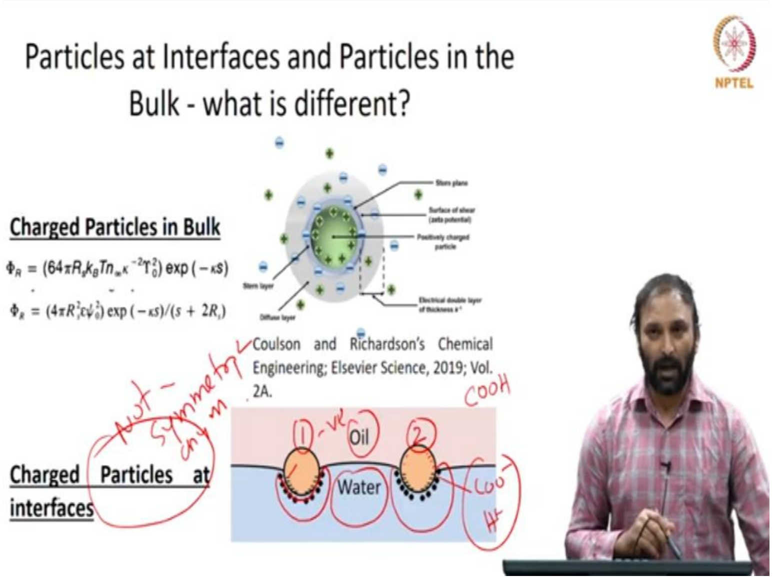

Particles at Interfaces and Particles in the Bulk - what is different?

Charged Particles in Bulk

$$\Phi_R = (64\pi R_i k_B T n_\infty \kappa^{-2} \Upsilon_0^2) \exp(-\kappa s)$$

$$\Phi_R = (4\pi R_i^2 \varepsilon \psi_0^2) \exp(-\kappa s)/(s + 2R_i)$$

Coulson and Richardson's Chemical Engineering; Elsevier Science, 2019; Vol. 2A.

Charged Particles at interfaces

Now, let us look at comparing, you know the particles in the bulk versus particles at interfaces, what is the difference now, so, we discuss that when you have charged particles dispersed in a fluid, there is going to be an electrical double layer that is formed the first thing is that the moment you have a charged particle dispersed in water or any other fluid medium, if there is going to be dissociation of charges, the particle is going to acquire some charge.

Right and, whatever ions are present in the vicinity of the charged particle, they are going to rearrange and they are going to give a an electrical double layer, and that electrical double layer is depicted here. So, you have stern layer and there is a surface of shear and there is an electrical double layer thickness associated with the thickness of the double layer and you have a stern layer where the counter ions are closed or tightly bound to the particle surface.

And you have a diffuse layer where the concentration of counter ions varies with the distance from the charge surface right. And in for such a configuration the interaction between two spherical particle is given by these two expressions, the first one is for a case where the Gouy Chapman theory has been used for the overlap of the electrical double layer, and the second one is for the case where we have a Debye Huckle approximation which is valid when the when the zeta potential is of the order of 25 millivolts.

Now, this is the picture that we have in the bulk that is the overlap of the electrical double layer it gives rise to electrostatic interactions of the electrical double layer interactions. One thing that is important to notice is that around the particle since this is a particle around the particle the electrical double layer is symmetric. Now, if you look at the particles sitting on the interface, what is shown here is a schematic of particle 1 and particle 2.

And they are sitting at the interface between the two fluids and this is a negatively charged particle that is the charges that are on the particle surface and you have the counter ions that are that are depicted here. And one thing that is to notice is that the electrical double layer or the distribution of counter ions around the charge surface is not symmetric anymore, that is because the dissociation of the charges occurs only across the surface that is in contact with water.

That means, so, although the particles would also have the surface charge groups you know, in the on the surface that is in contact with oil, the dissociation of the charges requires a suitable medium and a charge like say for example, C-O-O-H which would dissociate when it is in contact with water and under appropriate conditions. And therefore, the dissociation gives rise to C-O-O minus and H plus only in the region where the particle is in contact with water.

Therefore, there is an asymmetric distribution of counter ions in the case of particles or interfaces, and this difference is what is giving rise to long range interactions in the case of particles at interfaces.

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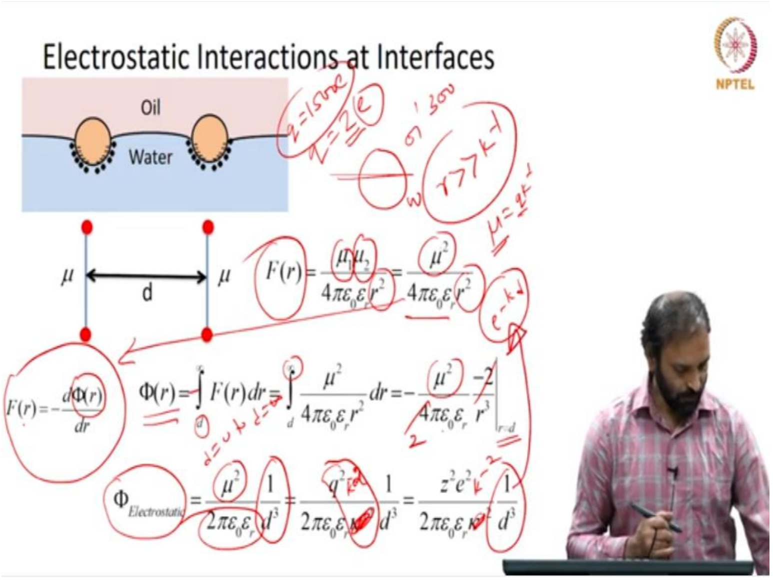

Electrostatic Interactions at Interfaces

$$F(r) = \frac{\mu_1\mu_2}{4\pi\varepsilon_0\varepsilon_r r^2} = \frac{\mu^2}{4\pi\varepsilon_0\varepsilon_r r^2}$$

$$F(r) = -\frac{d\Phi(r)}{dr}$$

$$\Phi(r) = -\int_{\infty}^{d} F(r)\,dr = \int_{d}^{\infty} \frac{\mu^2}{4\pi\varepsilon_0\varepsilon_r r^2}\,dr = -\frac{\mu^2}{4\pi\varepsilon_0\varepsilon_r}\left.\frac{-2}{r^3}\right|_{r=d}$$

$$\Phi_{Electrostatic} = \frac{\mu^2}{2\pi\varepsilon_0\varepsilon_r}\frac{1}{d^3} = \frac{q^2}{2\pi\varepsilon_0\varepsilon_r\kappa^2}\frac{1}{d^3} = \frac{z^2e^2}{2\pi\varepsilon_0\varepsilon_r\kappa^2}\frac{1}{d^3}$$

Now, this is a schematic, that there is a dissociation of charges only on the water side. Now, what one could do is that the So, because of the fact that the charges on the particle surface and the counter ions in solution, the fact that the charge density that is arising because of the in the charge density corresponding to the dissociation that occurs on the particle surface and the total number of counter ions in solution are going to be exactly the same.

Therefore, we can associate a charge minus q with the particle surface and similarly, for the for the ions in the double layer, we can associate a charge plus q and a typical length scale by which these two charges are separated is of the order of Debye screening length that is Kappa inverse. Therefore, so for every particle that is at the interface, there is a dipole, that is the dipole corresponding to particle 1 and that is a dipole that is corresponding to the particle 2.

And these dipoles depending upon what convention you use, they point in the same direction and they are along the axis that connects the center of the two particles right. So that means if they will be pointing out in this direction, right maybe I can just redraw. So, they will be pointing in the same direction and they are along the axis that connect the centers. Now, whenever we have two charges that are equal in magnitude, but opposite in sign, we can define a dipole moment q which is given by q times Kappa inverse that is mu.

And now, the force of repulsion between the two dipoles is given by if you have two dipoles mu 1 and mu 2 the force of repulsion is given by mu 1 mu 2 divided by 4 pi epsilon naught epsilon r into r square, where r is the separation distance between the two dipoles and if this expression can be written if the separation distance r is much greater than Kappa inverse and because the dipoles are of similar magnitude.

Therefore, the numerator becomes mu square and in the denominator you have 4 pi epsilon naught epsilon r into r square and because of the fact that so, this is the expression for the force and the force is the negative gradient of the potential therefore, if you want the repulsion the repulsive potential or the electrostatic interaction between the two particles, I need phi of r which I can obtain by integrating this you know from d to infinity and where d is the distance of separation between the two dipoles and it can vary from d is equal to 0 all the way up to d is equal to infinity.

So, therefore, if we work this out what you have is mu square 4 pi epsilon naught into epsilon r integral of 1 over r squared is minus 2 divided by r cube and that goes between the limits infinity and r is equal to d and because r cube is in the in the denominator the this term at infinity is 0 therefore, phi electrostatic essentially is given by the 2 and the 2 gets cancelled. Therefore, the final electrostatic is given by mu square divided by 2 pi epsilon naught epsilon r into 1 over d and because we have defined mu as q times Kappa inverse, I can substitute for mu in terms of q Kappa inverse.

So, therefore, we can write this as you know q divided by sorry this this is going to be q times Kappa inverse Kappa - 2 right q this is q times Kappa - 2 in the numerator that is Kappa - 2 therefore, and this charge q would depend on the total number of charges that are dissociated and you can write this q as z times e where e is the charge in the electron and z can take any value depending upon the total number of charges that are dissociated.

If for example, if you take a case where you have a particle that is sitting exactly with half of the surface in contact with oil and water in that case and if the total number of charges on the surface is like say for example 3000 then this q would become 1500 times e something of that that order

So, therefore, phi electrostatic goes as 1 over the distance to the power of 3 as against e power - Kappa times d for the case of interactions, colloidal interactions in the bulk. So, and this 1 over d q of dependence is what gives rise to the long range nature of the electrical double layer interactions compared to the similar interactions in the bulk.

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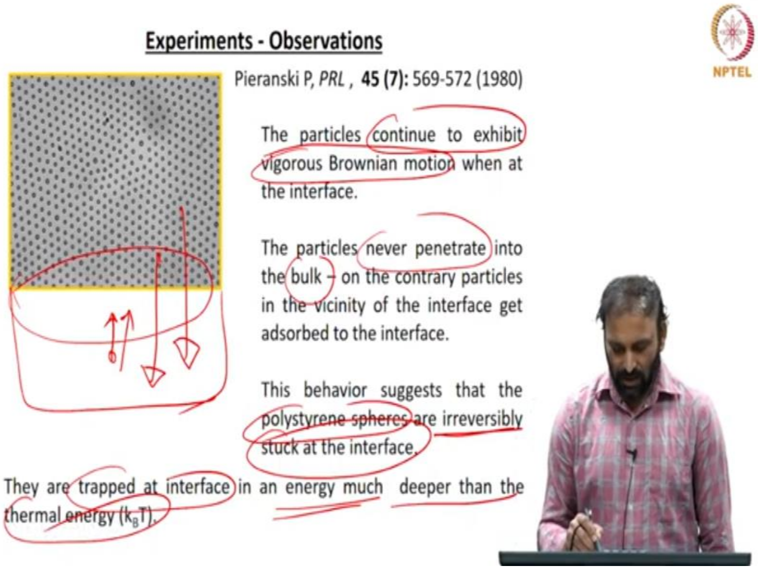

Experiments - Observations

Pieranski P, *PRL*, **45 (7):** 569-572 (1980)

The particles continue to exhibit vigorous Brownian motion when at the interface.

The particles never penetrate into the bulk – on the contrary particles in the vicinity of the interface get adsorbed to the interface.

This behavior suggests that the polystyrene spheres are irreversibly stuck at the interface.

They are trapped at interface in an energy much deeper than the thermal energy (k_BT).

Now, the other observations are that so, when the particles are trapped at the interface similar to you know, when they are in the bulk the particles continue to exhibit vigorous Brownian motion very similar to the particles in the bulk. And it is also observed that once they are at the interface, if you imagine this to be the interface and if you have, you know, this is a in a petri dish for example.

So, now, the particles they never penetrate into the bulk that means, once they are sitting at the interface, once they are absorbed at the interface, they continue to exist at the interface and they never go back into the, the bulk and moreover, if there is a the particle that is coming in the vicinity of the interface and experimental observations show that they can be drawn towards the interface and they can and that means, the transfer from the bulk to interface is possible.

However, the transfer from the interface to the bulk is practically impossible. This suggests that polystyrene particles are irreversibly stuck at the interface and the fact that they are in irreversibly stuck points to the fact that the particles are trapped at the interface in an energy that is much deeper than the thermal energy. So, now what we will do is will try and calculate what is the depth of the energy well, unit in which the particles are sitting at the interface.

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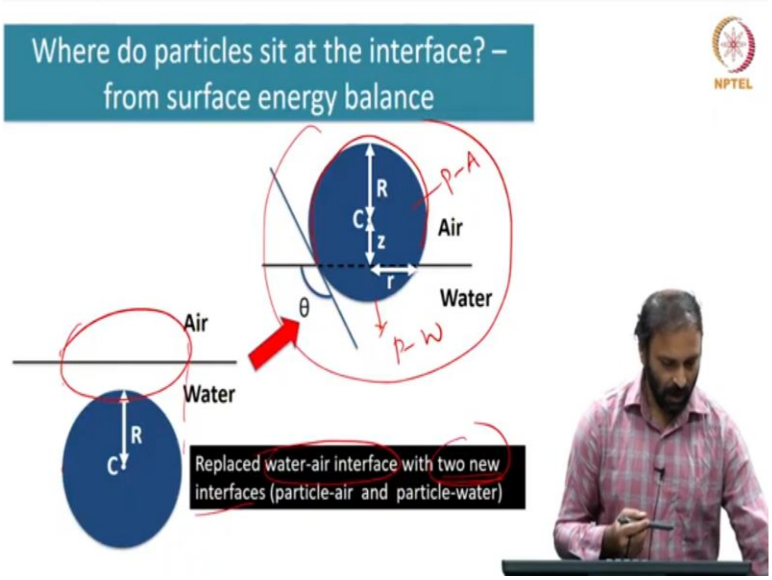

Where do particles sit at the interface? – from surface energy balance

Replaced water-air interface with two new interfaces (particle-air and particle-water)

So, we are going to do that by doing a very simple surface energy balance, which is just going to follow this reference for doing that. So, this is a schematic of like say a polystyrene particle in this case, which is sitting at the interface between air and water and theta is the, the contact angle. And so, the, the radius of the particle is R and the center of the particle is at C. And z refers to the location of it is a vertical distance that will tell us what is the location of the particle with respect to the interface.

z is equal to if I scale z with R that is the radius of the particle then I will get a z bar and this that bar is going to be plus 1 when the particle is in is completely in air, and z bar is minus 1 when the particle is completely in water.

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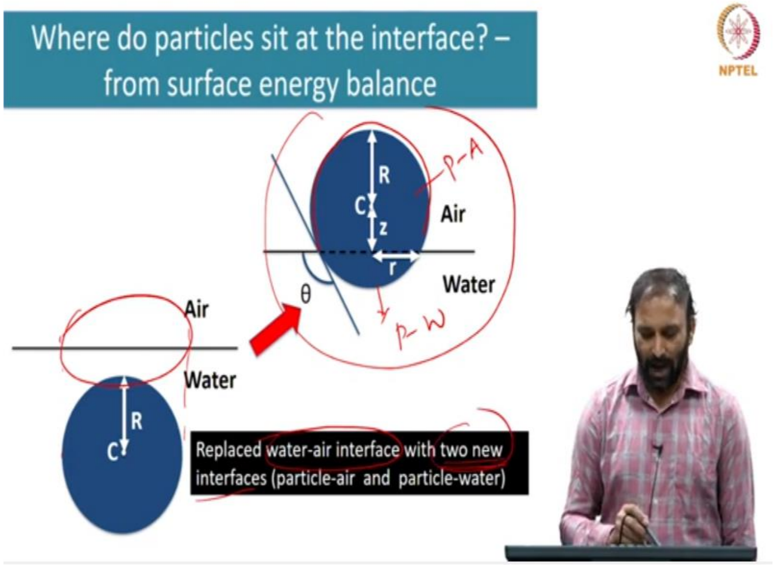

Where do particles sit at the interface? – from surface energy balance

Replaced water-air interface with two new interfaces (particle-air and particle-water)

So, now, if you have a configuration like this, now, so, when the particle is at the interface, right and initially imagine that you know there is a water air interface and you bring a particle either from you know the upper phase or the lower phase, and then you position them at the interface. Now, if you look at such a process, wherein you bring in a particle from one of the phases and position them at the interface.

So, what is done is that we have replaced in this configuration, we have replaced water air interface, with two new interfaces right. So, if I say that this is the, the water air interface, that was originally present, and the fact that you have placed the particle interface, you created two new interfaces, that is the interface between the particle and in this case, air and the interface between particle and water. We have created two new interfaces and we have removed the water air interface was originally present.

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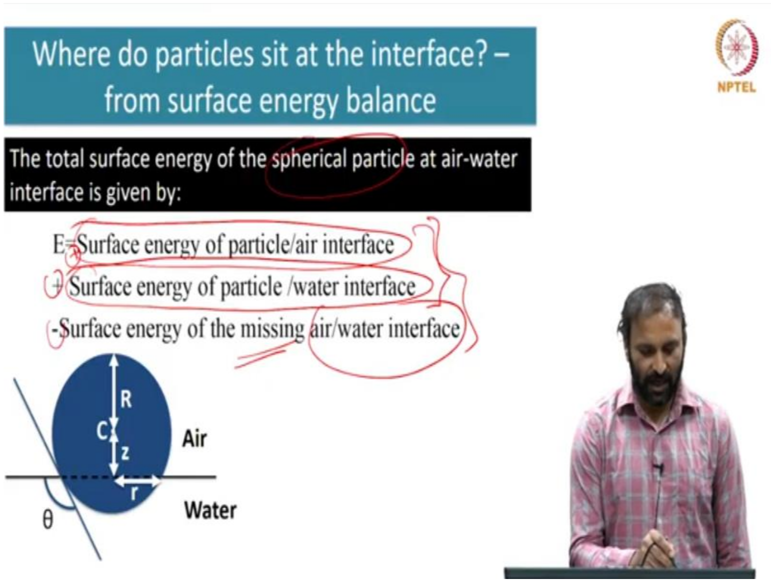

Where do particles sit at the interface? – from surface energy balance

The total surface energy of the spherical particle at air-water interface is given by:

E=Surface energy of particle/air interface
+Surface energy of particle /water interface
-Surface energy of the missing air/water interface

And therefore, the total surface energy when a spherical particle is at the interface is given by the summation of the three interfacial energies one is the surface energy of the particle-air interface, second is the surface energy of the particle-water interface and these are the surface energies that were newly created and they take the positive sign and however, we have replaced the air-water interface that is the energy of the missing interface that is negative because that has been lost.

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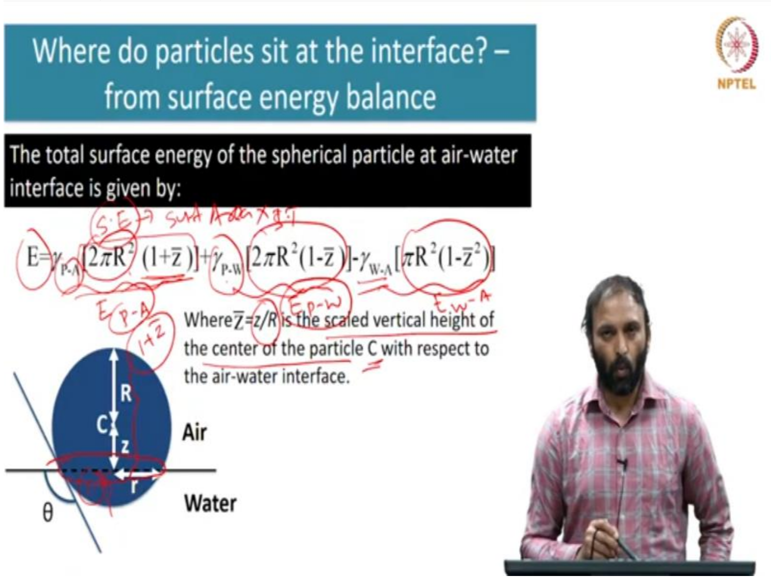

Where do particles sit at the interface? – from surface energy balance

The total surface energy of the spherical particle at air-water interface is given by:

$$E=\gamma_{P-A}[2\pi R^2(1+\bar{z})]+\gamma_{P-W}[2\pi R^2(1-\bar{z})]-\gamma_{W-A}[\pi R^2(1-\bar{z}^2)]$$

Where $\bar{z}=z/R$ is the scaled vertical height of the center of the particle C with respect to the air-water interface.

And so, for and the fact that the surface energy is given by surface area multiplied by surface tension you can write down the individual contribution to the to the total surface energy and this term E for the particle- air interface this term is E for the particle-water interface and this is the E term for water interface and if you look at the schematic So, we see that and we said that this distance is 1 + z bar.

And therefore, the total interfacial area that is available the total particle air interfacial area is given by 2 pi R square times 1 + z bar that is the particle-air interfacial area that multiplied by the particle-air interfacial tension or the surface tension will give me the surface energy that is associated with particle and air interface and the second term this 2 pi R square times 1 - z bar that this distance.

This is 1 – z bar is this distance that multiplied by 2 pi R square will give me what is the surface area of the particle-water interface that multiplied by the corresponding interfacial tension will give us what is the surface energy of the particle-water interface. Now, this pi R square into 1 - z bar tells us what is the interfacial area that that has been replaced and that multiplied by the interfacial tension between water and air will give us the contribution of the water-air interface to the total interfacial energy in this expression the z bar is z / R that is the scaled vertical distance of the center of the particle C with respect to the air water interface.

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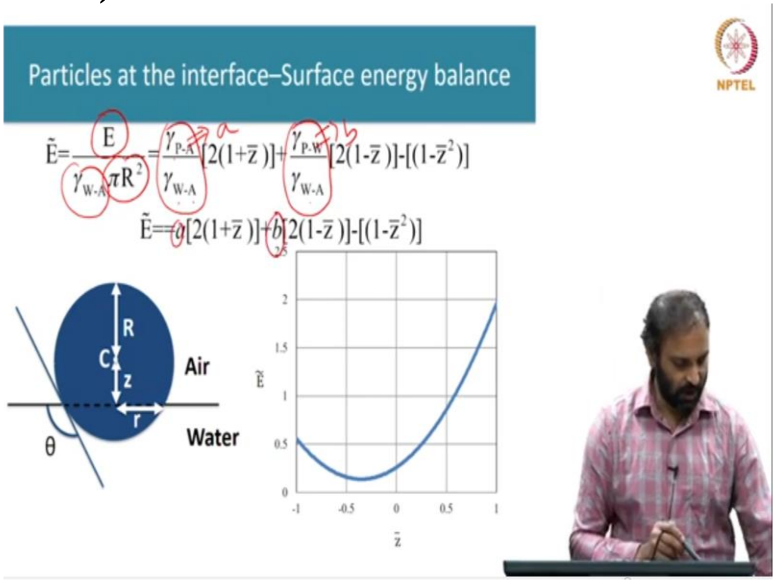

Particles at the interface–Surface energy balance

$$\tilde{E}=\frac{E}{\gamma_{W\text{-}A}\pi R^2}=\overset{\Rightarrow a}{\frac{\gamma_{P\text{-}A}}{\gamma_{W\text{-}A}}}[2(1+\bar{z})]+\overset{\Rightarrow b}{\frac{\gamma_{P\text{-}W}}{\gamma_{W\text{-}A}}}[2(1-\bar{z})]-[(1-\bar{z}^2)]$$

$$\tilde{E}=a[2(1+\bar{z})]+b[2(1-\bar{z})]-[(1-\bar{z}^2)]$$

Now, you can divide So, now, if you look at So, you have you know R square term that occurs in all the terms and because of the fact that gamma water-air is the interfacial tension of the water of the 2 immiscible fluids that are considered and it does not depend on any particles that one considers therefore, we can scale the total energy as by gamma water-air multiplied by pi R square.

Therefore, E bar becomes this is the ratio of the particle-air interfacial tension divided by what are air interfacial tension and this is the particle-water interfacial tension divided by particle sorry water-air interfacial tension therefore, and if we designate this as a and this as b, this E bar becomes a multiplied by 2 times 1 + z bar + b multiplied by 2 times 1 - z bar - 1 – z bar whole square.

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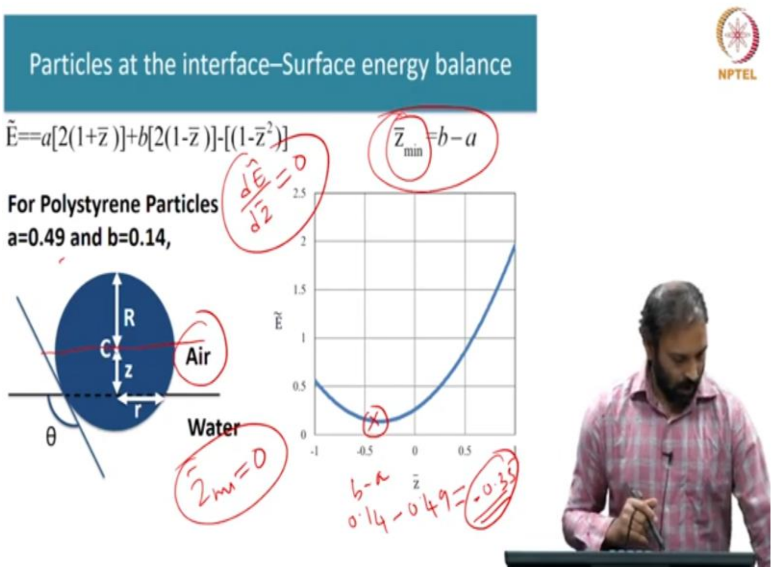

Particles at the interface–Surface energy balance

$\tilde{E} = a[2(1+\bar{z})] + b[2(1-\bar{z})] - [(1-\bar{z}^2)]$

$\bar{z}_{min} = b - a$

For Polystyrene Particles a=0.49 and b=0.14,

$\frac{d\tilde{E}}{d\bar{z}} = 0$

$\bar{z}_{m} = 0$

$b - a$

$0.14 - 0.49 = -0.35$

Now, because of the fact that a and b are known, that is, if we take typical these a and b values, which are the ratio of the interfacial tension of the particle-air with respect to interfacial tension of air-water and the polystyrene because of the fact that we are considered polystyrene particles, the polystyrene-air and polystyrene-water interfacial energies are known and, water air interfacial tension is 72 millinewton per meter.

So, therefore, we know what is the value of a and b and the z bar can go from plus 1 to minus 1. So, therefore, I can plot this E bar as a function of z bar. And what is interesting in this expression is that there is a minima at some location, it is a, this variation suggests that there is a energy well, and, and we can actually calculate the, the positions corresponding to that minima. So, all you need to do is take this expression that is E bar and we could differentiate this with respect to z bar.

So, that is d E bar divided by d z bar and if you set that equal to 0, so, we get what is z minima that is the coordinates that correspond to the minimum location that appears to be b - a and because we know what is the value of b that is 0.14 – a, that is 0.49 therefore, this becomes 0.35 with a negative sign, and the fact that the z bar minimum is negative for the considered case the particle it tells us that the particle is more in air.

And looking at this value one could make a conclusion as to whether the particle that is considered is hydrophilic or hydrophobic. So, that means, your z bar minimum if it is equal to I mean if the minimum occurs at z minimum is equal to 0 that means, the particle is such that the equal half of the particle are in contact with the two fluids therefore, the particle is going to be in neutrally wetting. So, therefore, z bar minimum value gives an indication as to whether the particle resides more in the water phase or more in the air or oil phase.

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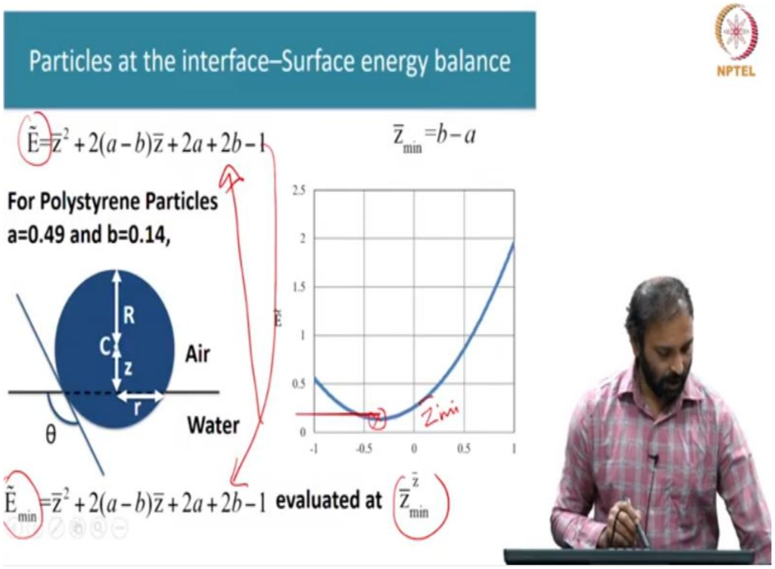

Particles at the interface–Surface energy balance

$\tilde{E}=\bar{z}^2+2(a-b)\bar{z}+2a+2b-1$

$\bar{z}_{min}=b-a$

For Polystyrene Particles
a=0.49 and b=0.14,

$\tilde{E}_{min}=\bar{z}^2+2(a-b)\bar{z}+2a+2b-1$ **evaluated at** $\bar{z}_{min}$

Now, and we can we can rearrange this and then write E bar as z bar square + 2 times a - b z bar + 2 a + 2 b - 1 and what we could do is we can actually evaluate. So, if you want the because we know what is the location of the particle with respect to the interface that is we know z bar minimum I can substitute the value of z bar minimum in this expression and calculate what is the energy that corresponds to this minimum position that means, I would have to evaluate this expression however, by replacing z bar with z bar minimum.

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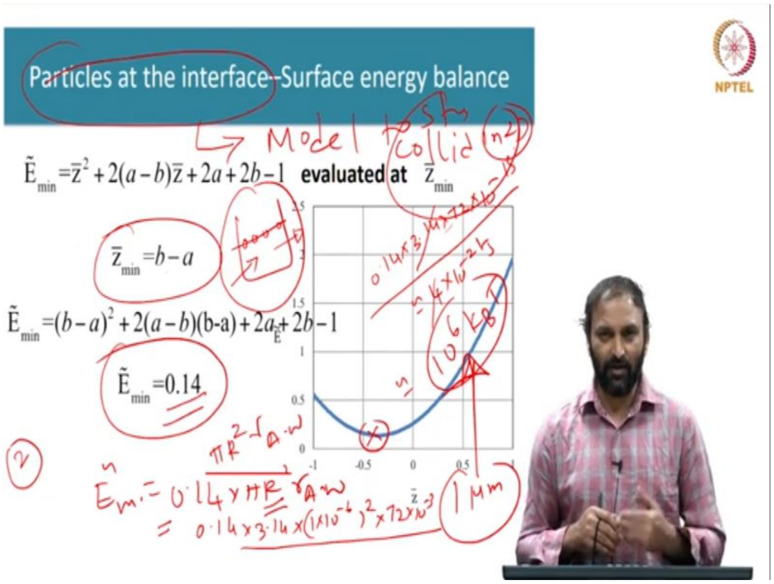
Particles at the interface--Surface energy balance

$\tilde{E}_{min} = \bar{z}^2 + 2(a-b)\bar{z} + 2a + 2b - 1$ **evaluated at** $\bar{z}_{min}$

$\bar{z}_{min} = b - a$

$\tilde{E}_{min} = (b-a)^2 + 2(a-b)(b-a) + 2a + 2b - 1$

$\tilde{E}_{min} = 0.14$

And if you substitute for z bar minimum as b - a, it turns out that E bar minimum is 0.14. And because we have scaled the energy with pi R square into gamma of air-water, if we can calculate the absolute value of E minimum by multiplying this 0.14 with this pi R square into gamma air-water and if we take particles that are like say for example 1 micro meter radius therefore, this E bar minimum becomes 0.14 into pi that is 3.14 multiplied by 1 10 power -6 whole square into 72 into 10 power -3 in SI units and divide.

Therefore, this becomes so, that is 0.14 times, 3.14 times, 72 into 10 power -15 and if we scale this with thermal energy at 298 Kelvin, which is the order of 4 into 10 power -21 joules therefore, what we end up with is So, this gets cancelled therefore, typically the number that you will get would be of the order of 10 power 6 K_BT that means, So, if you look at the coordinates of the minimum the coordinates of the minimum gives us two important parameters.

One is what is the location of the particle with respect to the interface, number two is that what is the depth of the energy Well, in which the particles are dispersed in which the particles are trapped and it turns out that for 1 micrometer particle this energy depth is of the order of 10 power 6 K_BT and this magnitude of energy magnitude of the energy well is important because the particles at interfaces are considered as model systems to study colloids in 2 d.

And that can only be said if the depth of energy well is much larger compared to K_BT that is, in this case 10 power 6 times K_BT, number two it So, happens that the particles that are trapped at an interface that is 2 dimensional colloidal systems they exhibit very high stability that means, if you create an interface containing particles and if you ensure that the evaporation of the fluid is minimized or you know or the condition such that the fluids do not evaporate.

And if you work with the clean fluids or the dust free in environment, it turns out that the particles at the interface there they continue to remain in the same arrangement for several months which is which is an indication that the particles once at the interface because of this very high energy well, they continue to exhibit ultra-high stability an important concept in you know which helps us to define, you know the particles at interfaces as a nice model system to look at colloids in 2 dimensions.