Fundamentals of Particle and Fluid Solid Processing

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Lecture - 58
Colloids and nanoparticles (Contd.)

Hello everyone and once again welcome back to the class of Fundamentals of Particle and Fluid Solid Processing. So, we were discussing on Colloids and nanoparticles.

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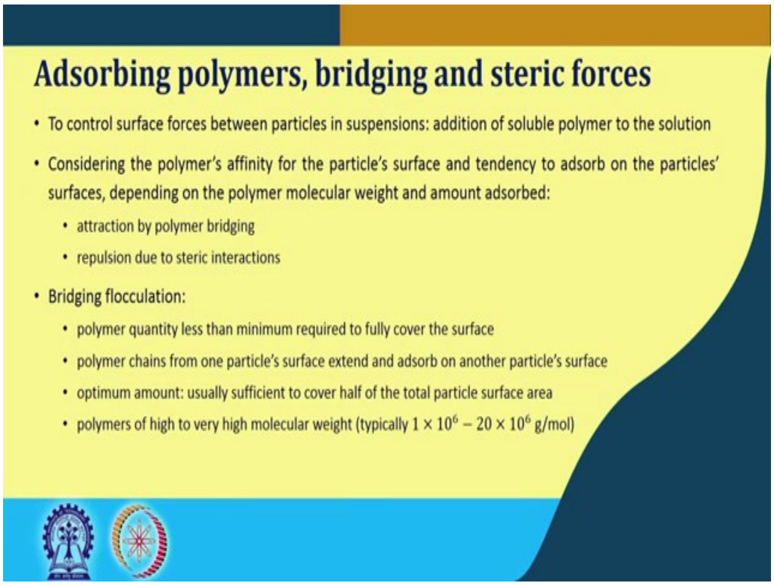

Adsorbing polymers, bridging and steric forces

- To control surface forces between particles in suspensions: addition of soluble polymer to the solution
- Considering the polymer's affinity for the particle's surface and tendency to adsorb on the particles' surfaces, depending on the polymer molecular weight and amount adsorbed:
  - attraction by polymer bridging
  - repulsion due to steric interactions
- Bridging flocculation:
  - polymer quantity less than minimum required to fully cover the surface
  - polymer chains from one particle's surface extend and adsorb on another particle's surface
  - optimum amount: usually sufficient to cover half of the total particle surface area
  - polymers of high to very high molecular weight (typically $1 \times 10^6 - 20 \times 10^6$ g/mol)

We came to this stage that, we have seen van der Waal forces, electrical double layer forces and we introduced the absorbing polymer bridging and the steric forces. So, the reason of these kinds of forces because if we want to control the surface force between the particles in suspension sometimes: we add soluble polymer into the solution. Now, the solutions and the polymer it has some interactions. Now how that happens is that this polymers affinity to the particles surface and its tendency to be adsorbed on the particle surface this creates this kind of forces.

Now, how it happens? Depending on the amount of polymer being adsorbed and its molecular weight we can have attraction or repulsion. Attraction happens by polymer bridging, the repulsion happens due to the steric interactions. So coming firstly, to the interaction part or the attraction part rather here; so, this is called the bridging flocculation.

Now when the polymer quantity, that is poured into the solution is less than the minimum that is required to cover the full surface of the particle.

In that case what happens the polymer chains from one particles surface extends and adsorbed on another particle surface, and this creates a polymeric bridge in between particles which is attractive in nature. Now, the optimal amount that is typically given for such kind of attraction to happen, usually which is sufficient to cover half of the totals particle surface area. That amount is we typically say the optimal amount or the optimum amount that is required to have such kind of attraction or the inter particle forces.

Now polymers the best quality or the best polymers that exhibit this kind of good attraction are of very high to very high molecular weight, typically in the range of $1\times10^{6}-20\times10^{6}$ g/mol.

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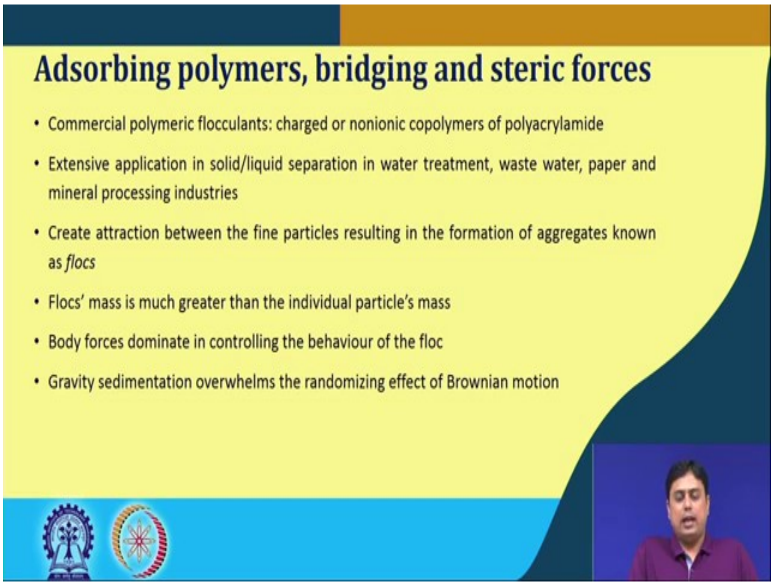

Adsorbing polymers, bridging and steric forces

- Commercial polymeric flocculants: charged or nonionic copolymers of polyacrylamide
- Extensive application in solid/liquid separation in water treatment, waste water, paper and mineral processing industries
- Create attraction between the fine particles resulting in the formation of aggregates known as *flocs*
- Flocs' mass is much greater than the individual particle's mass
- Body forces dominate in controlling the behaviour of the floc
- Gravity sedimentation overwhelms the randomizing effect of Brownian motion

The other aspect of this that when the it is used commercially these polymer flocculants are typically of charged or nonionic copolymers of polyacrylamide. It has immense application and several extensive applications in liquid solid separation, in water treatment, wastewater treatment paper and mineral processing industries.

What it does? It basically creates attraction between the fine particles that results in the formation of aggregates also known as flocs or from flocculation it is flocs. Now, once it is formed we have seen in the previous sections as well that once this flocs are formed these are of bigger in size ok, of our greater much then the origin fine particle sizes.

So, what happens the body force then becomes dominant in controlling the behavior of these flocs and then it helps us to separate from the solutions like the gravity sedimentation; it is actually then overwhelms the randomizing effect of Brownian motion. So, that it cannot diffuse further we can have easy separation of these fine particles in terms of aggregates for the flocs.

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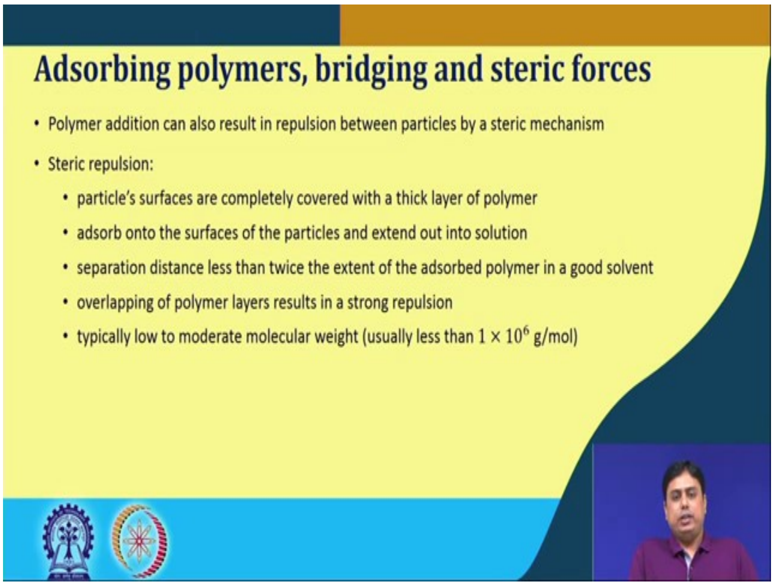

Adsorbing polymers, bridging and steric forces

- Polymer addition can also result in repulsion between particles by a steric mechanism
- Steric repulsion:
  - particle's surfaces are completely covered with a thick layer of polymer
  - adsorb onto the surfaces of the particles and extend out into solution
  - separation distance less than twice the extent of the adsorbed polymer in a good solvent
  - overlapping of polymer layers results in a strong repulsion
  - typically low to moderate molecular weight (usually less than 1×10^6 g/mol)

Now, this polymer addition can also result in repulsion that we mentioned or I mentioned as the steric repulsion or the steric forces, now it happens with the static mechanism. So, what is steric repulsion? Now when this the particle surfaces are fully covered with this polymers that is absorbed on the particle surface, it creates a thick layer of polymer and it also adsorbs into the surface of the particle and extend out to the solution.

And, then what happens when in a good solvent when the separation distance between the particles is less than twice the extent of these polymer or the adsorbed layer, then overlapping of these polymeric layer happens and that results in strong repulsion. A good polymeric solution or the polymer that exhibit this steric repulsion is typically low to moderate molecular weight polymers usually less than 1×10^6 g/mol of such molecular weight.

So which means these the property of these particles can be tailored based on the requirement, that the amount of polymeric material that is being absorbed on the surface and its molecular weight basically dictates whether that would be the attraction or there would be repulsion.

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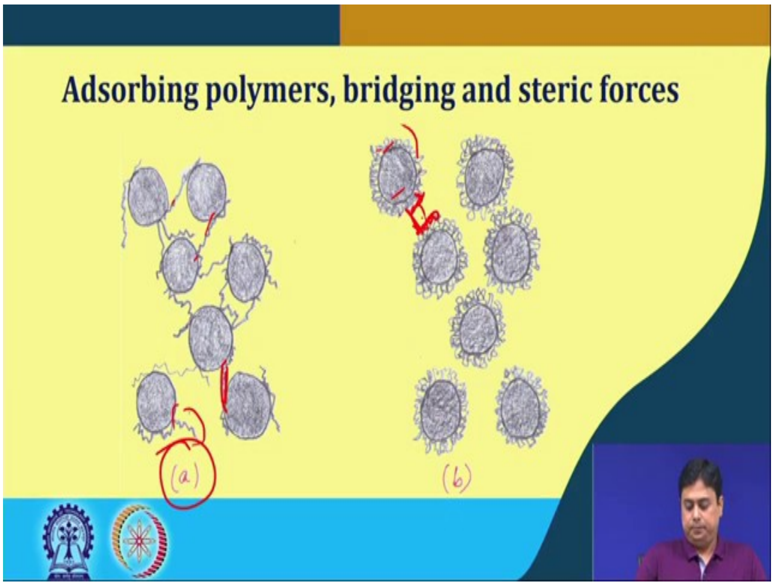

Adsorbing polymers, bridging and steric forces

Now, these two scenarios are summarized here in schematic. The figure a shows this polymer bridging where these, this is the extent of this polymers that is into the other particle; in this case it has been extended to the other particles from one particles. So, this is the bridge that has been formed. Now, this happens as I have mentioned the earlier when say it is partially covered, the surfaces are partially covered with this polymer. It is not fully and the optimal amount is the half of the area that has that can cover.

So, in that case it extends to the other particle and forms a bridge and then it is attractive in nature, but in case of steric repulsion when it is fully covered with the polymeric layer it only extend into the solution not on the other particle. And, when this inter particle distance is lower this cloud actually overlaps or this layer actually overlaps and then there is a strong repulsion due to this steric hindrance.

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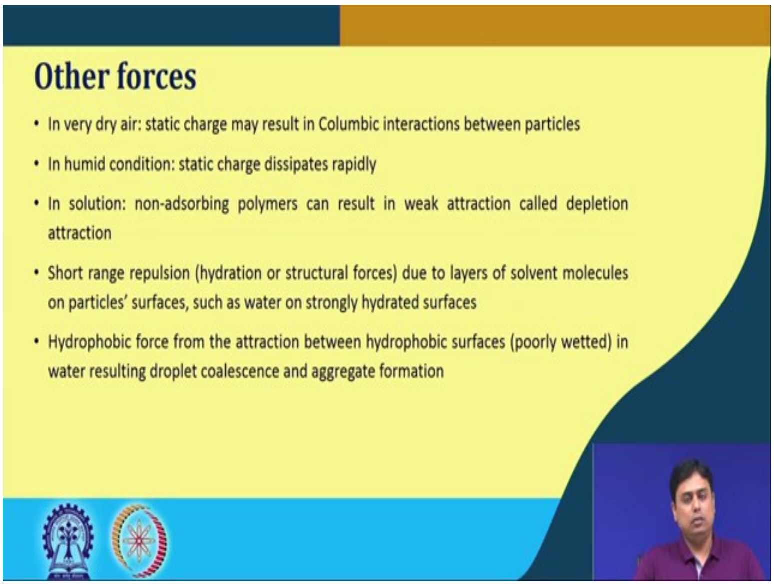

Other forces

- In very dry air: static charge may result in Columbic interactions between particles
- In humid condition: static charge dissipates rapidly
- In solution: non-adsorbing polymers can result in weak attraction called depletion attraction
- Short range repulsion (hydration or structural forces) due to layers of solvent molecules on particles' surfaces, such as water on strongly hydrated surfaces
- Hydrophobic force from the attraction between hydrophobic surfaces (poorly wetted) in water resulting droplet coalescence and aggregate formation

There are other forces that are involved in the surface force. For example, say in a very dry air static charge may result in Columbic interaction between the particles. But, in humid condition: the static charge dissipates rapidly and in solution: are non absorbing polymer can result in weak attraction called depletion attraction. In case of say the short range repulsion say the hydration or structural forces that happens due to the layer of solvent molecules on the particle surface such as say the water on strongly high rated surface.

In that case a short range repulsion can appear because we have a layer of solvent molecules around the particle surface. For example, say water layer that is on a hydrated surface. In case of hydrophobic material the hydrophobic force can be resulted from the attraction between hydrophobic surfaces; hydrophobic means poorly weighted surface that is affinity towards water is very very low. And so, for example, these hydrophobic surfaces in water can result in droplet coalescence and aggregate formation.

So, along with the forces the dominant forces that we have studied is that where the van der Waals, electrical double layer, steric forces, bridging force, adsorbed forces; we can have this kind of hydrophobic force. Short range repulsion force, non-adsorbing polymer that can result in weak attraction called the depletion attraction; these all the forces can be there.

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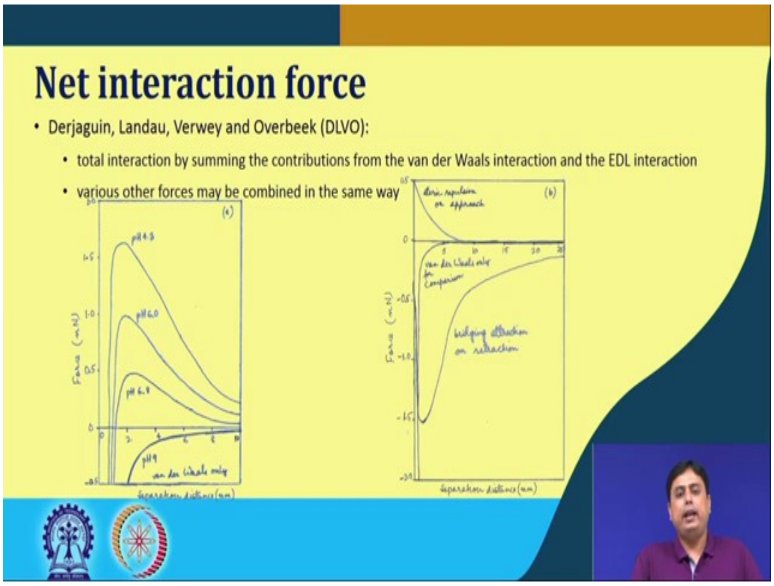

Net interaction force

- Derjaguin, Landau, Verwey and Overbeek (DLVO):
  - total interaction by summing the contributions from the van der Waals interaction and the EDL interaction
  - various other forces may be combined in the same way

Now, what would be the then net interaction force between the particles? So, Derjaguin, Landau, Verwey and Overbeek this together with these names of the scientists call the DLVO theory. It sums up that the total interaction is basically sum up the contribution of van der Waals and EDL interactions. And, similarly all other forces can be just added to those forces to have the total interaction between the two particles. So, basically it is the summation of all interaction forces, for which we can have the relation, the expression, theoretical derivations or empirical correlations.

So, this figure shows that the force versus the separation distance. Now, say for a certain particle at pH 9 you can see that only say the van der Waals dominates, this van der Waals attractive force dominates. As we increase the acidic nature of that solution say; that means, the pH is decreasing; in that case we can see the steric repulsion, the zeta potential is actually increases and that creates the repulsion. And then basically it overwhelms the van der Waal force, but at a shorter distance van der Waals always dominates.

This schematic shows the force versus separation distance for say the bridging attraction or on the retraction. So, say when there are two particles are there, there if we make them closer then there is a small amount of steric repulsion on approach. And, if we try to bring them to a separate distance, we try to separate or retract then we say we see that there is a long range repulsion attraction forces there.

So, long range attractive forces is there and this van der Waals is just for say to show you its magnitude. So, in this case we can have the long range attractive force on retraction or separation. And, in this case this is the short range repulsive force as per this polymer bridging or the steric repulsion.

$$V_{vdW} = \frac{-Ax}{24\,D}$$

$$V_{EDL} = \pi\varepsilon\,\varepsilon_0\,x\,\Psi_0^2 e^{-\kappa D}$$

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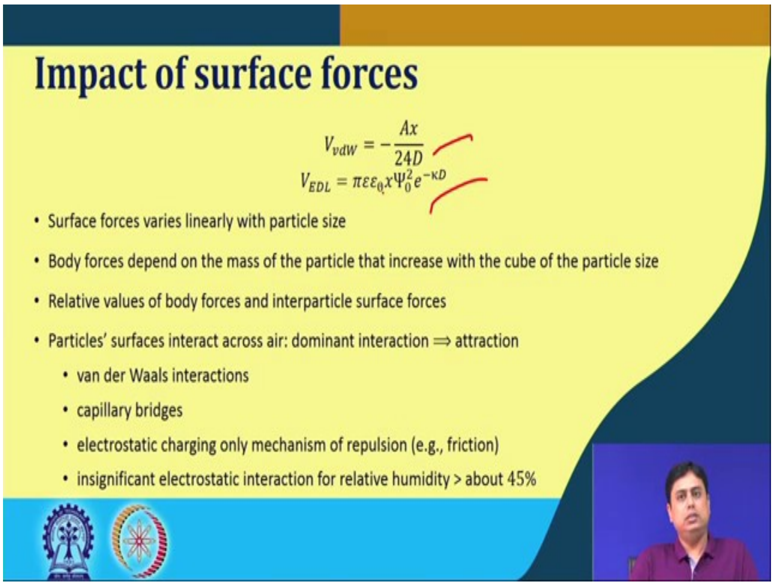

Impact of surface forces

$$V_{vdW} = -\frac{Ax}{24D}$$

$$V_{EDL} = \pi\varepsilon\varepsilon_0 x\Psi_0^2 e^{-\kappa D}$$

- Surface forces varies linearly with particle size
- Body forces depend on the mass of the particle that increase with the cube of the particle size
- Relative values of body forces and interparticle surface forces
- Particles' surfaces interact across air: dominant interaction ⟹ attraction
  - van der Waals interactions
  - capillary bridges
  - electrostatic charging only mechanism of repulsion (e.g., friction)
  - insignificant electrostatic interaction for relative humidity > about 45%

Now so, this is the overall forces, the overview on the overall forces. Now, how it impacts on handling the solids or the particles or the colloids. Now, we have seen that this is the potential energy van der Waal, for the van der Waals and this is the electrical double layer. So, in from both the expressions it is clear that the Surface forces varies linearly with the particle size where, x is the particle size, but the body force depends on the mass of the particle that increases with the cube of the particle size, because it is the volume multiplied by the density.

So, which means the particle is either smaller or bigger, it is the relative value of this body force and this inter particle surface force that is important. It is the relativeness of these two forces that actually dominates its behavior. So, for smaller particle although this body forces are smaller, but the surface force is what dominates its characteristics. So, say particle surfaces that are interacting with air, if nothing is there typically the dominant interaction is the attractive van der Waal forces.

Either it can happen by this van der Waal interaction or it can happen also through the capillary bridges that we have seen during the granulation studies. If you remember those the structures the funicular structures, pendular structures those are the bridges that can form between the particles. There is only mechanism for the repulsion to happen is the electrostatic charging and that can be caused say by friction. So, solid particles are in motion say with in a vasal or in a chamber.

So, during its rotation and all this stuff we can have friction and that can induce static charges, electrostatic charges. But, these have insignificant effect or these becomes non-significant when the relative humidity the atmosphere is greater than about 45 percent because, this electrostatic charge we have mentioned earlier rapidly decreases with humidity.

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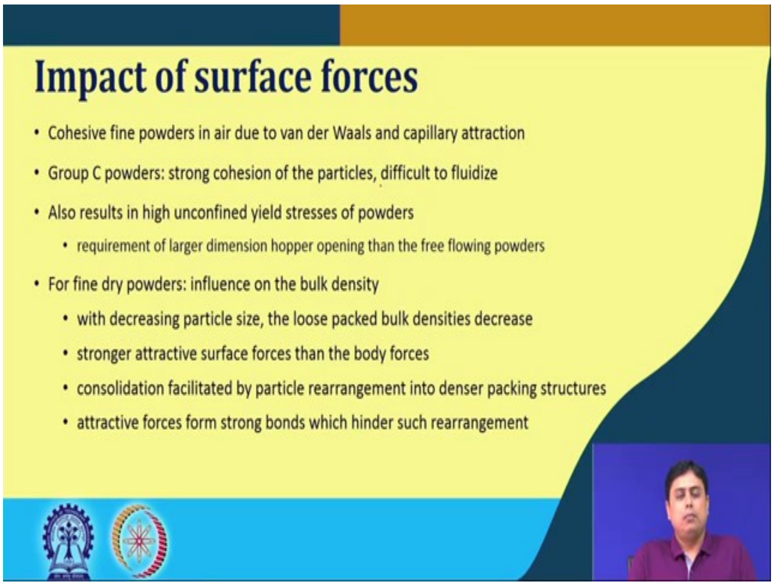

Impact of surface forces

- Cohesive fine powders in air due to van der Waals and capillary attraction
- Group C powders: strong cohesion of the particles, difficult to fluidize
- Also results in high unconfined yield stresses of powders
  - requirement of larger dimension hopper opening than the free flowing powders
- For fine dry powders: influence on the bulk density
  - with decreasing particle size, the loose packed bulk densities decrease
  - stronger attractive surface forces than the body forces
  - consolidation facilitated by particle rearrangement into denser packing structures
  - attractive forces form strong bonds which hinder such rearrangement

So; that means, this cohesive fine powder is the result when it is in contact with air because, of this van der Waals and the capillary attraction. And, this is also the reason why the group C Gilbert particles exhibited strong cohesion of the particles and it was difficult to fluidize, because of this attraction and the fine nature of the particle or the fine sizes of the particles.

Now, this surface forces also results in high unconfined illustrations of the powders which means it requires a larger dimension of the hopper, that is the storage of this fine particles for its discharge then the free flowing powders. It also influences the bulk density of the fine powders because, this bulk density of the fine powders is depend on the particle sizes. As the particle size decreases this loosely packed bulk density also decreases, which may sound a bit of counter inductive. Because say reducing the particle size one would expect a more and more compact densities.

But, the point is that this consolidation is facilitated by particle rearrangement into a more denser packing structure, but this stronger attractive forces than the body forces because these particles are very small, extreme small. So, there would be very strong attractive forces that would make it difficult to rearrange itself. So, attractive forces basically forms stronger bond which hinders such rearrangement that is required for consolidation. So, this is how it influences, it affects the fine particle properties.

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Impact of surface forces

- Dry fine powders vs. colloids in liquids:
  - usually minimal hydrodynamic drag forces for dry powders due to low viscosity of air
  - hydrodynamic drag forces strongly influence the particles in liquids
- For suspensions: control of the interaction forces through solution chemistry
  - suspension behaviour: stability, sedimentation rate, viscosity, and sediment density
  - use of additives – acids, bases, polymers and surfactants to develop the range and magnitude of either repulsion or attraction

Now, the difference between the fine powder and the colloids in the liquid is, that usually in air or say in the dry fine powder, when these are exposed to air or some other gases; there is very minimal hydrodynamic drag forces due to the very low viscosity of the air. But, in case of liquid hydrodynamic drag force is actually is a dominant mechanism and we have seen that in our earlier classes. So, it actually influences the particles in the liquid. Now, for a suspension; colloidal suspension or fine particle suspension we can control the interaction force through the solution chemistry, that dictates the suspension behavior. What are the suspension behavior?

That is say its stability, its sedimentation rate, suspension viscosity, suspension density; these behaviors can be controlled by the solution chemistry; that means use of say additives like acids, base, polymer surfactant. That with that addition and its influence we have seen that how pH can influence the surface charges, how the surface force can be controlled by varying the pH, how the counter ions helps in neutralizing this overall solution. So, this actually provides us a range and magnitude of either controlling repulsion or attraction.

So, which means if you want or if I want to have a dispersed suspension we have to tune its property, solution property in such a way that it can be suspended for a longer time. Or, it can be tuned to settle very quickly if that is required, if that is a solid liquid separation is desired we can change the solution property and it will quickly settle down. So, by varying the surface forces with the help of additives, we can have a control on the suspension.

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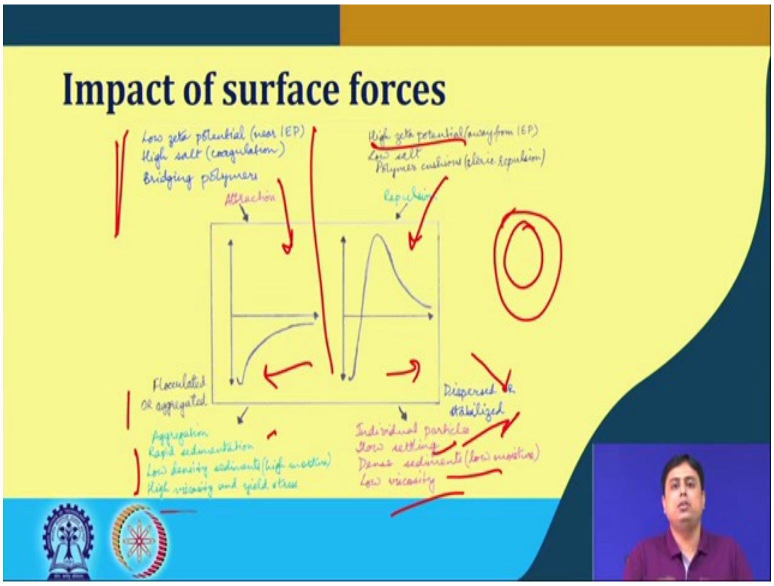

Impact of surface forces

Low zeta potential (near IEP)
High salt (coagulation)
Bridging polymers

High zeta potential (away from IEP)
Low salt
Polymer cushions (steric repulsion)

Flocculated OR aggregated

Aggregation
Rapid sedimentation
Low density sediments (high moisture)
High viscosity and yield stress

Dispersed OR stabilized

Individual particles
Slow settling
Dense sediments (low moisture)
Low viscosity

So, this schematic actually summarizes the properties that influences the solution behavior or the inter molecular forces, surface forces and this surface forces how it influences the overall solution property or the suspension property. So, here it says say this is the attractive force and this is the repulsive force summary.

So, here say the low zeta potential that is near iso electric point, if that the suspension is there with high salt that is the coagulation is happening and say bridging the polymers or actually results into attraction of the particles.

And, then the flocculation or the agglomeration happens, we have the aggregated form of the particles and this results in aggregation, rapid sedimentation, low density sedimentation; that means, that can have a high moisture content; all say the high viscosity and yield stress material or yield stress suspension. In case of high zeta potential that is away from this iso electric point low salt concentration and say there is polymer cushions; that means, whole surface is covered with the polymer that is adsorbed on the surface; that means, there is a steric repulsion we have the repulsive forces between the particles.

And, that results in the dispersed or say the stabilized dispersion which where the particles can remain suspended forever. So that results in individual particles, low settling rate, dense sedimentation or say the low moisture content and low viscosity suspension or material. So, this is how the solution property can control the attractive or repulsive nature of the force. And, respectively this attractive and repulsive force how then translate it into the solution behavior or the suspension behavior or the fine particle behavior.

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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

Now, if we go into the suspension rheology that that we are talking about its density viscosity and all this stuff. So, rheology is the area where we study the flow and the deformation of a matter. Now, it actually comprises of a wide range of mechanical behavior from say the elastic behavior to a simple Newtonian fluid. In elastic behavior it follows Hooke's law, from there it can cover the whole range of Newtonian fluid.

So that means, it can have the rheology can be studied for say water like viscosity of a Newtonian fluid or Newtonian liquid, to say the mortar or the concrete that kind of suspension and the material. So in this case is the Influencing parameter of this rheology is the volume fraction of the solids in the suspension. The viscosity of the fluid, the surface forces between the particles and the particle size and its shape; all these parameter influences or influence this suspension rheology.

Now, what we will do? We will start our understanding on this influence of the say first parameter which is the volume fraction of the solids without considering the surface forces. That means, when only there is hydrodynamic forces and the Brownian motion is there of the particles which means the particles are not interacting and we say typically this take is the hard sphere model or hard sphere approach.

So, we will start in the next class our discussion on this hard sphere model to understand the influence of volume fraction in a suspension. That means, the concentration of solid particles on inner suspension, how its viscosity mainly changes. There is some interesting behavior that we will be exploring and again we have to remember that this that discussion will be on assuming that these particles are non-interacting in nature. Once we understand that concept then we will couple this hard sphere approach with the particle interactions or the surface forces.

So, I will see you in the next class with that discussions.

Until then thank you for your attention.