Colloids and Surfaces
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Lecture – 48
Colloidal Interactions at Interfaces

So now, to end this module, we will start look at again some aspects of colloidal interactions.

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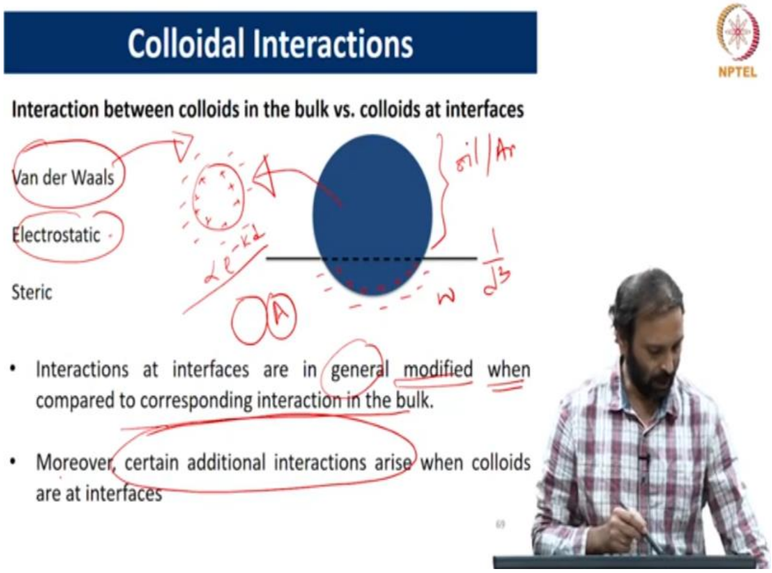

Colloidal Interactions

Interaction between colloids in the bulk vs. colloids at interfaces

Van der Waals

Electrostatic

Steric

- Interactions at interfaces are in general modified when compared to corresponding interaction in the bulk.
- Moreover, certain additional interactions arise when colloids are at interfaces

And we have seen several types of colloidal interactions in the bulk, Van der Waals interactions, electrostatic interactions, steric interactions and other and we saw that the colloidal interactions at the interfaces in general are modified, when compared to the corresponding interactions and the bulk is an example of that, we found that we discussed that you know in the case of a charged particle the electrical double layer around you know a charged particle is symmetric.

And However, when the particles are at the interface, because of the fact that the dissociation only happens in the region of the particle surface that is in contact with you know one of the phases depending upon the nature of the dissociable groups, we know that the electrostatic interactions instead you know being proportional to you know e power - Kappa times the separation distance they go as 1 over d cube right.

So, this is an example, where the electrical double layer interactions are in the at the interface are modified in when compared to corresponding interactions the bulk and similarly, the same would also hold although not discuss same would also hold good for the Van der Waals interactions as well because we know that the permittivity of the medium in which the particles are placed you know dictate the magnitude of the Hamaker constant.

And hence, the magnitude of the Van der Waals force of interaction now, that the particle is part in the oil phase, or the air phase, and part in the water phase, you know it will see different fluids that means different permittivity is you know across the interface and therefore, the Van der Waals interactions will also be modified in when the particular the interfaces. So, although certain interactions will get modified when the particles are at the interface.

There are also certain additional interactions that arise when the particles are at the interface. And these interactions are typically are not present or they are absent in a when we consider particles in the bulk.

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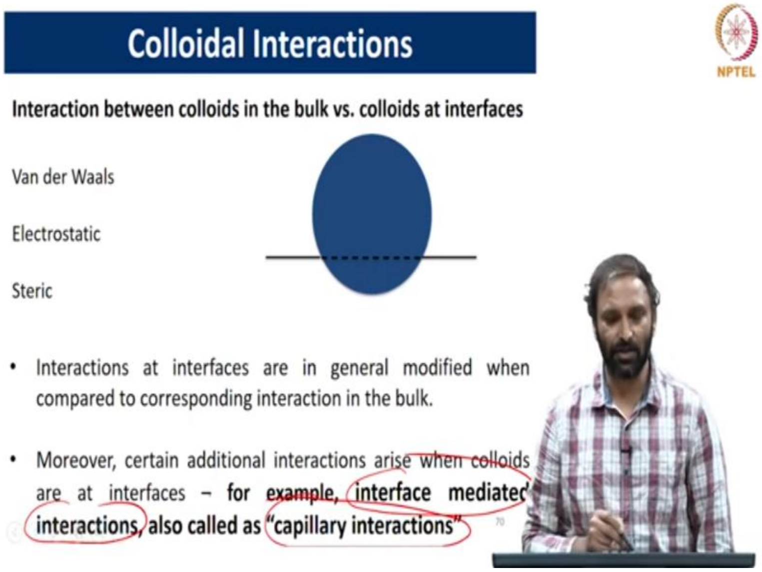

Colloidal Interactions

Interaction between colloids in the bulk vs. colloids at interfaces

Van der Waals

Electrostatic

Steric

- Interactions at interfaces are in general modified when compared to corresponding interaction in the bulk.
- Moreover, certain additional interactions arise when colloids are at interfaces – **for example, interface mediated interactions, also called as "capillary interactions"**

And these examples of these interactions are what are called as interface mediated interactions or capillary interactions.

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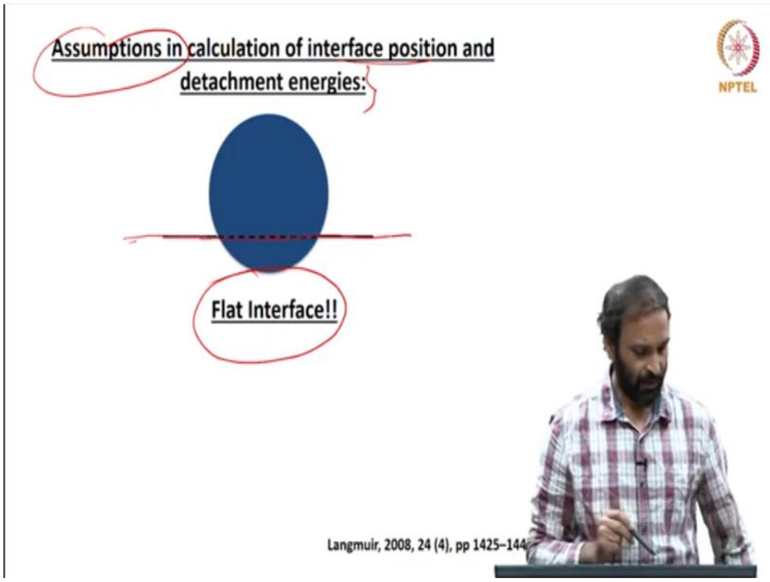

Assumptions in calculation of interface position and detachment energies:

Flat Interface!!

Langmuir, 2008, 24 (4), pp 1425–144

And before we talk about these interactions, I would like to point out to one of the assumption that we have been we have used in the calculation of the interfacial position and the detachment energies is that the interface is flat that means, the interfaces unperturbed by the presence of the particle.

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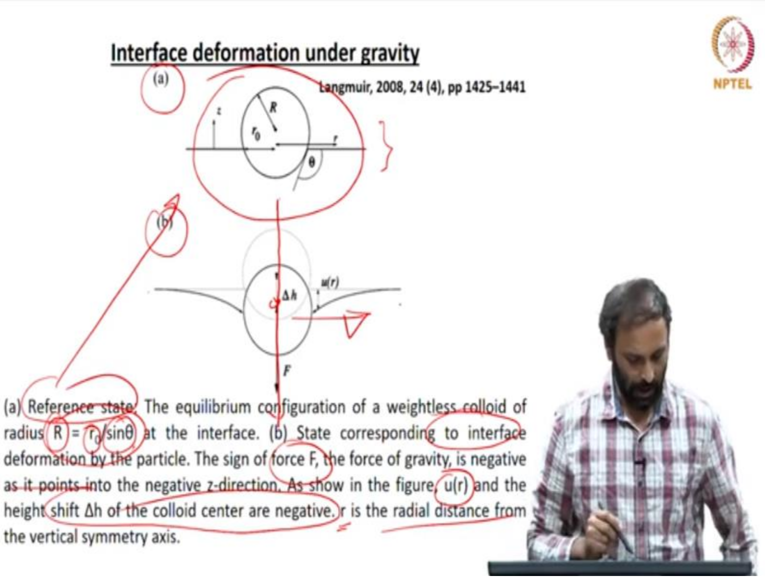

Interface deformation under gravity

Langmuir, 2008, 24 (4), pp 1425–1441

(a) Reference state: The equilibrium configuration of a weightless colloid of radius R = r_0/sinθ at the interface. (b) State corresponding to interface deformation by the particle. The sign of force F, the force of gravity, is negative as it points into the negative z-direction. As show in the figure, u(r) and the height shift Δh of the colloid center are negative. r is the radial distance from the vertical symmetry axis.

However, that need not be the case if you have so, the assumption that the presence of the particle the interface does not deform the interface is will hold good only for a weightless particle or when the particles are very small. So, what you are looking at is two cases one is a reference state and that shows the equilibrium configuration of a weightless particle that is the case where the gravitational forces on the particle can be neglected.

And if you have the radius of the particle is R and that is related to the radius of the contact line and sine of the contact angle by this expression and now, when you have so that is the this is for a weightless particle right the configuration a now, in b what you have is a particle when the interface is deformed. So, that is the dotted line that you see that is the equilibrium that is the location of the interface when we had a weightless particle.

Now we have a force F that is the gravitational force that is acting on the particle and that is pulling the particles down and because of which the interface is deformed, as shown by these lines. And what you also see in the figure is that there is this u of r that is the that captures what is the magnitude of the interface deformation and that is a function of r and this delta h it denotes what is the shift of the colloid center because of the gravitational forces that is acting on the particle.

And r is the radial distance from the vertical axis of symmetry that means, you know so, that is the vertical so, that is the vertical axis of symmetry that coincides with the center of the particle and r is measured perpendicular to this vertical axis.

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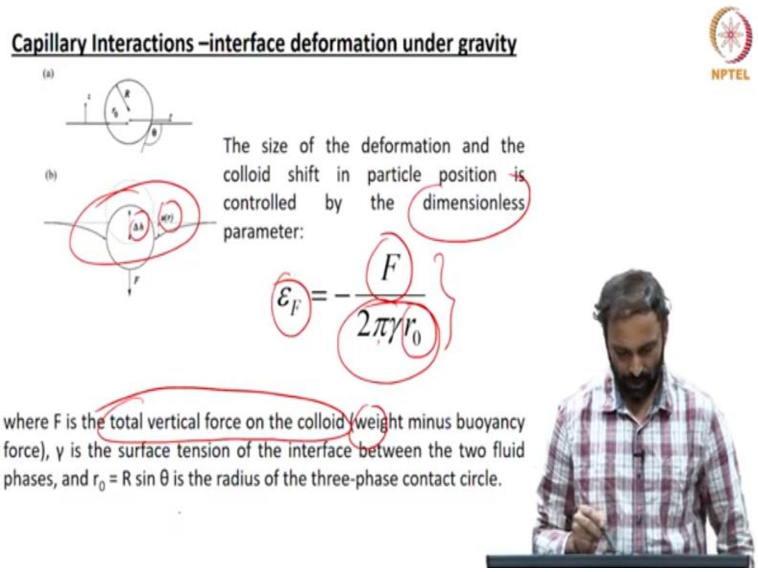

Capillary Interactions –interface deformation under gravity

The size of the deformation and the colloid shift in particle position is controlled by the dimensionless parameter:

$$\varepsilon_F = -\frac{F}{2\pi\gamma r_0}$$

where F is the total vertical force on the colloid (weight minus buoyancy force), γ is the surface tension of the interface between the two fluid phases, and $r_0 = R \sin\theta$ is the radius of the three-phase contact circle.

Now, the extent of the shift in the particle position that is delta h and the size of the deformation which is which is characterized by this u of r it depends on a dimensional parameter epsilon F which is defined as minus of F divided by 2 pi r times gamma into r naught, where r naught is the radius of the contact line this 2 pi r times gamma times r naught essentially gives us what is the surface tension force that is acting at the contact line and F is the gravitation force.

So, therefore, this E_F is defined as the ratio of the vertical force that is acting on the colloid that is weight minus buoyancy and the denominator is the surface tension force that is acting at the contact line right.

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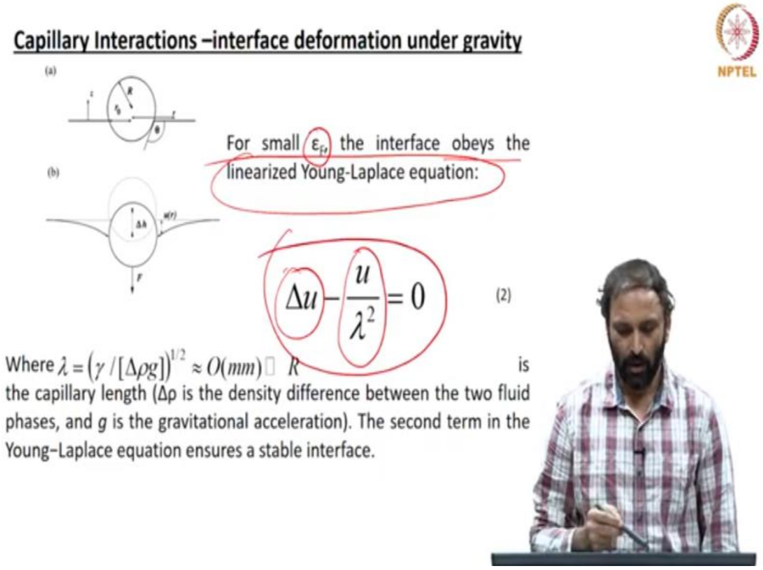

Capillary Interactions –interface deformation under gravity

For small ε_F, the interface obeys the linearized Young-Laplace equation:

$$\boxed{\Delta u - \frac{u}{\lambda^2} = 0} \qquad (2)$$

Where $\lambda = (\gamma/[\Delta\rho g])^{1/2} \approx O(mm)$ □ R is the capillary length (Δρ is the density difference between the two fluid phases, and g is the gravitational acceleration). The second term in the Young–Laplace equation ensures a stable interface.

When this epsilon F is very small that means, when the interfacial when this quantity is very small that means, when the surface tension forces are dominant then the interface deformation is given by the linearized Young Laplace equation and in this term there are 2 terms. So, this comes from the hydrostatic pressure contribution and this comes from the Laplace pressure contribution and so, essentially one could solve this linearized Young Laplace equation to find out the dependence of u of r with the radial distance r.

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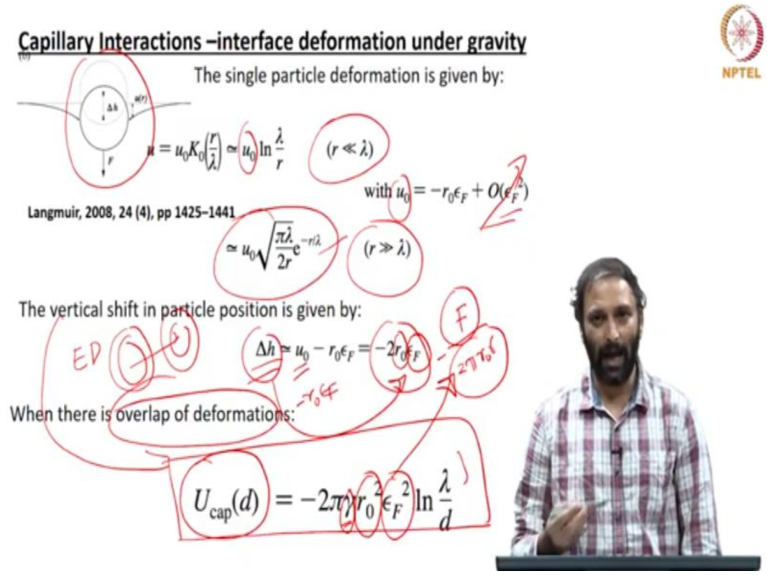

Capillary Interactions –interface deformation under gravity

The single particle deformation is given by:

$$u = u_0 K_0\left(\frac{r}{\lambda}\right) \simeq u_0 \ln\frac{\lambda}{r} \quad (r \ll \lambda)$$

with $u_0 = -r_0\epsilon_F + O(\epsilon_F^2)$

Langmuir, 2008, 24 (4), pp 1425–1441

$$\simeq u_0\sqrt{\frac{\pi\lambda}{2r}}e^{-r/\lambda} \quad (r \gg \lambda)$$

The vertical shift in particle position is given by:

$$\Delta h \simeq u_0 - r_0\epsilon_F = -2r_0\epsilon_F$$

When there is overlap of deformations:

$$U_{\mathrm{cap}}(d) = -2\pi\gamma r_0^2\epsilon_F^2 \ln\frac{\lambda}{d}$$

And the solution of if we consider the interfacial deformation by a single particle that means, when there are no particles in the immediate vicinity of the particle or for an isolated particle sitting at the interface, we can solve the linearized Young Laplace equation to obtain u going as u naught times ln of lambda / r, where lambda is what is called as a capillary length, which is again you know defined as the ratio of the interfacial tension contribution to the gravitation contribution

And this has units of length and typically for if you look at water oil or water air systems this lambda would be typically of the order of a millimeter in such a case u goes as u naught lambda ln of lambda / R, when r is much much less than lambda and with u going as u naught going as minus r naught epsilon F and higher order terms and for the case of r greater than lambda u essentially, the solution becomes of this form.

And the vertical shift in lambda is minus 2 times r naught epsilon F, if you neglect the higher order term this u naught is minus r naught epsilon F and which gives rise to delta h being minus 2 times r naught epsilon F therefore, if you know what is the gravitational force that is acting on the particle and if you know what is the surface tension force we and the radius of the contact line we can actually estimate what is the shift in the particle position.

And similar to the fact that the electrical double layer interactions originated when the electrical double layer between the 2 adjacent particles overlap when there is an overlap of the interface deformation that is when the capillary interactions come into picture and U capillary goes as minus 2 pi gamma, where gamma is the interfacial tension, r naught square, where r naught is the radius of the contact line, epsilon F square which is the non-dimensional quantity.

That we define which is the ratio of the gravitation force to the surface tension force times ln lambda divided by d. So, therefore, one could estimate capillary interaction between the particles when they are sufficiently close such that there is an interface deformation overlap between the 2 particles.

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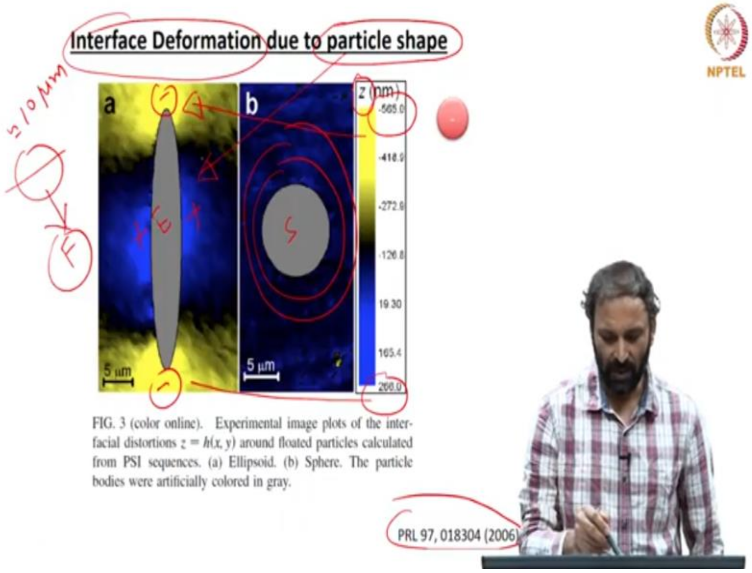

Interface Deformation due to particle shape

FIG. 3 (color online). Experimental image plots of the interfacial distortions $z = h(x, y)$ around floated particles calculated from PSI sequences. (a) Ellipsoid. (b) Sphere. The particle bodies were artificially colored in gray.

PRL 97, 018304 (2006)

Now, can we discuss that the interface deformation can occur when the gravitational force acts on the particle that is true for sufficiently big particles typically, of the order of 10 micrometer you know are larger however, the interface deformation can also occur due to particle shape what you are looking at is some results where what is shown is a interferometry experiments, where the deformation around an elliptical particle under a spherical particle is shown.

And so, yellow region corresponds to negative value of you know the position of the particle with respect to the interface and positive value corresponds to the positive you know that means to say that when So, if you look at the fact at this spherical particle case, no matter where we are around the particle, the interface deformation appears to be symmetric. That means, in this case, it is always positive value of the z.

That means, the interfaces in the case of spherical particles, the interface would either be elevated or depressed depending upon the nature of the particles that we are considering. However, if you look at non-spherical particle, there is the interface deformation is that means the value of the z is positive here and the value of the z is negative here that means, there could be interface elevations as well as depression around the particle when the particles are elliptical in shape.

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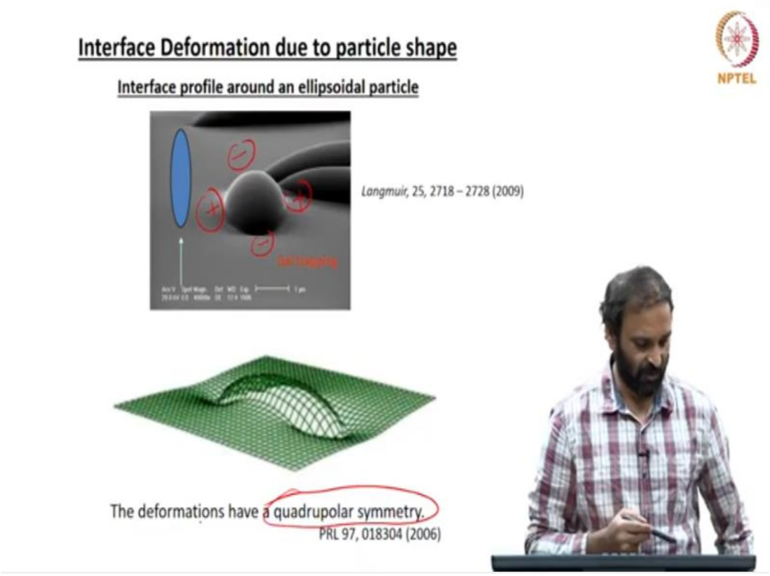

Interface Deformation due to particle shape

Interface profile around an ellipsoidal particle

Langmuir, 25, 2718 – 2728 (2009)

The deformations have a quadrupolar symmetry.

PRL 97, 018304 (2006)

There are been experiments which capture the interface deformation that it is the interface is elevated in at the side and the interfaces depressed at the edge of the ellipsoid right and such interface deformation are what are called as quadrupolar interface deformation.

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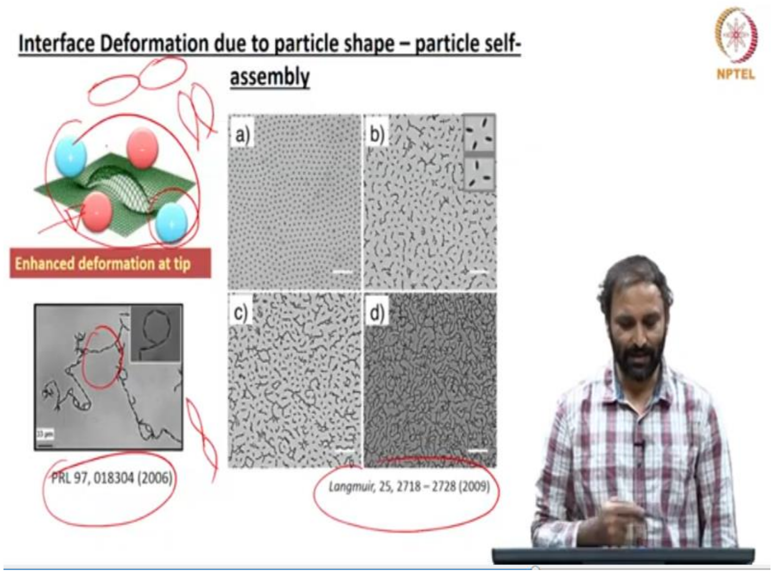

Interface Deformation due to particle shape – particle self-assembly

Enhanced deformation at tip

PRL 97, 018304 (2006)

Langmuir, 25, 2718 – 2728 (2009)

And these interface deformations have important implications in terms of the self-assembly of such particles. And whenever, there is an interface elevation you know that is typically referred to as a capillary negative charge and whenever there is an interface depression by convention it is referred to as capillary positive charge. And if you look at the nature of the self-assembly of particles with such deformation.

We see that there is always a tip-tip connection either in in different experiments and that is because of the rule that the like capillary charges attract therefore, whenever we you would see an assembly of particles with such quadrupolar symmetry you will all either see or tip-tip aggregation or side-side aggregation because, these are the only 2 configurations that lead to the minimization of the total energy free energy of the system and the fact that the like capillary charges attract lead to such assemblies.

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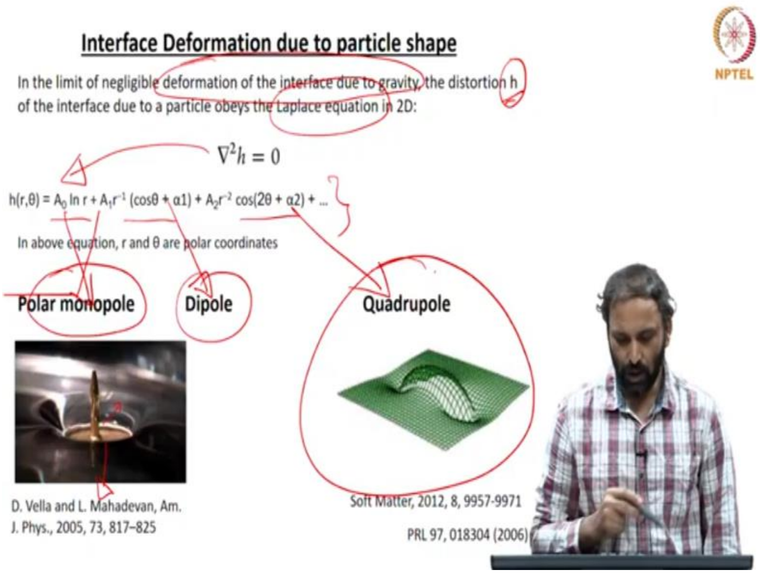

Interface Deformation due to particle shape

In the limit of negligible deformation of the interface due to gravity, the distortion h of the interface due to a particle obeys the Laplace equation in 2D:

$$\nabla^2 h = 0$$

$$h(r,\theta) = A_0 \ln r + A_1 r^{-1} (\cos\theta + \alpha 1) + A_2 r^{-2} \cos(2\theta + \alpha 2) + \ldots$$

In above equation, r and θ are polar coordinates

D. Vella and L. Mahadevan, Am. J. Phys., 2005, 73, 817–825

Soft Matter, 2012, 8, 9957-9971

PRL 97, 018304 (2006)

And in the case where the deformation of the interface is a little bit gravity is negligible, the distortion of the interface with respect to the planar condition that is h it obeys the Laplace equation 2 dimension and the solution of this Laplace equation is given by this and the different terms that you see here are what are called as capillary poles. The first term is what is called a capillary monopole, the second term is what is called a dipole, and the third one is what is called as quadrupolar deformation.

And we saw an example of that you know earlier and the monopolar deformations are typically observed when we have spherical particle at the interface. Now, also this is an example where there is a pin that is located that is positioned at the interface and because of the weight of the gravity that is acting on the plane you see that the interface is actually pulled up. And if you look at such monopolar deformation as I mentioned earlier, they will either be interface elevation at a given our location or they will be interface depression however, in the case of dipoles and higher order poles you will have both elevation and depression around you know isolated particles.

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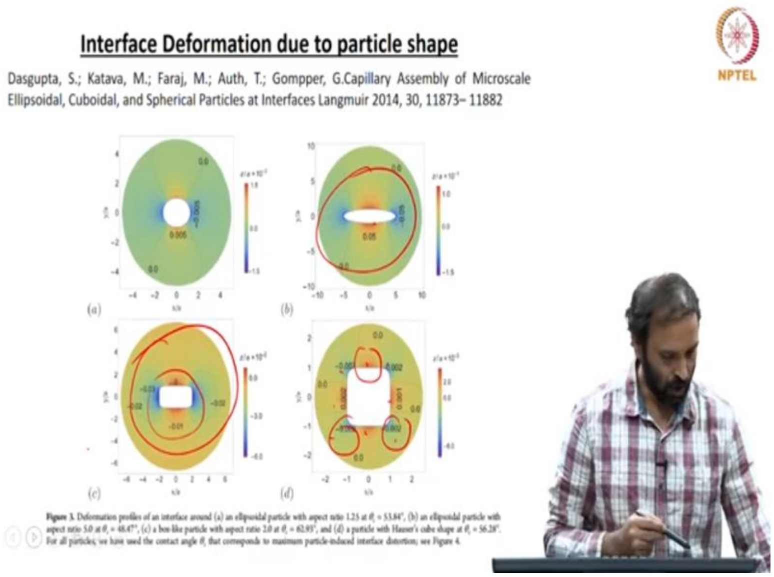

Interface Deformation due to particle shape

Dasgupta, S.; Katava, M.; Faraj, M.; Auth, T.; Gompper, G.Capillary Assembly of Microscale Ellipsoidal, Cuboidal, and Spherical Particles at Interfaces Langmuir 2014, 30, 11873– 11882

Figure 3. Deformation profiles of an interface around (a) an ellipsoidal particle with aspect ratio 1.25 at $\theta_c = 53.84°$, (b) an ellipsoidal particle with aspect ratio 5.0 at $\theta_c = 48.47°$, (c) a box-like particle with aspect ratio 2.0 at $\theta_c = 62.93°$, and (d) a particle with Hauser's cube shape at $\theta_c = 56.28°$. For all particles, we have used the contact angle θ_c that corresponds to maximum particle-induced interface distortion; see Figure 4.

And these are examples where higher order poles have been observed this is a case where there is an octopolar deformation that is that you have 8 regions that is 1, 2, 3, 4, 5, 6, 7, 8 where you know there is interface elevation and depression occur around a particle this is an example of again a quadrupolar deformation that occurs when you have elliptical and 2 dimensional rod like particles.

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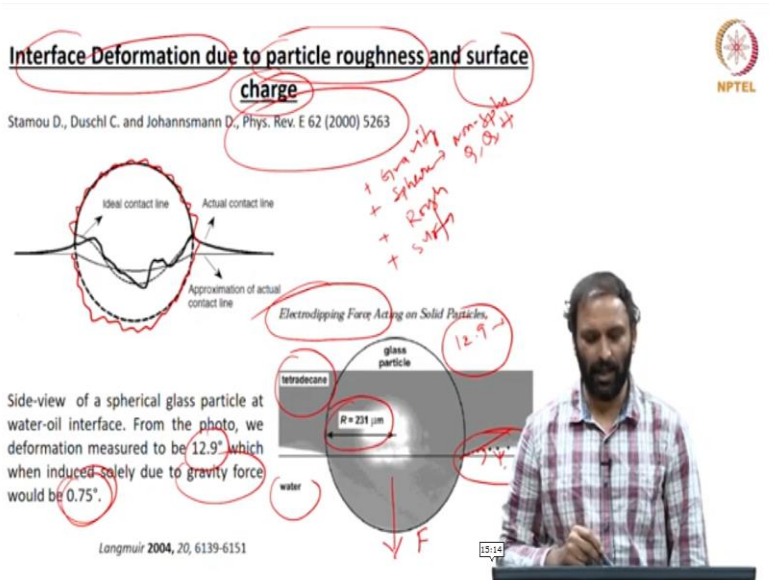

Interface Deformation due to particle roughness and surface charge

Stamou D., Duschl C. and Johannsmann D., Phys. Rev. E 62 (2000) 5263

Electrodipping Force Acting on Solid Particles,

Side-view of a spherical glass particle at water-oil interface. From the photo, we deformation measured to be 12.9° which when induced solely due to gravity force would be 0.75°.

Langmuir 2004, 20, 6139-6151

So, now going further so, the interface deformation can also occur in the case of when the particles are rough that means, if the particle are have some undulations on the surface and these undulations can help in pinning of the contact line around the particle surface and because of this roughness, the interface deformation need not be monopolar anymore and there have been calculations which showed that for a rough particle.

The interface deformation again is a quadrupolar in nature. So, would also be the case when we have particles with high surface charge what you are looking at is an example, where we have a really large particle located at water tetradecane interface and what is plotted is the fact that the interface these image captures that the interface is not planar anymore, and we can actually calculate this angle psi and it turns out to be 1.29 case where the particle is charged.

However, when there is a soul effect of gravity, and this angle is given by 0.75 therefore, so, the difference between the 2 cases is that, so, 12.9 psi is observed when the particle is charged as against 0.75 when the particle is deformed solely because of gravity, this additional deflection essentially comes from the fact that the particle is charged and such you know the deformation are arising because of what is called electro dipping force.

That is in addition to the force of gravity pulling the particle down, there could be contribution that comes from the charge of the particle and this also essentially gives rise to an additional deformation. Therefore, there are four different factors that can lead to the interface deformation;

one is purely because of gravity that occurs when the particles are sufficiently large. Second, when we have a particle that is not sphere that is when the particles are non-spherical in shape.

We can either have a quadrupolar or octopolar or you know hexapolara deformation of the interface, we can also have interface deformation that arise because of the particle roughness and because of surface charge in the form of electro dipping force.

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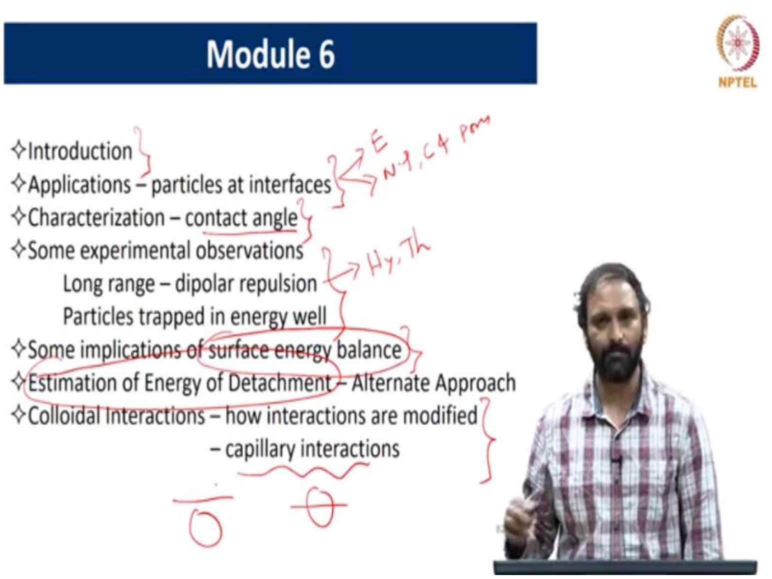

Module 6

- ✧Introduction
- ✧Applications – particles at interfaces
- ✧Characterization – contact angle
- ✧Some experimental observations
    - Long range – dipolar repulsion
    - Particles trapped in energy well
- ✧Some implications of surface energy balance
- ✧Estimation of Energy of Detachment – Alternate Approach
- ✧Colloidal Interactions – how interactions are modified
    - – capillary interactions

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So, just to conclude, so, in this module we have looked at we started with discussing how to position particles at the interface, we looked at some applications of particle at interfaces concept in the form of using this for emulsion stabilization in the creation of new type of particles and new materials such as colloidosomes, and also their application in the make in the making of porous materials as well. We looked at some additional characterization, how to obtain the equilibrium position of particles with respect to the interface.

We discuss some important experimental observations, which lead to some hypothesis followed by the development of theory for understanding the structure as well as the stability of particles interfaces. And we show that we discussed that the surface energy balance calculations have important implications in terms of understanding the structure of monolayers containing these particles.

We talked about calculation of energy of detachment followed by, how the interactions are modified, when the particles at interfaces. Finally, we discussed about interface deformation mediate interactions that arise only when the particles are at the interface compared to the fact that such interactions are absent when the particles are immersed in the bulk.