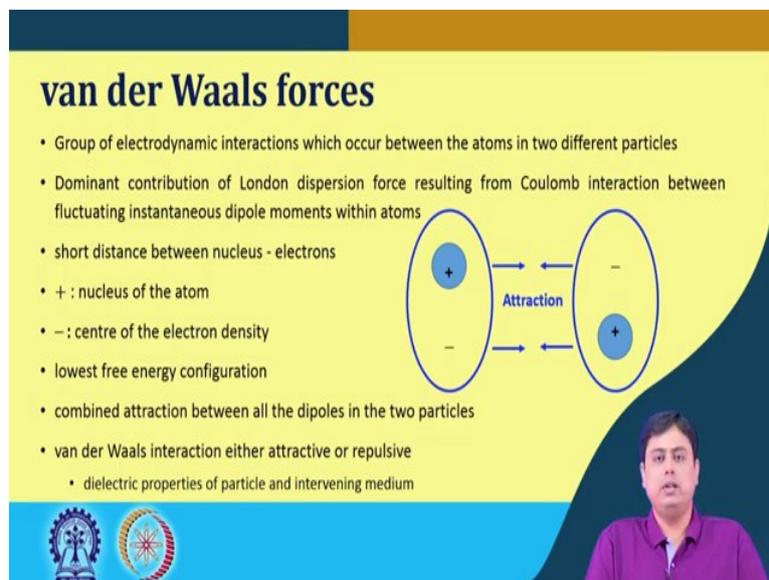


**Fundamentals of Particle and Fluid Solid Processing**  
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**Lecture - 57**  
**Colloids and nanoparticles (Contd.)**

Hello everyone and welcome back to our discussion on the Fundamentals of Particle and Fluid Solid Processing. And we started our discussion on the fundamentals of Colloid and nanoparticles. We started our discussion with a Brownian motion, the surface force at that we started with the van der Waals forces.

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**van der Waals forces**

- Group of electrodynamic interactions which occur between the atoms in two different particles
- Dominant contribution of London dispersion force resulting from Coulomb interaction between fluctuating instantaneous dipole moments within atoms
- short distance between nucleus - electrons
- + : nucleus of the atom
- - : centre of the electron density
- lowest free energy configuration
- combined attraction between all the dipoles in the two particles
- van der Waals interaction either attractive or repulsive
  - dielectric properties of particle and intervening medium

The diagram illustrates the attractive force between two dipoles. On the left, a dipole is shown with a positive nucleus (+) and a negative electron density center (-). On the right, another dipole is shown with a negative electron density center (-) and a positive nucleus (+). Arrows point from the positive nucleus of the left dipole to the negative electron density center of the right dipole, and from the negative electron density center of the left dipole to the positive nucleus of the right dipole. The word "Attraction" is written between the two dipoles.

We have seen the genesis of van der Waals force that is the dipole moment how it is created. And, how it achieve its lowest free energies configuration and that resulted in this van der Waal forces. The attractive forces between all the dipoles of the two particles resulted in the combined overall attraction. And this we say is the van der Waal interaction force. Now, this as I mentioned can be attractive or repulsive in nature depending on the dielectric properties of the particle and the intervening medium.

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**van der Waals forces**

- Pairwise summation of the interactions: overall interaction between two spherical particles of the same size ( $x$ ) separated by distance  $D (\ll x)$

$$V_{vdW} = \text{van der Waals interaction energy} = -\frac{Ax}{24D}$$

$$F_{vdW} = \text{van der Waals force} = -\frac{Ax}{24D^2}$$

$A = \text{Hamaker constant}$

- $A > 0$ : attractive interaction
- $A < 0$ : repulsive interaction

1 2 3

max-1 ② max-1

So, the pair wise summation of all the interactions, basically us; it provides us a simple expression that is analogous to the overall interaction between two spherical object or the vertical particles of same size. And that are separated by your distance which is very small compared to the size. So, in this criteria, the van der Waal is introduction energy can be expressed or has been estimated by this expression.

$$V_{vdW} = \text{van der Waals interaction energy} = \frac{-Ax}{24D}$$

$$F_{vdW} = \text{van der Waals force} = \frac{-Ax}{24D^2}$$

So, this is the van der Waal interaction energy and this is the van der Waal force expression, where  $A$  is the Hamaker constant. Now, this is schematic shows that the particles say are of two different material; that is particular 1 and 3 are separated by an intervening media that is 2. Now this positive value or the negative value of this force; that means, at attractive or repulsive nature and its magnitude would depend on the value of this Hamaker constant here.

Now, this if Hamaker constant is greater than 0, the interaction is attractive. If Hamaker constant is less than 0, then this interaction is repulsive in nature. So, which means this Hamaker constant is calculated for this system say two materials separated by an intervening medium. Now, this in this case the material 1 can be of this 3 is equals to 1, this can happen; that means, there can be two materials; material 1 and material 1 separated by material 2. But

this is more generic configuration say two different particles separated by a intervening media Hamaker constant is calculated based on such scenario.

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Material 1	Material 2	Material 3	Hamaker constant (approx.) [J]
Alumina	Air	Alumina	$15 \times 10^{-20}$
Silica	Air	Silica	$6.5 \times 10^{-20}$
Alumina	Water	Alumina	$5.0 \times 10^{-20}$
Silica	Water	Silica	$0.7 \times 10^{-20}$
Metals	Water	Metals	$40 \times 10^{-20}$
Air	Water	Air	$3.7 \times 10^{-20}$
Octane	Water	Octane	$0.4 \times 10^{-20}$
Water	Octane	Water	$0.4 \times 10^{-20}$
Silica	Water	Air	$-0.9 \times 10^{-20}$

Martin Rhodes, Introduction to Particle Technology, 2<sup>nd</sup> Edition, John Wiley & Sons Ltd.

Now, a typical values of these Hamaker constants are given in this table. What is noteworthy in this table; in this table actually we have different material say the aluminium; alumina and aluimina are separated by air. In this case we have a certain Hamaker constant value which is in the order of  $15 \times 10^{-20}$  Joule. In case of silica this value is lower, which is  $6.5 \times 10^{-20}$ .

The interesting point is that when we change the intervening media say for alumina; alumina when we change from air to water this Hamaker value goes down. It is the positive the attraction is there, but it is of a lower attraction or lower force attractive force in practice. Now, this has the implication in our application. The scenario is that so, this fine powders of alumina, when they are in contact with air they are in cohesive in nature.

And that is done by this van der Waals introduction of having higher Hamaker constant which means higher interactions and that is there these are more cohesive in nature difficult to flow. As we change the intervening medium to water, we say the attractive forces has decreased, which means these particles are now easier to separate. The attractive forces has been reduced, it can now be easy to separate them.

Similarly for silica particles, we can see the similar difference. From 6.5, 2.7 it has been reduced when we change the medium from air to water. So, this metals when they are in

water, this has a significantly higher Hamaker constant value which means they are attractive in nature. So, this air, these are the air bubbles say in water this also now, we have spoken about this solid particles

Now, in this case this air and water this air bubbles or say the oil droplets also can be considered as particles to estimate the interaction in between them by this theory. And that is why the Hamaker constants are listed here as well to prove a to give you an idea of their strength between say the air bubbles in water or say the oil in water emulsion and water in oil moisture.

Now, the point here in the rare case that I have mentioned that the van der Waals can be repulsive in nature; if we have the Hamaker constant as negative value which is shown here. So, here the scenario is something like that, that the silica particle ok, attached to say to a air bubble and being separated from water in that case the separation becomes difficult.

So, then we have the negative Hamaker constant and as we mentioned here; that means, there is repulsive interaction. So, this provides us an idea or the reason behind that why separation in off say alumina or silicone particles in water becomes easier than when that is in air, or why the fine particles in contact with air is more cohesive than it is in water.

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**Electrical double layer forces**

- Development of surface charge in particles immersed in a liquid

EDL

(a) vacuum

(b) water at IEP

(c) low pH

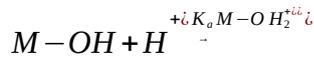
(d) high pH

$$M-OH + H^+ \xrightleftharpoons{K_a} M-OH_2^+$$

$$M-OH + OH^- \xrightleftharpoons{K_b} M-O^- + H_2O$$

Now, the other force that is very critical or dominant is the electrical double layer force we say it is the EDL force in short. Now, the particles can develop a surface charge when it is

immersed in a liquid. Say in the case of a metal oxide particle, when this is exposed in air or in contact with air, ok. The atoms at its surface will have some insufficient or say unsatisfied bonds and they will try to arrange themselves.



Like here in this one where  $M$  stands for the metal iron this is positive and oxide is negative. So, something like this  $M-O$ ,  $M-O$ ,  $M-O$  this kind of configuration when it is in simple air or pure air or in vacuum. Now, when there is moisture in air or some humidity in air beyond a certain percentage. This will react with the water or say it is immersed in water then in that case, this will react with water and will create the metal hydroxyl groups.

And then these metal hydroxyl groups depending on the pH of the solution, which means higher pH means alkaline solution, lower pH means as acidic solution. Depending on these two medium it will further react with those  $H^+$  ion or the  $OH^-$  ion.



And in case of low pH the configuration would look like this kind of a scenario where it would create  $M-OH_2^+$  something like this on the surface. And in case of high pH that is alkaline medium, it would create  $M-O^-$  or higher density of this kind of surface charges.

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### Electrical double layer forces

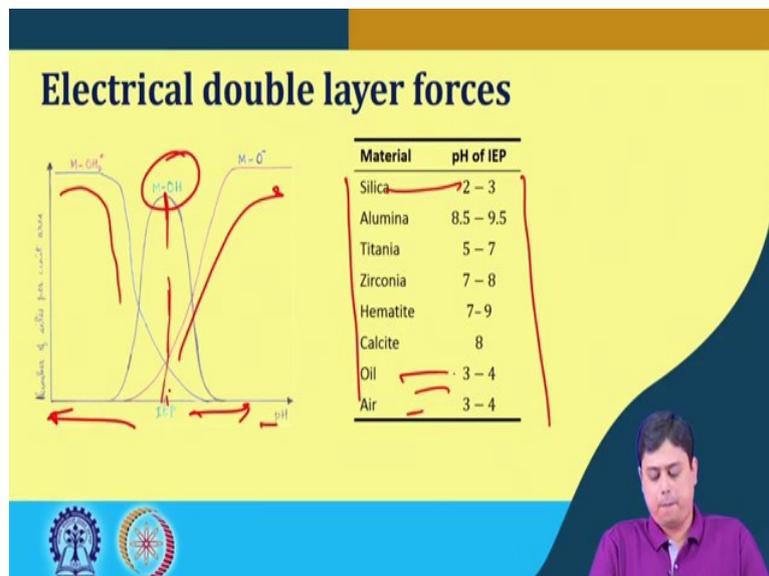
- Surface ionization reaction constants ( $K_a$  and  $K_b$ ) are material properties
- Isoelectric point (IEP): neutral sites dominate, zero net charge on the surface
- At low pH: surface hydroxyl groups react with  $H^+$  and form positively charged surface ( $M-OH_2^+$ )
- At high pH: surface hydroxyl groups react with  $OH^-$  and form negatively charged surface ( $M-O^-$ )

Now the point is that, this surface ionization reaction constant which are  $K_a$  and  $K_b$  in this case are the material properties; it depends on the properties of the material for example, it changes with silica oxide, it changes with alumina oxide they have the different values. So, the point is there is an ISO electric points which is called IEP, where do we have the mostly neutral sites on the surface that is 0 net charge on the surface which is this kind of a scenario.

Here we have mentioned that as water considering pH as 7, but this is again materials specific there will be a different value of IEP for each and every material; under which there will be the net surface charges and the neutral sites will dominate. But there will be occurrence this positively charged ion and the negatively charged ion, but the total balance of between these two will be nullified; the numbers will be same., But at low pH the surface hydroxyl groups as I mentioned will react with  $H^{+}$  and form the positively charged surface this is the low pH case, which is means the acidic medium.

And at high pH this hydroxyl groups will react with  $OH^{-}$  and we will form negatively charged surface which is  $M-O^{-}$ . So, the density of this charges on the surface is negatively charged and here we have positively charged surfaces.

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Now, this schematic shows the variation of pH d; pH and the number of sites per unit area. And this point where the maximum numbers of O hydroxyl simple hydroxyl group exist is the IEP or ISO electric point. At the low pH, then this dominance of positively charged

surface higher than that IEP we have negative discharge surface. And these are the different materials and their approximate IEP values.

So, we can see the silica has the IEP of 2 to 3, alumina on the other hand we have 8.5 to 9.5 that is on the higher side; oil and air is in the order of 3 point, 3 to 4 so; that means, depending on this material we have different IEP values. And if the media is higher than that or lower than that depending on that we have a surface charge development on the surface of these particles.

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**Electrical double layer forces**

- Surface potential ( $\Psi_0$ ): potential difference due to separation of charge between the surface and the bulk solution
- Diffuse cloud formed by the counterions around each particle to maintain electrical neutrality of the system
- Overlapping of counterion clouds  $\Rightarrow$  increase in the concentration of counterions in the gap between the particles
- Particles of same charge  $\Rightarrow$  repulsive potential due to the osmotic pressure of the counterions
- Known as electrical double layer (EDL) repulsion
- Debye length ( $\kappa^{-1}$ ): measure of the EDL thickness  $\Rightarrow$  range of the repulsion
- Debye screening parameter ( $\kappa$ ) for monovalent salts:  
$$\kappa = 3.29\sqrt{[c]} \text{ nm}^{-1}$$
  
[c] = molar concentration of monovalent electrolyte
- Large Debye length (small counterion concentration): repulsive particles at large separation
- Addition of salt: compressed EDL due to increased concentration of the counterions
- Sufficient salt: EDL repulsion decreased and van der Waals attraction dominates

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Now, when we try to separate the charge between the surface and the bulk solution, there is a potential difference that is called the surface potential. Now, these counter ions that actually forms a diffused cloud around each particles maintains the neutrality of the system. And, each solution or say that each particle or each surface charge will have its counter ions; that means, say here we have the positively charged surfaces.

So, which means the counter ions in this positive cases it can be the KOH solution which will provide us the  $OH^{-}$  ion. When that there is say negatively charged  $O^{-}$  are there the counter ions can be the HCl solution, which will provide us the  $H^{+}$  ion. So, this counter ions actually keeps this solution or the particles electrically neutral state.

Now, when we try to say bring them closer there will be the overlapping of this counter ion clouds, and that actual increases the concentration of the counter ions in the gap between the

particles. If the particles are of same charge, then there will be a repulsive potential due to this osmotic pressure of the counter ions. This repulsion is known as the electrical double layer repulsion.

So, surface charge has been developed, but these are kept neutral by the addition of counter ions. This counter ions creates a cloud around each and every particle. Now, when we try to keep these or put these particles together or in the close proximity of them then this overlapping of these diffuse clouds or the counter ion clouds increases the concentration in between the particles; concentration of the counter ions.

And if the particles are of same charge then it actually repulses them. This counter ion and the thickness and it is a repulsion we call the electric double layer repulsion; it is quantified by the Debye length. So, it is a measure of this electrical double layer thickness basically this Debye length.

And it also provides a measure or estimate on the range of this repulsion force or the repulsive force,

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

where this kappa is the device screening parameter and for monovalent salts this is written in this form; or this has a relation with the molar concentration of the monovalent electrolyte. So, Debye length provides the measure of this electrical double layer thickness, which also tells us the measure the range of this repulsive force.

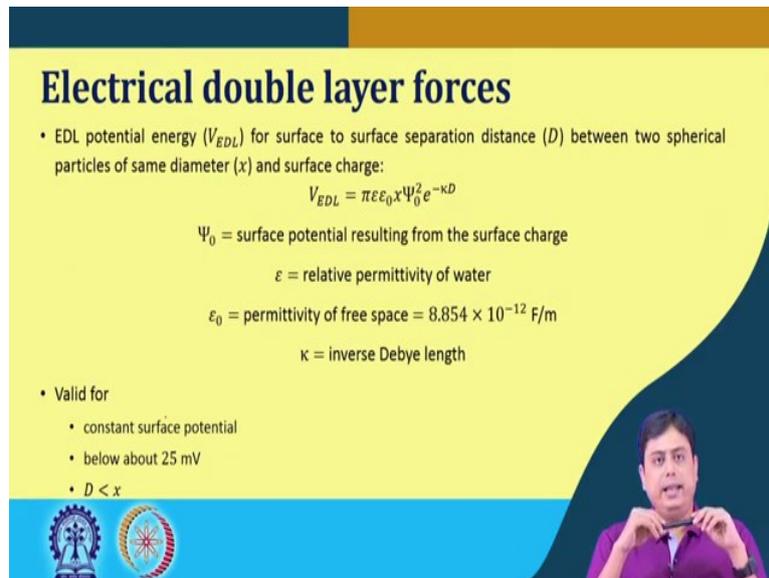
So, large divisor length that means, the small counter ion concentration; which means, if the particles are repulsive in a large separation. And if we add some salt to it compresses the electrical double layer; because there will be an increase in concentration of the counter ions. Once the sufficient amount of salt is added, this electrical double layer repulsion then decreases and the van der Waal interaction becomes dominant.

So, the concept here is that when this Debye length is large, which means we have small concentration of the counter ions around the particles; the particles are repulsive say at a larger distance. Once we add the salt say we have added some salt, then this double layered thickness is compressed, because now we have increased the concentration of the counter

ions. Now, if we add sufficient amount of salt this EDL repulsion decreases and the van der Waals attraction again dominates.

$$V_{EDL} = \pi \epsilon \epsilon_0 x \Psi_0^2 e^{-\kappa D}$$

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**Electrical double layer forces**

- EDL potential energy ( $V_{EDL}$ ) for surface to surface separation distance ( $D$ ) between two spherical particles of same diameter ( $x$ ) and surface charge:
$$V_{EDL} = \pi \epsilon \epsilon_0 x \Psi_0^2 e^{-\kappa D}$$

$\Psi_0$  = surface potential resulting from the surface charge

$\epsilon$  = relative permittivity of water

$\epsilon_0$  = permittivity of free space =  $8.854 \times 10^{-12}$  F/m

$\kappa$  = inverse Debye length

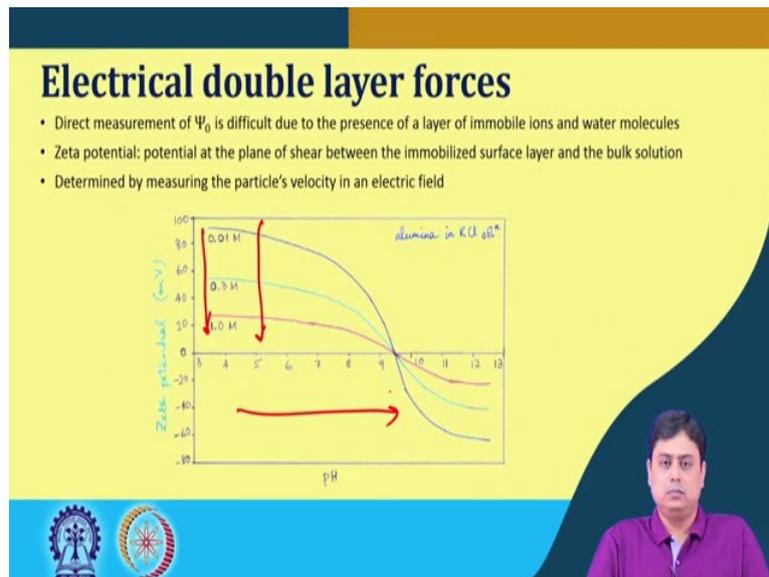
- Valid for
  - constant surface potential
  - below about 25 mV
  - $D < x$

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So, this EDL for surface to surface separation distance of  $D$  in between two spherical particles of same diameter and surface charge can be written in this form or has an expression of this one. Where  $\epsilon$  is the relative permittivity of water and  $\epsilon_0$  is the permittivity of the pre space, which is related here the energy for the potential energy for electrical double layer is related with the surface potential. So, which means we have to measure the surface potential as well in order to have its magnitude.

Now, this expression is valid for constant surface potential which is below about 25 mV and the other criteria is that the separation distance is much smaller than the particle size; if it is not, then it creates some complex expression. So, which means to estimate this EDL potential energy we have to know now the surface potential, that results from the surface charges.

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So, this surface potential direct measurement of it is not trivial. It is difficult, because there is a layer of immobile ion and say the water molecule layer is present. Instead, we measure zeta potential, which is the potential at the plane of shear between this immobilized ion surface layer and the bulk solution. And the distance between this actual surface and this ion layer surface is of about few angstroms.

So, it provides us a near about accurate measure of the surface potential as well. This zeta potential can be measured by measuring the velocity of the particles under a electrical field. So, this schematic shows the variation of zeta potential with salt concentration and pH. We see as the salt concentration increases zeta potential decreases, as the pH increases the zeta potential also decreases. And this is how a solution or suspension is manipulated for its surface charges to create say aggregates, to create flocculates.

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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)

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So, the other force that is important is to control the surface between the particles in suspension by addition of soluble polymer to the solution. Now, say we consider the polymers affinity towards the particle surface and it adsorbs on the particle surfaces depending on the molecule weight and the amount that is being absorbed.

So, depending on these parameters that is the polymer molecular weight and the amount it is being absorbed on the particle surface. There we can have attraction or repulsion; attraction due to polymer bridging or repulsion due to steric interactions. So, when we try to control the surface force, we can also add some soluble polymers to the solution.

If we consider say the polymer has affinity towards the particles surface and it adsorbs on the particular surface. And then depending on the amount it is being absorbed and its molecular weight; that means, polymers molecular weight we can have attractive force or the repulsive force between the particles. These are the separate forces then these van der Waal force and the EDL forces. And this adsorbing polymer layer that creates the interactions can be repulsive or attractive in nature. Based on this say the attraction we have bridging flocculation or the steric repulsion.

So, we will continue discussing on these two aspects that is the bridging flocculation or the attraction and the repulsion or the repulsion, ok. Why this happens? How it happens? We will continue our discussion in the next class till then.

Thank you for your attention.