Fundamentals of Particle and Fluid Solid Processing
Prof. Arnab Atta
Department of Chemical Engineering
Indian Institute of Technology, Kharagpur

Lecture - 59
Colloids and nanoparticles (Contd.)

Hello everyone and welcome back to the penultimate class or the lecture of Fundamentals of Particle of Particle and Fluid Solid Processing. And, we were discussing about the Colloids and the nanoparticles. We have seen the surface forces, the net or the resulting force and how it impacts on the suspension that we will see today.

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Suspension rheology

- Rheology: study of flow and deformation of matter
- Wide range of mechanical behaviour: elastic to Newtonian fluid
- Influencing parameters
  - volume fraction of solids
  - viscosity of the fluid
  - surface forces between particles
  - particle size and shape
- Understand the influence of volume fraction without surface forces
  - hydrodynamic forces
  - Brownian motion
  - non-interacting hard sphere model

So, for that we have introduced this suspension rheology in the last class. So, where we I mentioned that the rheology is the study of flow and deformation of a matter. Now, it encompasses a wide range of behavior starting from Newtonian to the very elastic nature of the fluid.

So, now, the influencing parameter of this suspension rheologies are typically the volume fraction of the solids, viscosity of the fluid, surface forces between the particles and particle shape as well as it is size. So, these are the critical or the main influencing parameters, that we will see today that how it actually influences the rheology.

Now, foremost important thing is the surface force between the particles when it comes to the fine particles or the nanoparticles and the colloids. Now, we have seen those kind of forces that what are the contributing forces to the surface forces. So, we will broadly mention this now, as a clubbed term is the inter particle interaction, ok.

Now, to understand this influence say we take one by one; first let us understand the influence of volume fraction without any surface force or without any inter particle forces; which means, in the such scenario can happen when the hydrodynamic forces are the dominant forces, it dictates the behavior of the particles including the suspension. And, there is since we are talking about the fine particles, there is the movement due to Brownian motion, but these are non interacting particle.

And, we typically say this approach to understand the behavior of a suspension is the hard sphere model; that means, when there is no interaction between the particles.

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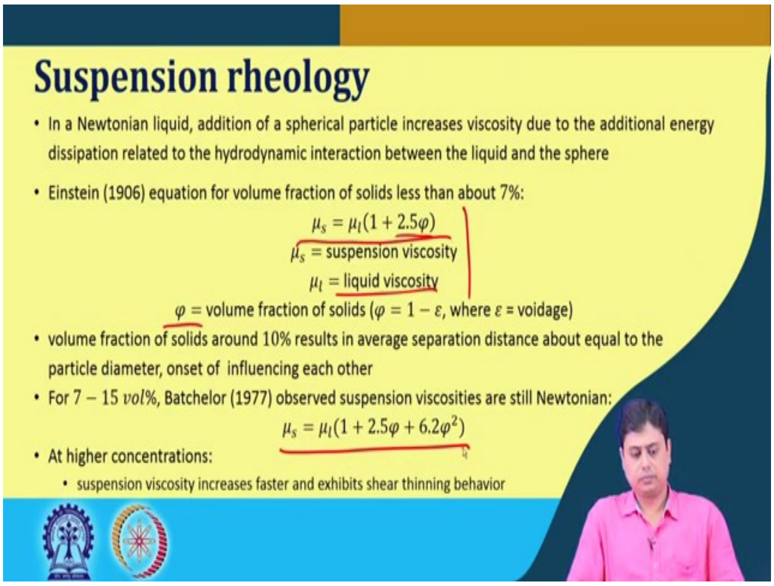

Suspension rheology

- In a Newtonian liquid, addition of a spherical particle increases viscosity due to the additional energy dissipation related to the hydrodynamic interaction between the liquid and the sphere
- Einstein (1906) equation for volume fraction of solids less than about 7%:

$$\mu_s = \mu_l(1 + 2.5\varphi)$$

μ_s = suspension viscosity

μ_l = liquid viscosity

φ = volume fraction of solids ($\varphi = 1 - \varepsilon$, where ε = voidage)

- volume fraction of solids around 10% results in average separation distance about equal to the particle diameter, onset of influencing each other
- For 7 – 15 *vol*%, Batchelor (1977) observed suspension viscosities are still Newtonian:

$$\mu_s = \mu_l(1 + 2.5\varphi + 6.2\varphi^2)$$

- At higher concentrations:
  - suspension viscosity increases faster and exhibits shear thinning behavior

So, in this hard sphere approach or hard sphere modeling say in a Newtonian liquid. This addition of spherical particle increases the viscosity due to the additional energy dissipation that would happen that related to this hydrodynamic interaction between the liquid and the sphere. So, as we increase the solids concentration in a Newtonian suspension say the viscosity typically increases.

Now, Einstein proposes a relation of this suspension viscosity and the liquid viscosity that is when it was without any liquid solid particles. Now, that expression or this expression that is mentioned here,

$$\mu_s = \mu_l (1 + 2.5\varphi)$$

where μ_s is the suspension viscosity, μ_l is the liquid viscosity and it is related by a volume fraction of the solids which is 1 minus epsilon where epsilon is the voidage. Because, if this is the voidage so; that means, $1 - \varepsilon$ would naturally be the volume fraction. So, 2.5 times of the volume fraction plus 1 multiplied by mu l gives us the mu suspension.

Now, this expression holds true for very dilute suspension for near about when the solids concentrations are less than 7% by volume. Now, the basic assumption that was made while proposing this expression was that these particles are far away from each other so, there is no influence of one particle on another. So, that was the definition of very dilute suspension.

Now, for that these expressions it has been tested by several experimental process, methods and it holds true. Now, the volume fraction of solids when it is around 10 percent then the average separation distance between the particle becomes near about equal to that of the particle diameter, and that triggers the influencing of one particle to the other or influenced of one particle the presence of the other.

So, in this range say moderately concentrated suspension to 7 to 15% in the range, bachelor further expanded this expression

$$\mu_s = \mu_l (1 + 2.5\varphi + 6.2\varphi^2)$$

and proposed that the suspension viscosity remains still in Newtonian design, but it does not just vary linearly like it was proposed by Einstein. So, that expression is mentioned here.

So, again this has been tested and has been seen that it is reasonably feeds several experimental data. Now, at higher concentration than this that whatever is mentioned here that is here about 15 percent by volume when we go above that when we add some solid more solids to the suspension, then the suspension viscosity increases faster; it is rapidly increases and it exhibits shear thinning behavior; that means, it is viscosity goes down as we increase the shear rate on that suspension.

So, this interesting behavior we will see that why this happens? Now, remember we are talking about the hard sphere model or the hard sphere approach, in which there is no inter particle interaction. So, what happens here? That while I traced this moderately suspended suspension; the concentrated suspension, in the particles will have it is Brownian motion, and now this Brownian motion actually dictates the suspension rheology.

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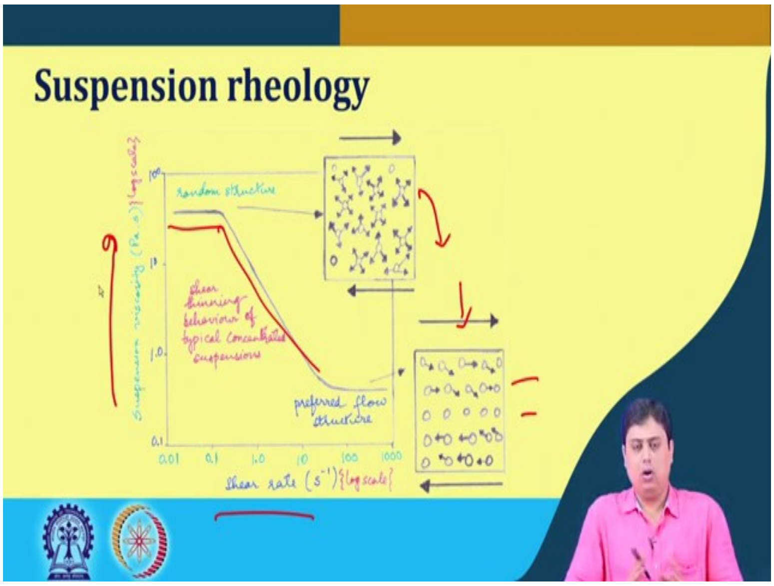

Suspension rheology

So, any addition of the concentration or the solids concentration in that suspension it is viscosity is dictated by that amount of the concentration. So, initially for a particular say concentration, it will have a Newtonian like plateau at the lower shear rate and as the shear rate is increased. The hydrodynamic interactions will be higher and higher will become more dominant than this Brownian motion and it the particles will be in a more arranged manner or say it will be in a kind of layered state, which was also called a preferred flow structure which is shown here.

So, from a random position of the particles it becomes more organized, and quite naturally then the viscosity becomes smoother or lower. So, this transition from low shear rate Newtonian plateau to a high shear Newtonian plateau is the shear thinning behavior. So; that means, at lower shear rate we have the Brownian motions that dictates the suspension geology, as we increase the shear rate these hard spheres.

Or say hard sphere means, this and as I mentioned the in non-interacting particles; they are now more organized say kind of sheets or layer, and then the flow becomes much smoother;

that means, the viscosity goes down. So, this decrease this transition is the shear thinning behavior. So, here it is the shear rate versus the suspension viscosity both in log scale. So, this is what happens in case of the non interacting particles?

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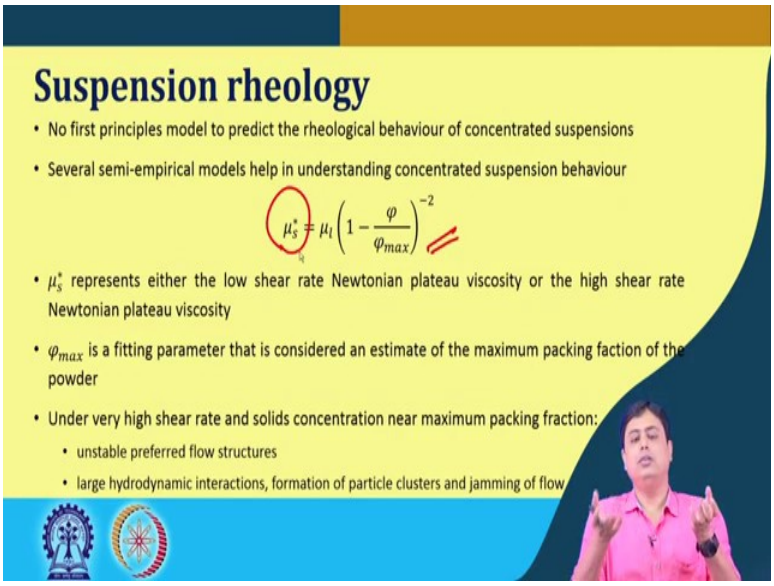

Suspension rheology

- No first principles model to predict the rheological behaviour of concentrated suspensions
- Several semi-empirical models help in understanding concentrated suspension behaviour

$$\mu_s^* = \mu_l\left(1-\frac{\varphi}{\varphi_{max}}\right)^{-2}$$

- μ_s^* represents either the low shear rate Newtonian plateau viscosity or the high shear rate Newtonian plateau viscosity
- φ_{max} is a fitting parameter that is considered an estimate of the maximum packing faction of th powder
- Under very high shear rate and solids concentration near maximum packing fraction:
  - unstable preferred flow structures
  - large hydrodynamic interactions, formation of particle clusters and jamming of flow

Now, for highly concentrated suspensions there is no as such first principle model to predict the geological behavior of such concentrations. But, there are like in other sections we mentioned several semi empirical models are available; which helps to understand this concentrated suspension behavior and one of such is mentioned here a simplified form.

$$\mu_s^{\text{¿}}=\mu_l\left(1-\frac{\varphi}{\varphi_{max}}\right)^{-2}$$

Where, this first term represents either the low shear rate Newtonian plateau viscosity or the high shear rate Newtonian plateau viscosity. And, this phi max is a fitting parameter that is considered as a measure of maximum packing limit or packing fraction of that fine particles or the powders.

So, such suspension under very high shear rate and high solids concentration that leads to it is maximum packing fraction, what happens? That the structure that was developed or say the sheets or the layers that was developed at the high shear in Newtonian plateau that becomes unstable. Because now, here we have more solid concentration and very high shear rate. So, this what it does? It destabilizes that preferred flow state or structure. There is very large hydro dynamic interaction, which leads to formation of particle clusters, which also is called the hydrodynamic clusters.

And, then these clusters makes the flow more difficult; which means, again the viscosity goes high and this clusters at times blocks the 4 or say it jams the flow. So, that is called the jamming phenomena and this whole observation is called the shear thickening behavior; that means, the viscosity is now, increasing as we increase the shear rate. And, this is the common occurrence in case of concentrated suspension by hard sphere approach.

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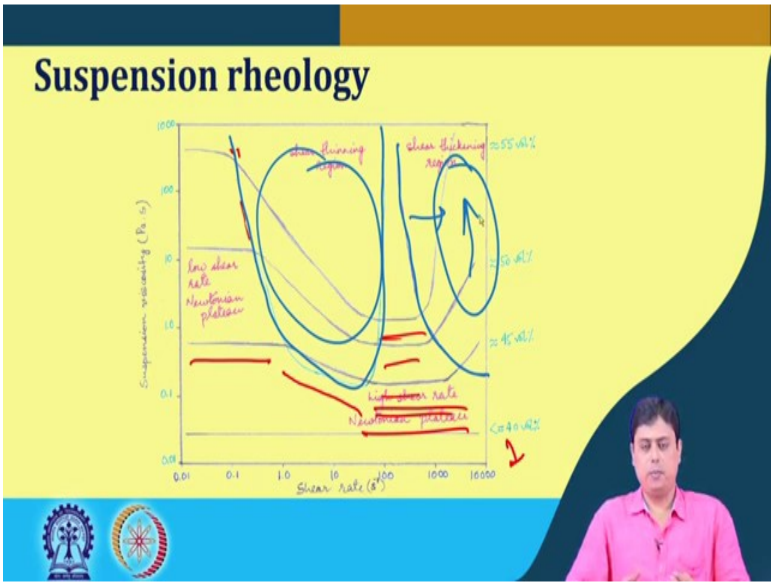

Suspension rheology

So, this is what something happens in schematically? So, here say below are certain volume fraction; it is Newtonian that the viscosity does not change with the shear. Now, it is having a constant viscosity system. Now, as the shear rate increases with the concentration; so, say we have this low shear rate Newtonian plateau initiative and then it exhibits shear thinning behavior followed by high shear rate Newtonian plateau.

And, this is all happening, because of the arrangement or the rearrangement of the particles in the suspension from Brownian state to a more organized state, layer kind of state. So, this with the increasing sheer there is a smooth movement of the fluid, but at a very high so, this high shear in Newtonian plateau is arrived, when it has reached this preferred flow structure limit.

So, for a time being this state is not further improved or if there is no space to improve it further; which means, that stage is remained for a certain time that also depends on the particle size apart not particle size the particle type.

Now, after that it again increases, because this preferred state is now, unstable due to the higher concentration and or this happens due to high shear rate. So, we can see that this state becomes more narrower, the range becomes more narrower as we increase the concentration that is high shear rate Newtonian plateau, and, the onset of shear thickening resign goes higher and higher. So, these lines are basically having a zone or it is showing a zone of shear thinning and this is the shear thickening zone. So, which means, here in this region we can see that the viscosity is going down and in this region we can see the viscosity is going higher.

So, this is all happening again for the particle rearrangement in layers and after that that layer is broken due to the high a hydrodynamic interaction and that leads to the cluster or the aggregates of the particles, which called the hydrodynamic cluster, it then blocks the flow it makes the flow more difficult.

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Influence of surface forces on suspension rheology

Repulsive forces

- Similarity with hard sphere approach when interparticle distance is larger than the range of repulsive force
- As in low volume fraction and/or relatively larger particles
- High volume fraction: overlapping of repulsive force field ⇒ increased viscosity compared to hard spheres
- In very small (100 nm or less) particles, the average interparticle distance (even at moderate volume fraction) is in the order of the range of the repulsion
- Consequently, the repulsive force fields overlap resulting in increased viscosity

Now, when there are repulsive part force; now, the particles we are now talking about that the particles are there in the suspension, but the interaction between them is repulsive in nature. So, then what happens? It similarly, behaves as of the height a hard sphere approach or the hard sphere behavior when they are separated at a larger distance, that in the range of repulsive force. Because then there is proper dispersion is there, because we have seen that this attractive force tends to form aggregates.

Now, if the particles are separated at our long range repulsive force then these are more dispersive in nature or there is say I would say more dispersion is there uniform dispersion can happen with these repulsive forces. And, this is indeed true for low volume fraction or relatively large particle, because at the low volume fraction these particles are separated far away from each other. Once we increase the volume fraction there is the overlapping of this repulsive force field and that leads to the increase in viscosity compared to the hard sphere.

So, even say there is a same particle and same volume fraction in two suspensions; in one case we are considering repulsive force or say the surface force included phenomena, the other one is simply hard sphere model method. In both the cases in the second one there will be a reduced viscosity, because we have not considered there the particle interaction.

So, here due to this repulsive force and it is overlapping there will be enhanced viscosity compared to that of the hard sphere of same material and same volume fraction. Now, means, very small particles say 100 nanometer or less the average inter particle distance, even at moderate volume fraction is in the order of the range of this repulsion; that means, in this case we will have enhanced or increased viscosity, because the repulsive force fields are overlapping. So, that leads to increased viscosity.

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Influence of surface forces on suspension rheology

- Also for dilute suspensions of repulsive particles, larger viscosity than hard spheres
  - due to additional viscous dissipation of the fluid flow through the repulsive region around the particle
- Primary electro-viscous effect: for particles with EDL repulsion
- Total drag on the particle and the EDL > drag on a hard sphere
- Insignificant increase in viscosity due to the primary electro-viscous effect
- Concentrated suspensions: significantly elevated viscosities compared to hard spheres at the same volume fraction) due to the interaction between overlapping EDLs
- Secondary electro-viscous effect: double layer must be distorted to push particles

Now, also for dilute suspension of repulsive particles; we will have this larger viscosity than these higher spheres, because of this additional viscous dissipation of the fluid flow through this repulsive region around the particle. Now, such phenomena in case of suspension having electric double layer is called the primary electro viscous effect; that means, even this is the very dilute suspension of the particles, there would be larger viscosity although the behavior I have mentioned as similar, but there would be the larger viscosity compared to the simple hard spheres, because of this additional viscous dissipation that would happen in the repulsive force field.

So, a suspension having electric double layer this phenomena is called the primary electro viscous effect, and the total drag on the particle and the EDL is greater than the drag that was considered or that happened in case of simple hard sphere model. However, there is insignificant increase in viscosity due to this primary electro viscous effect.

Now, when the concentration goes higher with such particles there is significantly elevated viscosities compared to that of the hard sphere model of same volume fraction and same material due to this interaction between the overlapping EDLs.

Now, in the EDL suspension, the EDLs are overlapping that has tremendous repulsion. So, this I mean, when we try to push them the particles closer there is the secondary electro viscous, because effect that this electrical double layer must be distorted in order to keep them in contact and that phenomena is called a secondary electro viscous effect.

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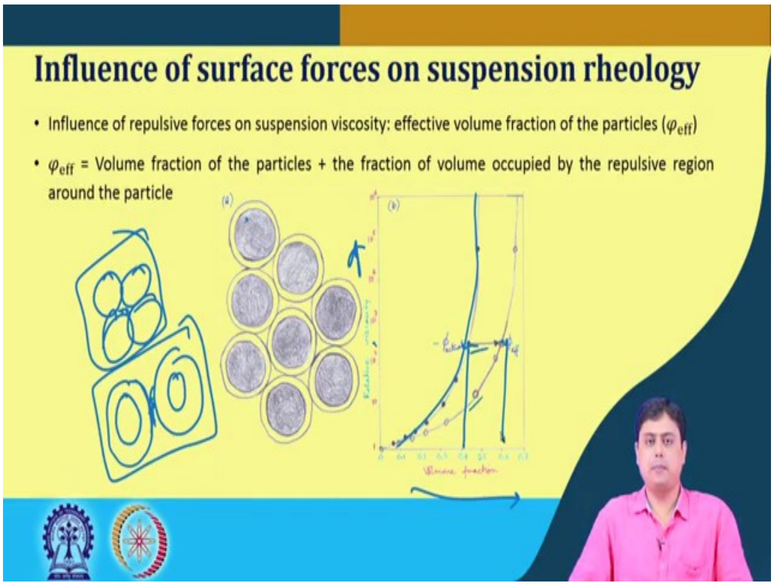

Influence of surface forces on suspension rheology

- Influence of repulsive forces on suspension viscosity: effective volume fraction of the particles (φ_{eff})
- φ_{eff} = Volume fraction of the particles + the fraction of volume occupied by the repulsive region around the particle

So, the influence of repulsive force in suspension basically can be also measured in terms of effective volume fraction of the particle. What is effective volume fraction of the particle? It is the volume fraction of the particle plus the fraction of the volume occupied by the repulsive region around the particle.

So, this EDL layer says; so, for example, in this schematic, this is this what could have been the actual particle arrangement and the voidage calculations in between these, but with the repulsive forces, there is or say the EDL layer there are this layer, which actually occupying some virtual space. So, this total volume becomes the effective volume than the actual volume of the particles. So, the volume fraction of the particles plus the fraction of volume occupied by the repulsive region around the particle is the effective volume.

Now, the previous expression that we have seen for the concentrated suspension; if this expression it is expression so, this one if it is replaced the phi with the phi effective it actually predicts the behavior of such suspension. And here this schematic shows that the volume fraction and relative viscosity and we see that this is actually the volume fraction and this is basically the effective volume fraction. So, for a relative particular velocity we have basically higher effective limit, volume fraction. So, for actual volume fraction we have higher effective volume, because of these layers or the force field that is there.

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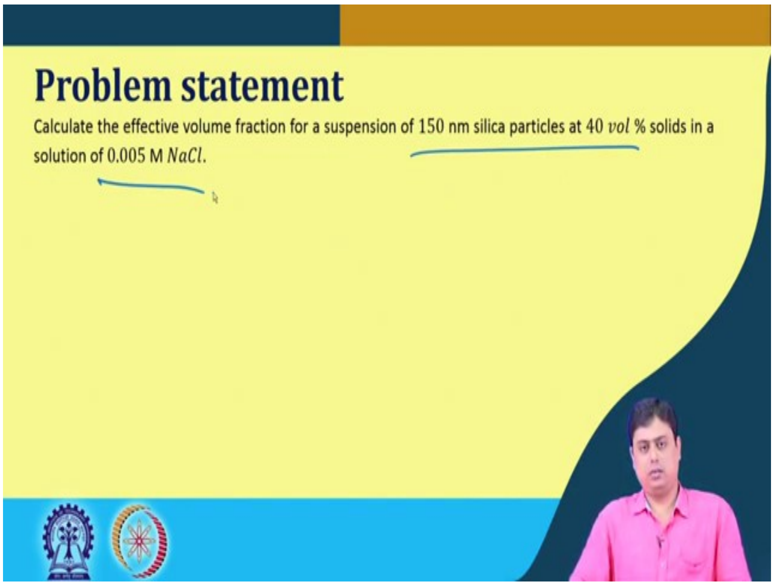

Problem statement

Calculate the effective volume fraction for a suspension of 150 nm silica particles at 40 *vol* % solids in a solution of 0.005 M *NaCl*.

So, how does it matter? So, say this problem statement; you have to calculate the effective volume fraction for a suspension of 150 nm silica particles, at 40 *vol* % solids in a solution of

0.005 M *NaCl* solution. So, this is say the actual volume fraction of the of silica particles of known diameter, in electrolyte what is the effective volume fraction? So, how do we calculate such scenario?

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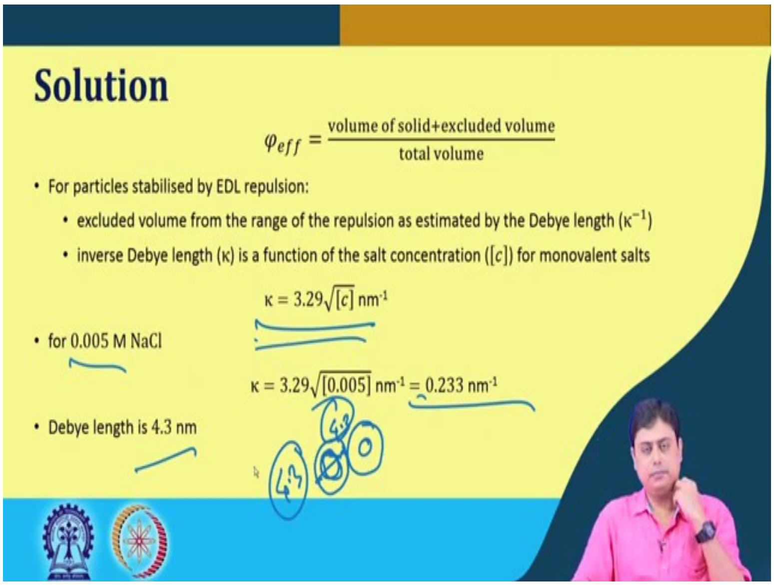

Solution

$$\varphi_{eff} = \frac{\text{volume of solid+excluded volume}}{\text{total volume}}$$

- For particles stabilised by EDL repulsion:
  - excluded volume from the range of the repulsion as estimated by the Debye length (κ^{-1})
  - inverse Debye length (κ) is a function of the salt concentration ($[c]$) for monovalent salts

$$\kappa = 3.29\sqrt{[c]}\ \text{nm}^{-1}$$

- for 0.005 M NaCl

$$\kappa = 3.29\sqrt{[0.005]}\ \text{nm}^{-1} = 0.233\ \text{nm}^{-1}$$

- Debye length is 4.3 nm

If we use our this knowledge that we have just seen that

$$\varphi_{eff} = \frac{volume\ of\ solid + excluded\ volume}{total\ volume}$$

So, for particles stabilized by the EDL repulsion, excluded volume from the range of repulsion can be estimated by the Debye length that we have seen earlier; that it is a measure of the range of this EDL force as well as it is thickness. So, inverse Debye length we have seen this as a function of the salt concentration and for monovalent salt this was the relation that we have seen earlier, and it provides this inverse Debye length.

$$\kappa = 3.29\sqrt{[c]}\ \text{nm}^{-1}$$

So, for 0.005 molar NaCl, we have this as the kappa; so, which means, the Debye length the inverse of that is

$$\kappa = 3.29\sqrt{[0.005]}\ \text{nm}^{-1}\ \text{¿}\, 0.233\ \text{nm}^{-1}$$

Once we know the Debye length now; that means, a particle would be in contact with the other particle including it is Debye length, the thickness of the EDL. So, which means, the effective particle size say; so, for a single particle this would be the total diameter or the total size of the particle. So, which means, on both the sides we have the thickness of 4.3 nm.

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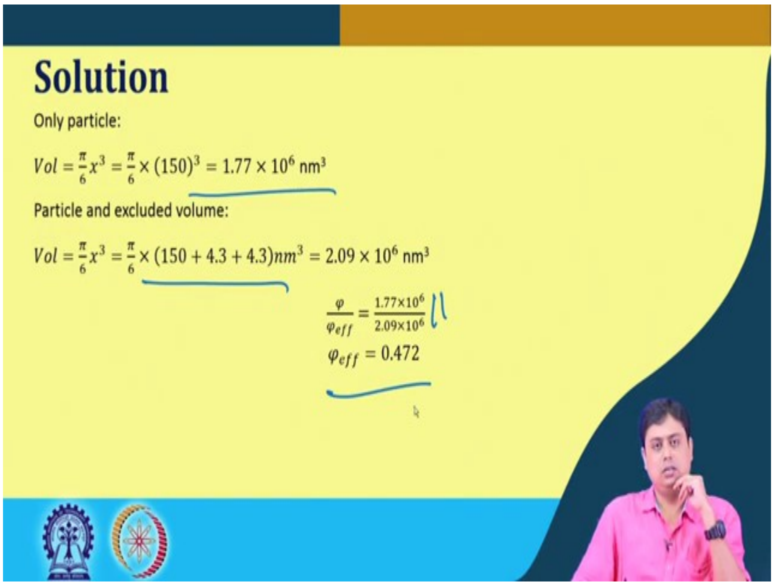

Solution

Only particle:

$$Vol = \frac{\pi}{6}x^3 = \frac{\pi}{6} \times (150)^3 = 1.77 \times 10^6\ nm^3$$

Particle and excluded volume:

$$Vol = \frac{\pi}{6}x^3 = \frac{\pi}{6} \times (150 + 4.3 + 4.3)nm^3 = 2.09 \times 10^6\ nm^3$$

$$\frac{\varphi}{\varphi_{eff}} = \frac{1.77\times10^6}{2.09\times10^6}$$

$$\varphi_{eff} = 0.472$$

So, the effective diameter becomes it is original diameter, which is 150+4.3+4.3 nm and, such a manner all other particles are there. So, for only one particle, if we consider only one particle then the volume of a single particle is this one. But, the particle with the excluded volume, excluded means; excluded during the consideration of calculating it is volume fraction would be this one and the ratio of these two is basically we have the effective volume fraction. So, this is how those knowledge is useful in this case.

Only particle:

$$Vol = \frac{\pi}{6}x^3 = \frac{\pi}{6} \times (150)^3 = 1.77 \times 10^6\ \text{nm}^3$$

Particle and excluded volume:

$$Vol = \frac{\pi}{6}x^3 = \frac{\pi}{6} \times (150 + 4.3 + 4.3)nm^3 = 2.09 \times 10^6\ \text{nm}^3$$

$$\frac{\varphi}{\varphi_{eff}} = \frac{1.77 \times 10^6}{2.09 \times 10^6}$$

$$\varphi_{eff} = 0.472$$

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Influence of surface forces on suspension rheology

Attractive Forces

- fundamental difference with hard sphere or repulsive particle suspensions:
  - bonds between particles must be broken
- attractive bonds between particles ⟹ attractive particle network at rest
- material behaviour: viscoelasticity, yield stress and shear thinning
- more pronounced shear thinning of the same particles and volume fraction
- different mechanism for shear thinning

And, now, we will see what will happen in case of attractive forces. So, after hard force; hard sphere approach we have seen if the particles are repulsive in nature, it behaves similarly, but what will happen in case of attractive particle? So, this we will continue in our next class and we will see that how the overall influence of these forces happens on a particular case see the sedimentation; which is the liquid solid separation that is one of our intention initially, and how this knowledge helps in that, from that perspective. So, we will be continue our discussion in the next class with these attractive forces till then

Thank you for your attention.