Colloids and Surfaces
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Lecture – 47
Implications from surface energy balances and Estimation of energy required for detachment

So far we have looked at some important experimental observations concerning particles located at fluid-fluid interface. And we have also looked at the hypothesis as well as the theory that has been put forward to explain these experimental observations. So, which are the facts that the long range repulsion for the charged particles positioned at the interface arises due to what is called as a dipolar nature of a dipolar that is associated with every particle at the interface.

And the dipolar-dipolar repulsion is what gives rise to long range repulsive forces. The second aspect that was also discussed was that the particles are trapped in an energy well and typical you know the magnitude of this energy well is of the order of 10 power 6 times the thermal energy for 1 micrometer particles and on such a high energy well, in which the particles are trapped is important in the context of defining colloids at interfaces as a model system to look at particles at interfaces to study particles at interfaces. What we will do now is to look at some important implications of surface energy balance that we have done.

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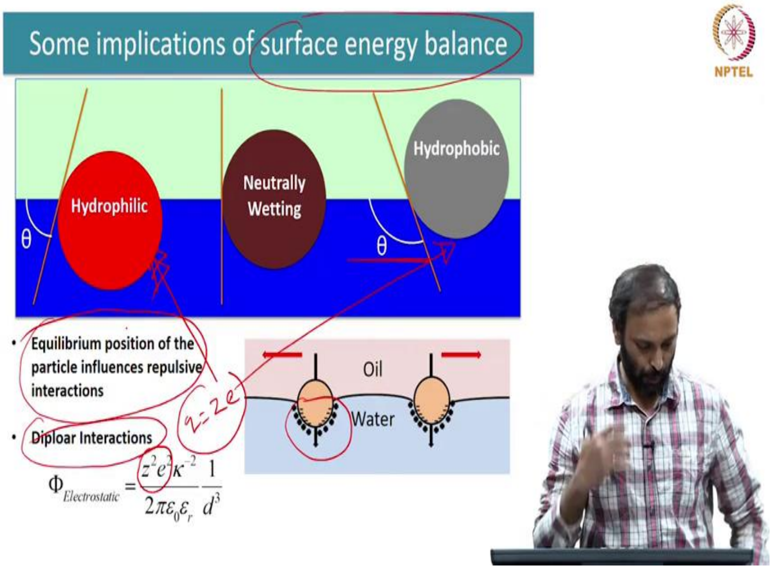

Some implications of surface energy balance

- Equilibrium position of the particle influences repulsive interactions
- Diploar Interactions

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

So, what the surface energy balance that we have looked at it provides an estimate of the equilibrium position of the particle. So, we just plotted the scaled energy that is E bar you know as a function of the scaled distance and it turns out that, you know, there is a minima in the surface energy plot and that position provides us an estimate of the equilibrium position it will tell us whether the particle is more residing in the aqueous phase or the water phase.

That is the particle hydrophilic or is it that the particle is residing more in the oil phase or is it that the particles are hydrophobic and this information is important because, depending upon whether the particle resides more in the aqua phase or more in the oil phase, one could predict the emulsion type that is formed when such particles are used for emulsification. For example, what you are looking at is two pictures where you have a particle that resides more in the water phase.

That is, because, if you look at the portion of the particle that is in water is more such a particles would give rise to oil in water emulsion, that means, if the particles resides more in a particular phase, that phase becomes the continuous phase. So, therefore, hydrophilic particles give rise to oil in water emulsion and typical example of the particles that give all in water emulsion are silica particles or hematite particles or any particle where the contact angle is less than 90 and the particles are hydrophobic.

That means, if they prefer to sit in sit more in the oil phase such particles would give rise to water in oil emulsion and therefore, the surface energy balance can be used to estimate the equilibrium position of the particle which in turn can be used to predict or a prior check what kind of emulsion form when such particles are used for emulsification process and the equilibrium position of the part. Because that is again estimated by surface energy balance is also important.

because of the fact that we know that the dipolar interactions they arise because of the dissociation of charges on the side of the particle that is in contact with the water and depending upon you know what is the extent of immersion of particle in the water phase, there could be this is z times q is that times e and that depends depending upon you know what is the total surface here that is in contact with water.

This q can be higher if the particles are more hydrophilic and if the particles are hydrophobic, the q would be lower therefore, the magnitude of the electrostatic interactions would do depend on you know the what is the location of the particle with respect to the interface and surface energy balance provides as an estimate of finding out what you know what is the typical area of the particle that is in contact with ether of the fluids.

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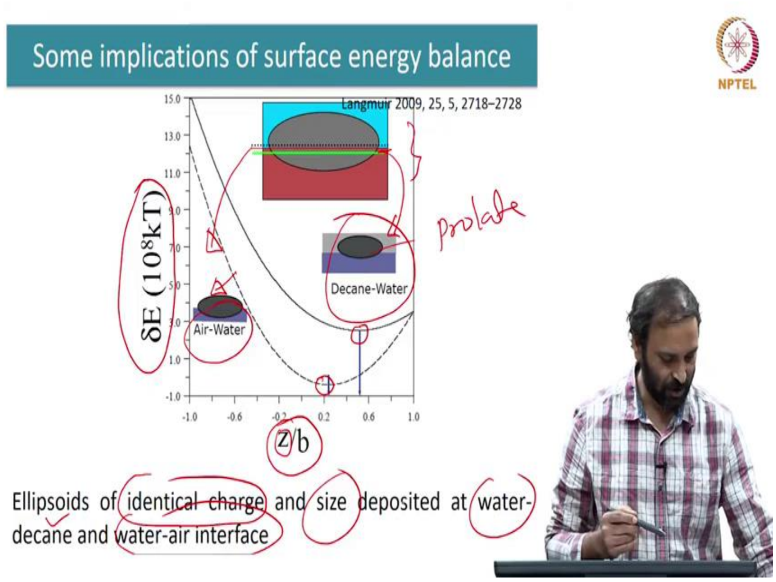

Some implications of surface energy balance

Langmuir 2009, 25, 5, 2718–2728

Ellipsoids of identical charge and size deposited at water-decane and water-air interface

Now, so, what is plotted here is the surface energy as a function of scaled immersion depth, so, z is immersion depth and what you see is two plots one generated for a particle sitting at water-decane interface and the other generated for a same particle that is sitting at air-water interface. So, these are ellipsoids you know or prolate ellipsoids and these are having identical charges and size and they are at two different interfaces.

One is water-decane and water-air and as you can see that the minima in the surface energy plot occurs at a different location that means, the in one case there you know for example, in this particular case, this green line corresponds to the case where the particle is sitting at water-decane interface and this red line corresponds to the case where the particle is sitting at air-water interface in the equilibrium position. Therefore, such simple surface energy balance can be used to access if there is a shift in the particle position with respect to the interface when you are doing experiments at by using particles that are that are of identical charge and size however, at different interfaces.

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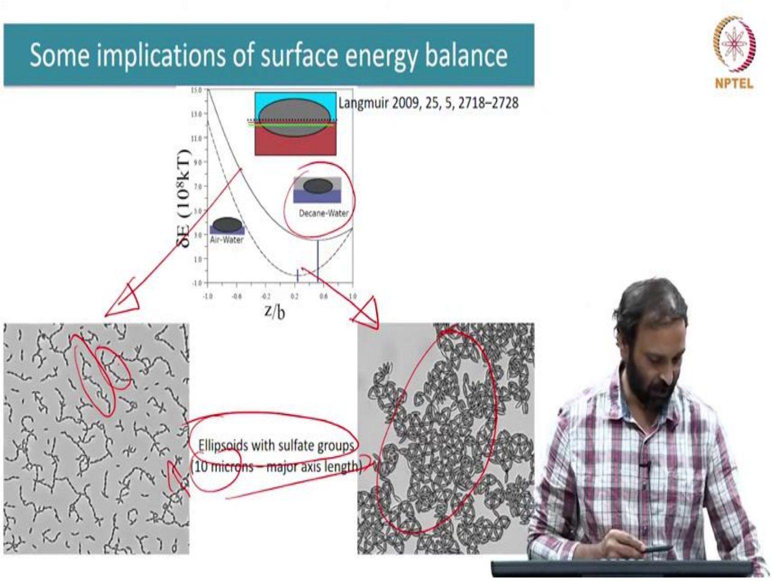
Some implications of surface energy balance

Langmuir 2009, 25, 5, 2718–2728

Ellipsoids with sulfate groups (10 microns – major axis length)

So, the implication of this shift in the particle position with respect to the interface is that depending upon whether the particle is you know at water-decane or water-air interface, they can give rise to very different self-assembly of particles. So, what you are looking at is ellipsoids that have sulfate groups and the major axis of the ellipsoids is 10 micrometer in both the cases in one case where that is for the water-decane interface.

You kind of more see linear aggregates that are formed and if you look at water-air interface, you know the particles are more clustered and they form much larger aggregates. So, therefore, this shift in the one way to think about this would be that the shift in the position of the particle with respect to the interface does affect colloidal interactions, and which in turn can lead to different structure at the interface.

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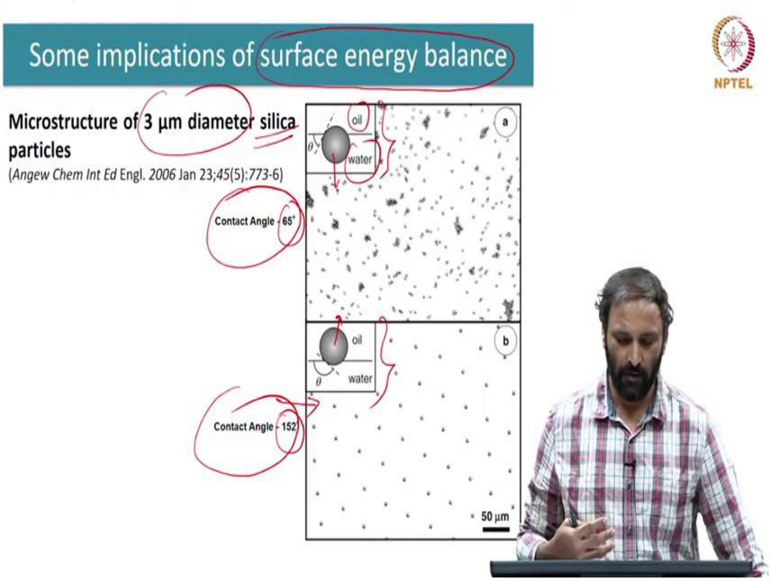
Some implications of surface energy balance

Microstructure of 3 μm diameter silica particles

(*Angew Chem Int Ed Engl. 2006* Jan 23;45(5):773-6)

Contact Angle - 65°

Contact Angle - 152

And this is another example, where 3 micrometer silica particles have been placed at the same type of oil water interface. So, the oil-water interface in this case, oil-water interface in the next case, however, the contact angle of the particle at the interface is different in one case, the contact angle is 65 or the case a contact angle is 152. In this case, the particle sits more in the water phase, here the particle sits more in the oil phase and it can we can clearly see that all other condition being same.

The microstructure that you get with the contact angle 65 is very different from the microstructure that you get at when the contact angle is 150 therefore, we can use the surface energy balance calculations in a way to understand the influence of various different parameters on the microstructure of the particle at the interfaces as well as to predict the emulsions that form when such particles are used in for interface stabilization. Now, what we are going to do now is to kind of use the surface energy balance that we have done to calculate what is the energy that is required to detach a particle from the interface.

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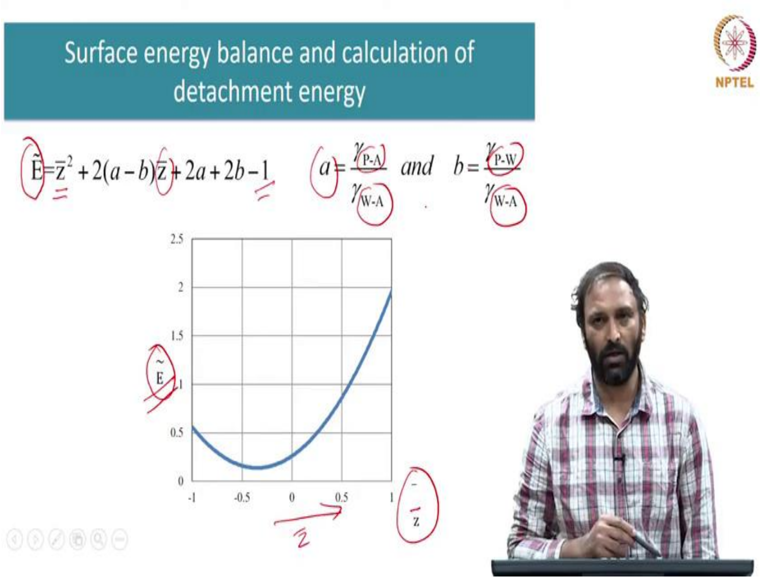

Surface energy balance and calculation of detachment energy

$$\tilde{E} = \bar{z}^2 + 2(a-b)\bar{z} + 2a + 2b - 1 \qquad a = \frac{\gamma_{P\text{-}A}}{\gamma_{W\text{-}A}} \text{ and } b = \frac{\gamma_{P\text{-}W}}{\gamma_{W\text{-}A}}$$

So, for that, we will again use this plot of the surface energy that is a scaled total surface energy as a function of immersion depth that is z bar here and we derived this expression that the scaled surface energy goes as z bar square times 2 times a - b z bar + 2 a + 2 b - 1 where a is given us the ratio of the interfacial tension that of particle air to the water-air and particle and b that of particle-water to water-air.

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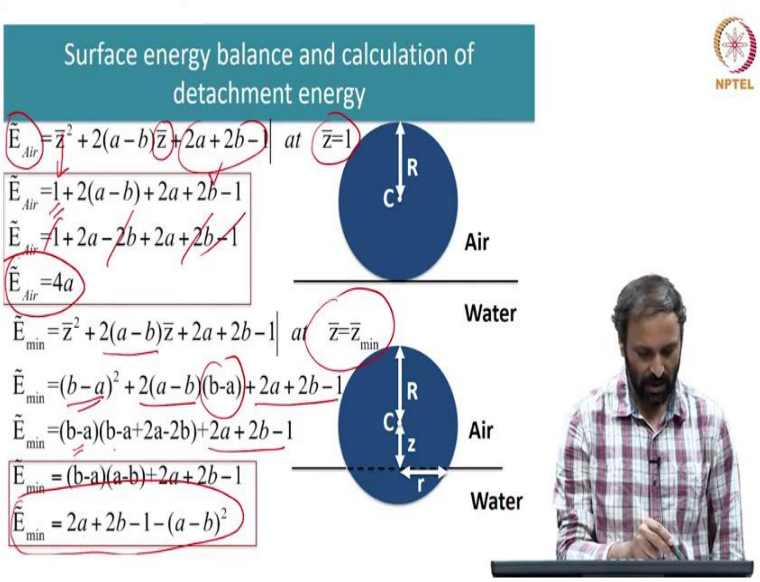

Surface energy balance and calculation of detachment energy

$$\tilde{E}_{Air} = \bar{z}^2 + 2(a-b)\bar{z} + 2a + 2b - 1 \Big| \; at \; \bar{z}=1$$

$$\boxed{\begin{aligned} \tilde{E}_{Air} &= 1 + 2(a-b) + 2a + 2b - 1 \\ \tilde{E}_{Air} &= \cancel{1} + 2a - \cancel{2b} + 2a + \cancel{2b} - \cancel{1} \\ \tilde{E}_{Air} &= 4a \end{aligned}}$$

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

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

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

$$\boxed{\begin{aligned} \tilde{E}_{min} &= (b\text{-}a)(a\text{-}b) + 2a + 2b - 1 \\ \tilde{E}_{min} &= 2a + 2b - 1 - (a-b)^2 \end{aligned}}$$

Now, what we will do is, so, this particular point corresponds to the total energy or the total surface energy of the particle when the particle is immersed completely in air. So, is this is what the configuration looks like you have air water interface and the so, in such a case the particle center is at a distance R you know from the interface therefore, the scaled therefore, z is actually R that is the location of the particles center with respect to the interface is the radius of the particle itself.

And now, this the equilibrium configuration corresponds to the case where the particle is located at the interface and we know that the energy corresponding to that is given by E bar minimum and the energy that corresponds to when the particle is shifted and put completely in the air phase is given by E bar air and therefore, the energy that is required to detach a particle is given by what is the energy total surface energy when the particle is in air phase minus what is the energy that corresponds to the equilibrium position.

Now, and because of the fact that this z is R the scaled height z bar is going to be z r divided by R that is going to be 1. So, therefore, we can take the total surface energy of the particle that is corresponding of the system and then if we substitute z bar is equal to 1 we end up with what is the energy surface energy corresponding to the particle when it is completely in air phase and similarly, for E bar minimum.

So, I will have to take this expression and then substitute is z bar with z bar minimum that is the coordinate that corresponds to the minimum position. So, we have already estimated that in the previous lecture, so, what we will do is, so, we will get E bar air by substituting z bar is equal to 1 therefore, you have z bar square that becomes 1 and becausez bar is 1, so, the second term is 2 times a - b and this term remains as it is.

So, therefore, this this gets canceled, so, you end up with E bar a as 4 times a that means, when the particle is completely in the air phase, the total interfacial energy or the total surface energy is given by 4 times a. And similarly, if we substitute for z bar with z bar minima, we know z bar minimum is given by b - a therefore, this becomes b - a whole square plus you have 2 times a - b multiplied by b - a and this term is as it is and I can take b - a to be common here.

So, therefore, I end up with b - a + 2 a - 2 b and this remains as it is. So, therefore, this E bar if you do simplification E bar minimum essentially becomes 2 a + 2 b - 1 - of a - b whole square. So, therefore, now that we have been able to calculate what is E bar air and E bar minimum.

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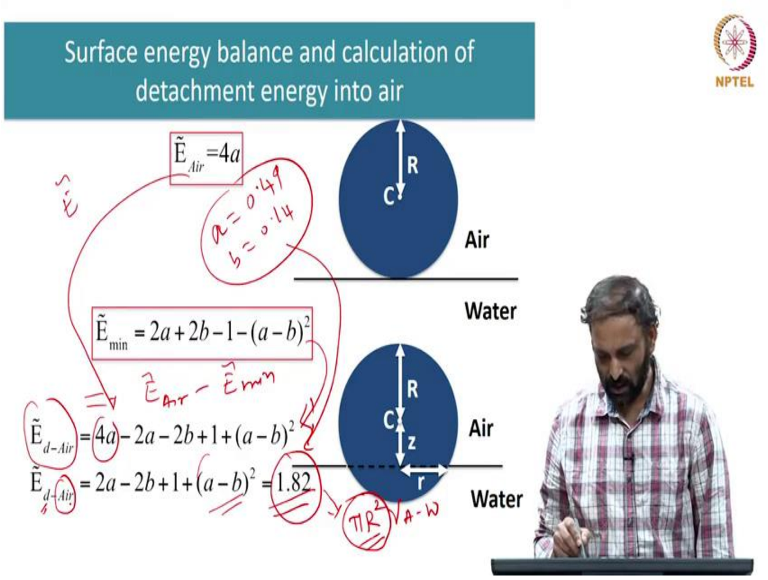

Surface energy balance and calculation of detachment energy into air

$\tilde{E}_{Air} = 4a$

$a = 0.49$
$b = 0.14$

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

$\tilde{E}_{Air} - \tilde{E}_{min}$

$\tilde{E}_{d-Air} = 4a - 2a - 2b + 1 + (a-b)^2$

$\tilde{E}_{d-Air} = 2a - 2b + 1 + (a-b)^2 = 1.82$

$\pi R^2 \gamma_{A-W}$

So, we can calculate what is the detachment energy which essentially is E bar air - E bar minimum therefore, this becomes 4 a that is E bar a - E bar minimum term therefore, E_d air that corresponds to the energy that is required for detaching a particle into the air phase is given by 2 times a - 2 b + 1 + 1 a - b whole square and because we know that a is 0.49 and b is 0.14 we can substitute these values and we obtain energy that is required for detaching the particle into the air phase is 1.82.

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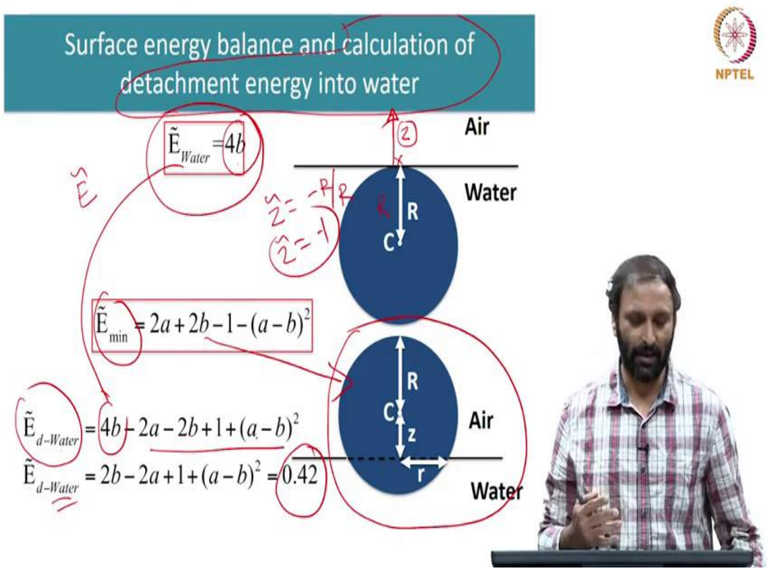

Surface energy balance and calculation of detachment energy into water

$$\tilde{E}_{Water} = 4b$$

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

$$\tilde{E}_{d-Water} = 4b - 2a - 2b + 1 + (a-b)^2$$

$$\tilde{E}_{d-Water} = 2b - 2a + 1 + (a-b)^2 = 0.42$$

Of course, this is the scale energy if you want the absolute values of the energy, you would have to multiply this term with pi R square into gamma of air water that is the area that is because we had scaled that the expression for E bar with pi R square times gamma air-water therefore, if you want the absolute value of the energy that is required to detach a part into the air phase, you would have to multiply this with this term.

Similarly, we can calculate what is the energy that is required to move the particle into the water phase in this case, the equilibrium configuration remains the same and that is given by 2 times a + 2 b - 1 - a - b whole square, but, the now the particle is shifted into the water phase and therefore, the particle now is such that, it is at a distance again R from the interface. However, because we have defined z in a particular way.

Therefore, z bar becomes - R divided by R, therefore, z bar becomes - 1 therefore, if you substitute for z bar is equal to - 1 in the expression for the total surface energy, you end up with the energy of the total surface energy of the particle when it is in water phase to be 4 b therefore, energy that is required for detaching the particle into the water phase is given by 4 b that is this term - E bar minimum and if you substitute for a and b E detachment into water phase turns out to be 0.42.

So, therefore this surface energy balance calculation can also be used to estimate what is the energy that is required for detaching a particle into one of the phases depending upon the fluid particle system that no one is dealing with. There are alternate approaches for estimating the energy of detachment. We will try and take a look at that now.

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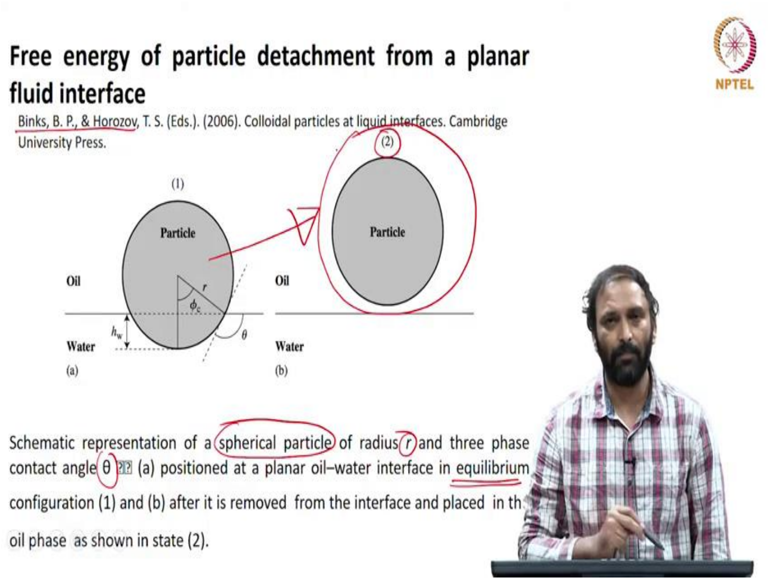

Free energy of particle detachment from a planar fluid interface

Binks, B. P., & Horozov, T. S. (Eds.). (2006). Colloidal particles at liquid interfaces. Cambridge University Press.

Schematic representation of a spherical particle of radius r and three phase contact angle θ ⍰⍰ (a) positioned at a planar oil–water interface in equilibrium configuration (1) and (b) after it is removed from the interface and placed in th oil phase as shown in state (2).

So, what the concept that I am going to discuss is from the book that is edited by you know, these guys. So, what you are looking at is a schematic where there is a spherical particle of radius a, sorry radius r and that is the radius of the particle and the contact angle is theta and you have case 1 here and case 2 and case 1 corresponds to when the particle is at equilibrium configuration.

That means, the spherical particles is positioned at the interface and it is allowed to reach an equilibrium position and this configuration corresponds to the equilibrium configuration of a spherical particle of radius r contact angle theta positioned at the interface. Now, this case 2 corresponds to when the particle is removed from the interface and it is positioned in the oil phase that means, the particles that is positioned the interface that is shifted and then that is placed completely such that completely in the oil phase and that is shown in this schematic 2.

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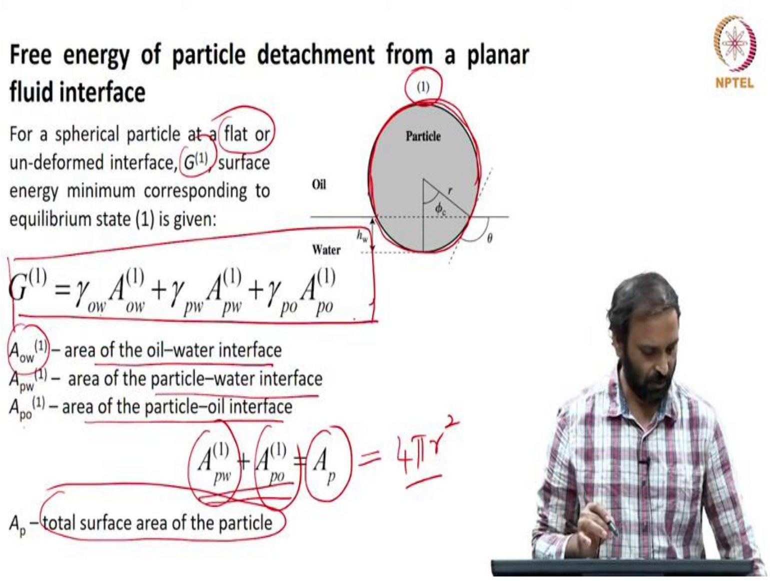

Free energy of particle detachment from a planar fluid interface

For a spherical particle at a flat or un-deformed interface, $G^{(1)}$ surface energy minimum corresponding to equilibrium state (1) is given:

$$G^{(1)} = \gamma_{ow}A_{ow}^{(1)} + \gamma_{pw}A_{pw}^{(1)} + \gamma_{po}A_{po}^{(1)}$$

$A_{ow}^{(1)}$ – area of the oil–water interface

$A_{pw}^{(1)}$ – area of the particle–water interface

$A_{po}^{(1)}$ – area of the particle–oil interface

$$A_{pw}^{(1)} + A_{po}^{(1)} = A_p = 4\pi r^2$$

A_p – total surface area of the particle

Now, what we can do is we can write an expression for configuration 1 that is when the particle is in configuration 1 and we are going to assume that the interface is flat that means, the interface is not deformed and G of 1 that is the interfacial energy corresponding to the equilibrium position of the particle which we know that it is the minimum energy configuration and that is essentially given by the summation of the three interfacial energies.

Where gamma oil-water times A oil-water is the total interfacial energy of the oil-water interface, particle-water interfacial tension multiplied by the particle-water area is the interfacial energy corresponding to the particle-water interface. And similarly, there is an interfacial energy contribution that comes from the particle-oil interface. So, where A oil-water superscript 1 is the area of the oil-water interface.

Similarly, A pw is the area of the particle-water interface and A po is the area of the particle-oil interface and if we sum up the interfacial area that is in this the surface here the particle that is in contact with oil that is this interfacial area and the surface area of the particle that is in contact with water the summation of the two interfacial areas is equal to Ap which is the total surface area of the particle which for a spherical particle is going to be 4 pi r square. So, that is the surface energy. So, this is the surface energy that corresponds to the energy minimum configuration when the particle is at its equilibrium position.

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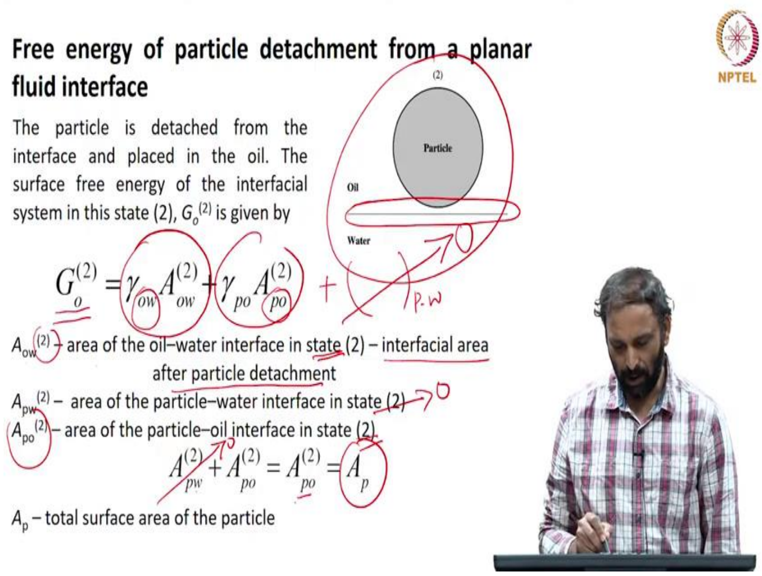

Free energy of particle detachment from a planar fluid interface

The particle is detached from the interface and placed in the oil. The surface free energy of the interfacial system in this state (2), $G_o^{(2)}$ is given by

$$G_o^{(2)} = \gamma_{ow} A_{ow}^{(2)} + \gamma_{po} A_{po}^{(2)} + \cancel{(\quad)}_{P.W} \rightarrow 0$$

$A_{ow}^{(2)}$ – area of the oil–water interface in state (2) – interfacial area after particle detachment

$A_{pw}^{(2)}$ – area of the particle–water interface in state (2) $\rightarrow 0$

$A_{po}^{(2)}$ – area of the particle–oil interface in state (2)

$$\cancel{A_{pw}^{(2)}} \rightarrow 0 + A_{po}^{(2)} = A_{po}^{(2)} = A_p$$

A_p – total surface area of the particle

Similarly, we can write an expression of the total interfacial energy of the system when the particle is detached and placed in the oil phase. And in that case, the total interfacial energy is given by there are only two contribution because the particle is no more in contact with water. Therefore, the interfacial energy conservation that comes from the particle-water interface is essentially 0 now, and we have only contribution that comes from the oil-water interface and the particle-oil interface.

And in this case A ow superscript 2 is the area of the oil-water interface in state 2 and that is the area of the interfacial area after the particle is detached that means, so, the particle was occupying certain area initially now, when it is removed there is only there is the total interfacial area of the oil-water interface is what is A ow superscript 2 and particle-water interfacial area as we said it is 0.

In this case and A po superscript 2 is the area of the particle-oil interface in state 2 and similarly, we can write that A pw superscript 2 plus A po subscript 2 should be equal to A p and because of the fact that this is 0 essentially A particle-oil superscript 2 is going to be A p that is the total surface area of the particle.

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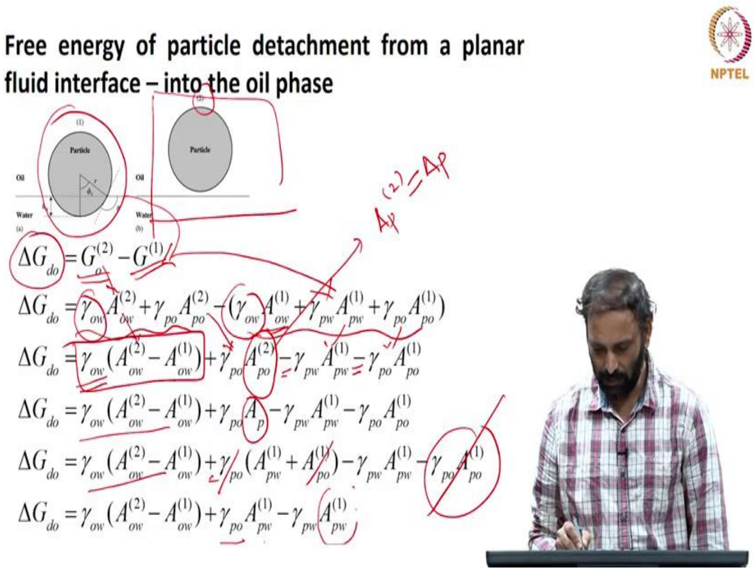

Free energy of particle detachment from a planar fluid interface – into the oil phase

$$\Delta G_{do} = G^{(2)} - G^{(1)}$$

$$\Delta G_{do} = \gamma_{ow} A_{ow}^{(2)} + \gamma_{po} A_{po}^{(2)} - (\gamma_{ow} A_{ow}^{(1)} + \gamma_{pw} A_{pw}^{(1)} + \gamma_{po} A_{po}^{(1)})$$

$$\Delta G_{do} = \gamma_{ow} (A_{ow}^{(2)} - A_{ow}^{(1)}) + \gamma_{po} A_{po}^{(2)} - \gamma_{pw} A_{pw}^{(1)} - \gamma_{po} A_{po}^{(1)}$$

$$\Delta G_{do} = \gamma_{ow} (A_{ow}^{(2)} - A_{ow}^{(1)}) + \gamma_{po} A_{p} - \gamma_{pw} A_{pw}^{(1)} - \gamma_{po} A_{po}^{(1)}$$

$$\Delta G_{do} = \gamma_{ow} (A_{ow}^{(2)} - A_{ow}^{(1)}) + \gamma_{po} (A_{pw}^{(1)} + \cancel{A_{po}^{(1)}}) - \gamma_{pw} A_{pw}^{(1)} - \cancel{\gamma_{po} A_{po}^{(1)}}$$

$$\Delta G_{do} = \gamma_{ow} (A_{ow}^{(2)} - A_{ow}^{(1)}) + \gamma_{po} A_{pw}^{(1)} - \gamma_{pw} A_{pw}^{(1)}$$

Now, the energy of detachment it is defined as the energy the total surface energy of the fluid interface particle system in state 2 minus the this interfacial energy of the system corresponding to the equilibrium configuration that is G superscript 1. So, therefore, we can substitute the corresponding terms for each of these terms and because we have A oil-water common. So, we are going to take that you know outside the parentheses.

This is so, you have A oil-water superscript 2 - A oil-water superscript 1 that is the term with oil, water interfacial tension and so, we are going to retain this term as it is and because you have a negative sign here. So, we have to you know basically you have these 2 terms with negative sign and this term will continue to remain the same and because of the fact that a particle-water superscript 2 particle-oil superscript 2.

That is the interfacial area of the particle oil interface we have said that because the particle is only in contact with oil phase it is same as Ap therefore, we can substitute for Ap instead of A po superscript 2 and we know that A po is same as the Ap is same as a particle-water in configuration 1 plus A particle-oil in configuration 1 and therefore, these 2 terms gets cancelled. So, this term and sorry about that.

So, this should be so, you have not the term. We know that this term, this term, that is positive sign here and this term this negative sign. So, therefore, these 2 terms gets cancelled. So, what we end up with is particle-oil interfacial tension times A pw 1 minus particle-water interfacial tension multiplied by A pw superscript 1.

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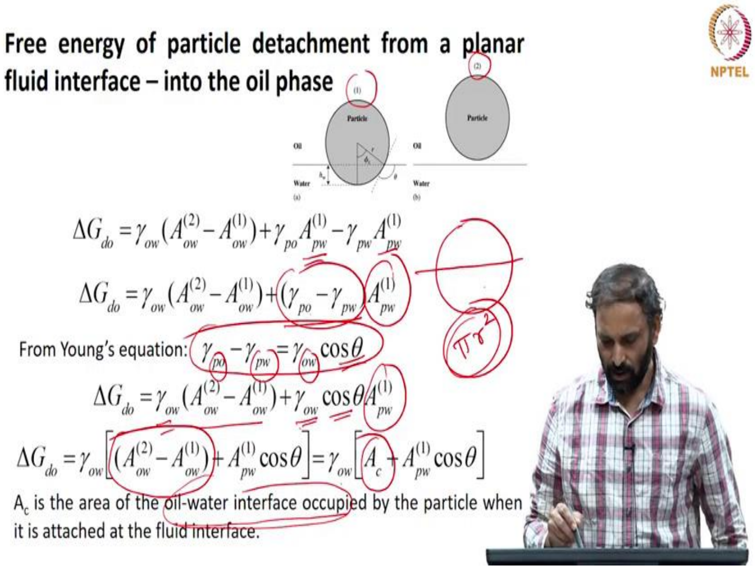

Free energy of particle detachment from a planar fluid interface – into the oil phase

$$\Delta G_{do} = \gamma_{ow}(A_{ow}^{(2)} - A_{ow}^{(1)}) + \gamma_{po}A_{pw}^{(1)} - \gamma_{pw}A_{pw}^{(1)}$$

$$\Delta G_{do} = \gamma_{ow}(A_{ow}^{(2)} - A_{ow}^{(1)}) + (\gamma_{po} - \gamma_{pw})A_{pw}^{(1)}$$

From Young's equation: $\gamma_{po} - \gamma_{pw} = \gamma_{ow}\cos\theta$

$$\Delta G_{do} = \gamma_{ow}(A_{ow}^{(2)} - A_{ow}^{(1)}) + \gamma_{ow}\cos\theta A_{pw}^{(1)}$$

$$\Delta G_{do} = \gamma_{ow}\left[(A_{ow}^{(2)} - A_{ow}^{(1)}) + A_{pw}^{(1)}\cos\theta\right] = \gamma_{ow}\left[A_c + A_{pw}^{(1)}\cos\theta\right]$$

A_c is the area of the oil-water interface occupied by the particle when it is attached at the fluid interface.

And because A pw superscript 1 is common, I can take it out of the parenthesis you end up with gamma particle oil minus gamma particle water term and we can use Young's equation which relates the interfacial tension of the particle oil interface, particle water interface and oil water interface with the contact angle so, therefore we can replace this term with the right hand side of Young's equation.

Therefore, we have delta G d_o is gamma-oil water times A oil water superscript 2 - A oil-water superscript 1 - gamma oil-water A cos theta times a particle water superscript 1 and this term which is which is the oil-water interfacial area in configuration 2 – oil-water interfacial area in configuration 1 it is what is called as the contact area c for contact. A c is the area of the oil-water interface occupied by the particle when it is at the fluid-fluid interface.

Now, if the particle is such that the particle is the half of the particle is in one phase and half of the particle in the other phase, then the area that the particle occupies at the interface it is essentially pi r square because the intersection of the particle and the interface at the equilibrium configuration gives in the area gives a circle whose area is pi r square this would depend on what is the contact angle of the particle with respect to the interface and this A_c which is A oil-water in configuration 2 – A oil-water in configuration 1 it is the area of the oil-water interface that is occupied by the particle when it is at the interface.

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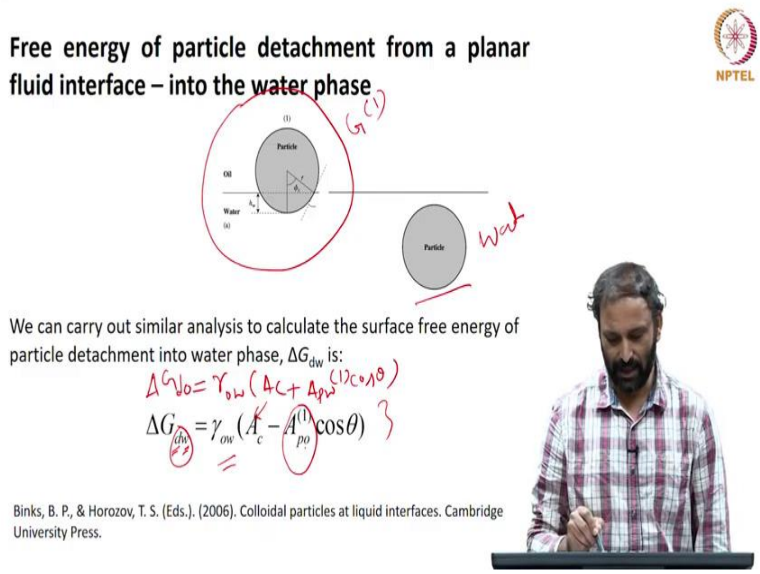

Free energy of particle detachment from a planar fluid interface – into the water phase

We can carry out similar analysis to calculate the surface free energy of particle detachment into water phase, ΔG_{dw} is:

$$\Delta G_{do} = \gamma_{ow}(A_c + A_{pw}^{(1)}\cos\theta)$$

$$\Delta G_{dw} = \gamma_{ow}(A_c - A_{po}^{(1)}\cos\theta)$$

Binks, B. P., & Horozov, T. S. (Eds.). (2006). Colloidal particles at liquid interfaces. Cambridge University Press.

And so, therefore, we can similarly, we can also derive an expression for detaching a particle into the water phase. So, detaching the particle into oil phase we obtained an expression which is gamma oil-water into Ac + A particle water you know in configuration 1 multiplied by cos theta that is what we obtain in the previous you know slide and similarly, we can write the interfacial energy for the system.

When the particle is in equilibrium position that is again it will still be G1 and when the particle is completely in the water phase, and we can do a similar surface energy calculation and it turns out that for detaching a particle into the water phase, the interfacial the energy that is required for detachment is given by again gamma oil-water the contact area that is the area that the particle occupies at the interface and minus the particle-oil interfacial area in configuration times cos theta where theta is the contact angle.

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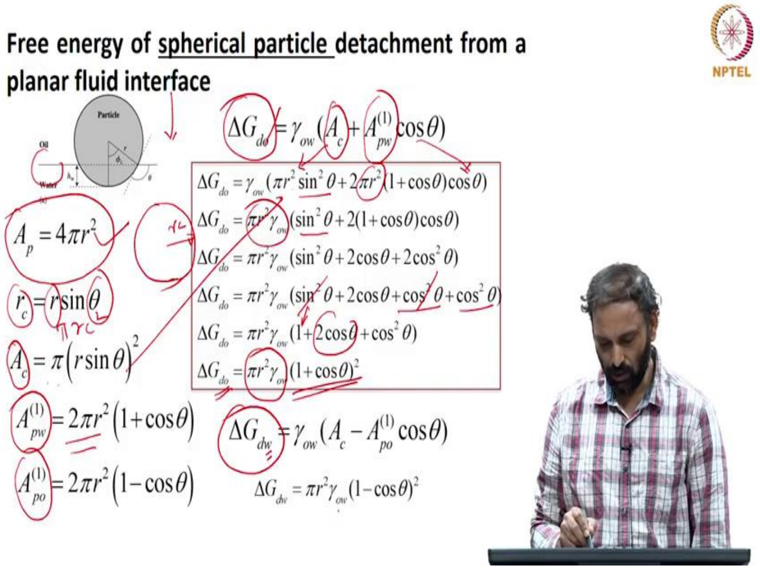

Free energy of spherical particle detachment from a planar fluid interface

$$\Delta G_{do} = \gamma_{ow}(A_c + A_{pw}^{(1)}\cos\theta)$$

$$A_p = 4\pi r^2$$

$$r_c = r\sin\theta$$

$$A_c = \pi(r\sin\theta)^2$$

$$A_{pw}^{(1)} = 2\pi r^2(1+\cos\theta)$$

$$A_{po}^{(1)} = 2\pi r^2(1-\cos\theta)$$

$$\Delta G_{do} = \gamma_{ow}(\pi r^2\sin^2\theta + 2\pi r^2(1+\cos\theta)\cos\theta)$$

$$\Delta G_{do} = \pi r^2\gamma_{ow}(\sin^2\theta + 2(1+\cos\theta)\cos\theta)$$

$$\Delta G_{do} = \pi r^2\gamma_{ow}(\sin^2\theta + 2\cos\theta + 2\cos^2\theta)$$

$$\Delta G_{do} = \pi r^2\gamma_{ow}(\sin^2\theta + 2\cos\theta + \cos^2\theta + \cos^2\theta)$$

$$\Delta G_{do} = \pi r^2\gamma_{ow}(1 + 2\cos\theta + \cos^2\theta)$$

$$\Delta G_{do} = \pi r^2\gamma_{ow}(1+\cos\theta)^2$$

$$\Delta G_{dw} = \gamma_{ow}(A_c - A_{po}^{(1)}\cos\theta)$$

$$\Delta G_{dw} = \pi r^2\gamma_{ow}(1-\cos\theta)^2$$

Now, if we are working with spherical particles, so, we know that Ap that is the total surface area of the particle is 4 pi r square and this Rc it is the radius of the contact line. So, what we mean by that is that, if you look at the intersection of the interface and the particle, if you see from the top we will have a circular contact line and the radius this is given by Rc and this Rc is related to the contact angle theta and R as Rc is equal to r time sin theta.

Therefore, the area that the particle occupies the area of the oil-water interface that the particle occupies when is the interface is given by pi times Rc square or pi times r sin theta the square and now that we know the contact angle theta we can do some simple geometry and then show that A particle water in configuration 1 is 2 pi r square into 1 + cos theta and a particle-oil in configured in 1 is 2 pi r square into 1 - cos theta.

And therefore, the energy that is required for detaching a particle into oil phase, we can obtain in definite expression, where we are going to replace Ac by the contact area that is pi r square into sine square theta + A po, it is 2 pi r square into 1 + cos theta multiplied by cos theta because we have pi r square and as common so, we can take that out. So, we have pi r square times gamma oil water into sine square theta plus 2 times 1 + cos theta multiplied by cos theta and we can write this as cos square theta + cos square theta.

This becomes one that is what you have here and 2 times cos theta + cos theta square which is essentially becomes delta theta delta G detachment into oil phase is pi r square into gamma-oil water multiplied by 1 + cos theta whole square. And similarly, we can show that detachment energy into the water phase is given by pi r square into gamma oil-water into 1 - cos theta square.

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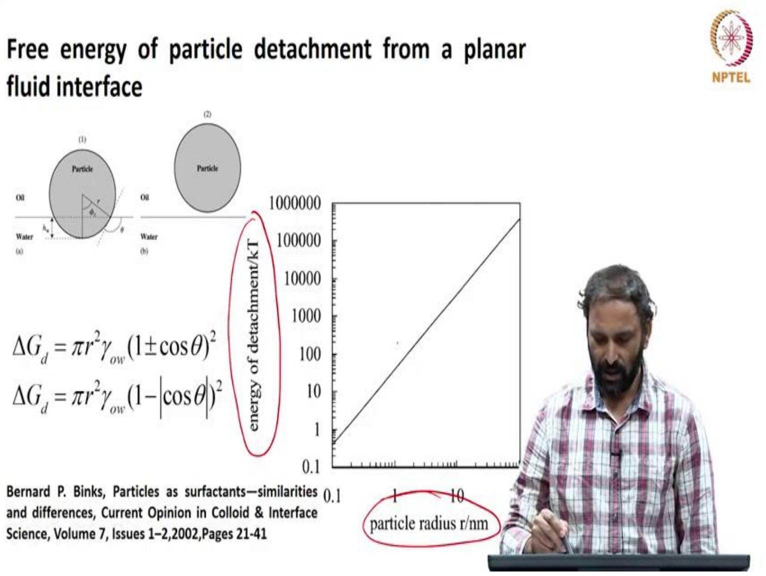

Free energy of particle detachment from a planar fluid interface

$$\Delta G_d = \pi r^2 \gamma_{ow} (1 \pm \cos\theta)^2$$

$$\Delta G_d = \pi r^2 \gamma_{ow} (1 - |\cos\theta|)^2$$

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

Therefore, the energy of detachment either into the oil phase or the water phase is given by pi r square gamma oil-water into 1 + or - cos theta square or 1 - or this you can write it as 1 - mod of cos theta square. So, therefore, there are 2 approaches to obtaining the energy that is required for detaching a particle into one of the fluids either by, doing a surface energy balance. We will find out what is the energy that corresponds to the minimum.

And what is the energy that is when the particle is in one of the phases and the difference between the 2 or you can both of them of course, you know, you can our analog is so, or you can write an expression for the total free energy of the system when the particle is in the equilibrium position and you shift the particle into one of the phases and then write an expression for the total interfacial energy and the difference of that is the energy.

That is required for detaching the particle into one of the phases and this is an expression you know a plot of the, the energy of detachment as a function of particle size that we have already seen. And you will see that the energy of detachment essentially increases with increase in the, the particle dimension and it goes as radius of the particle to the power 2.