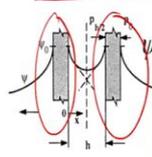**Colloids and Surfaces**
Prof. Basavaraj Madivala Gurappa
Department of Chemical Engineering
Indian Institute of Technology, Madras

Lecture – 39
Potential Energy of Repulsion between Planar Double Layers and DLVO Theory

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So, far we have derived an expression for repulsive force between two interacting surfaces, when we say interacting surfaces it means that there is a overlap of electrical double layer and the expression that we been able to obtain is this that is the excess pressure or the force per unit area with which the particles are the two surfaces that we are considering that is this and this are pushed apart as a result of overlap of electrical double layer is given by this.

$F_R = 2 k_B T$ n infinity cos hyperbolic z e psi at h / 2 / k_B T - 1 and because we can express cos hyperbolic x as a series expansion in this form instead of cos hyperbolic x - 1 I can substitute for cos hyperbolic x - 1 = x square / 2 factorial and I can neglect the higher order terms. So, if I do that, in the end the expression for repulsion becomes something like this 64 k_BT n infinity gamma not square exponent of - h / kappa inverse that is what we have derived so far.

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Repulsive force between interacting surfaces
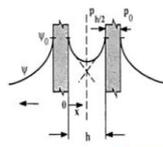
$$F_R = 64 k_B T n_\infty \Upsilon_0^2 \exp(-h / \kappa^{-1})$$

We know that $\kappa^2 = [(e^2 / \varepsilon k_B T) \sum_i z_i^2 n_{i\infty}]$

Since κ varies with $n_\infty^{1/2}$

$$F_R = C_1 n_\infty \exp(-C_2 n_\infty^{1/2})$$

The force of repulsion decreases with increasing electrolyte concentration between two surfaces compared at same distance (valid at relatively large separation)

The addition of electrolyte to a dispersion in many cases will induce the coagulation of colloids

Now, if you look at this expression, if we what we would like to do now is to look at a case where the distance of separation between the two plates is fixed that is, h is fixed and because we know that kappa square you know depends on you know the permittivity temperature and iron concentration in a particular way therefore, kappa varies as n infinity power of half kappa square goes n infinity therefore, kappa varies as n infinity to the power of half.

So, that is essentially is so, if this is kappa, therefore, kappa goes as if I take square on both sides, they essentially kappa goes as n infinity to the power of half. So, I can so, this is a constant for a given because if you are working at a given temperature, this is constant and if the surface potential is fixed, this gamma not square would also be fixed therefore, I can write the expression for the force of repulsion as some constant C_1 times n infinity exponent minus some constant multiplied by n infinity to power of form 1 half.

Therefore, from this expression what we can conclude is that, the force of repulsion decreases with increase in electrolyte concentration between the 2 surfaces compared at same distance, that means for a given distance, because you have there is a pre exponent term and there is an exponent term because of the fact that this decreases much more drastically with increasing the electrolyte concentration.

Therefore, the overall effect is essentially governed by this term. Therefore, the force of repulsion decreases with increase in the electrolyte concentration. And the other point that we can make is that the addition of the other way of saying this same point would be the addition

of electrolyte to dispersion in many cases is known to induce that coagulation of colloids that means, if you have the particles nicely dispersed.

The addition of electrolyte like salt for example, it gives rise to the coagulation or aggregation of particles that arises because of the fact that increase the electrolyte concentration leads to a reduction in the repulsive forces, which will make a colloid to go from a stable state to a destabilized or unstable state.

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Since we know that, the potential is given by the force times distance through which it operates, for change for an increment the change or the increment in the potential arising from a change in the separation distance, you can actually calculate by knowing F of R therefore, because d phi of R goes as $-F_R$ time dh therefore, one could integrate this expression to obtain an expression for the potential of repulsion between the two charge surfaces.

And if I use the boundary condition that the potential becomes 0 when the distance of separation is very very large at a separation distance which is much larger than k inverse or if you consider the distance of separation to be very very high, the force of repulsion would be 0 therefore, phi of R essentially goes as 64 k_BT n infinity kappa inverse is a factor that comes when you integrate this term and of course, you going to have the exponent - h / kappa inverse term intact.

So, therefore, now, what you have is that so, if you look at n infinity here n infinity goes as let us go back to the previous expression. So, you have a kappa inverse here. So, therefore, you had kappa which goes as n infinity power half n infinity power half and you have kappa inverse which goes as n infinity power of minus half so, because you have n infinity here and kappa inverse goes as n infinity power of minus half.

So, let me just quickly so, you have n infinity to the power of 1 that is this term and kappa inverse goes as n infinity power minus half therefore, overall this phi R the energy of repulsion or the interaction potential goes as some constant times n infinity to the power of half and exponent of minus C_2 some other constant times n infinity to the power of half and again this expression is written for a given separation distance of course, this expression is again valid when the distance of separation between the surfaces are large.

Again the same conclusions can be drawn that the potential energy of repulsion decreases with increasing electrolyte concentration because of a strong dependence of the exponential term on the concentration of the electrolyte that are being considered.

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So, we have been able to derive this expression for the overall potential or the total electrical double layer potential if we were able to do it or it was possible to obtain this expression because of the relatively simple approximation for the potential at the midpoint. So, we said that it is not the potential at the surface, but the potential at the mid plane, the potential that h/2 is what governs the electrical double layer repulsion.

And of course, we did use a superposition approximation to say that psi at h/2 = psi 1 + psi 2. So, we essentially used this approximation to obtain how the phi of R quantitatively depends on the several parameters in what however, general method for the evaluation of the potential energy of repulsion, it was derived by or it was put forward by Verwey and Overbeek in which a numerical simulation was used to capture.

How does the potential energy of repulsion varies with separation distance for any charge stabilized colloidal system for a very general case of the conclusions from these numerical integration procedure or that the potential energy of repulsion may extend appreciable distances from surfaces, but its range is compressed by increasing the electrolyte concentration of the system.

So, when we say that the electric potential energy of repulsion can extend to appreciable distances from the surfaces, we are talking about distances of the order of kappa inverse are less or of the distances of that order and however, the strength of the repulsion is reduced or compressed or decreased by decreases by increasing the concentration of electrolyte in the system.

The second point is the condition under which approaching particles first influence one another are at large separation distance for which the approximate relationship is given by this. So, therefore, the general solution that has been developed by numerical integration it kind of reduces to this particular expression when we are considering a moderate overlap or when the overlap is such that the distance between the particles is sufficiently larger.

The sensitivity of aqueous hydrophobic colloids to electrolyte concentration is due to the dependence of the inter particle repulsion on this concentration. So, there are several systems where lyophobic that means, the colloidal particles which do not disperse well in solutions are considered and the colloidal stability of such particles and the dependence of the stability on the electrolyte concentration is kind of captured by this particular theory. So, that is about the overlap of electrical double layers and how does that manifest into the repulsion between the particles.

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Colloidal interactions – charged suspensions
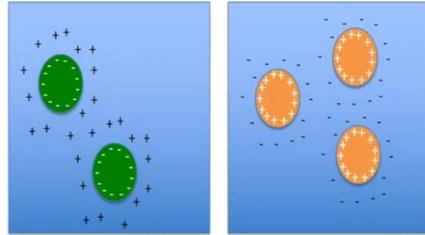
Attractive Interactions – van der Waals (Module 2)

Repulsive Interactions – Overlap of Electrical Double Layers (this module, Module 4)

$$\Phi_{Total}(d) = \Phi_{vdW}(d) + \Phi_{Electrostatic}(d)$$

So, now, we will move on to looking at colloidal interactions in charge stabilized suspensions. So, what we are have is a schematic 1 and 2 in which what is considered is you have a dispersion of and negatively charged particles and a dispersion of positively charged particles in a fluid medium and whenever you have a system of charge stabilized colloidal system.

So, you have to think about the attractive interactions between the particles and that comes from the contribution of the Van der Waals forces, which were discussed in module 2 and the repulsive interactions, which come about because of the overlap of electrical double layers which has been discussed in this module or the module 4. So, in such a system of charge stabilized colloids. The total interaction as a function of separation distance d is given by the summation of the Vander Waals contribution and the electrostatic or the electrical double layer contribution.

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Colloidal interactions – charged suspensions

$$\Phi_{DLVO}(d) = \Phi_{vdW}(d) + \Phi_{Electrostatic}(d)$$

The DLVO theory is named after Derjaguin and Landau, Verwey and Overbeek. This theory is put forward to explain the stability of charge stabilized colloidal dispersions.

Fig. 1.1 Schematic plot of a typical double layer repulsion between charged colloidal spheres (*top*), of the Van der Waals attraction (*bottom*) and their sum, which is the DLVO interaction potential
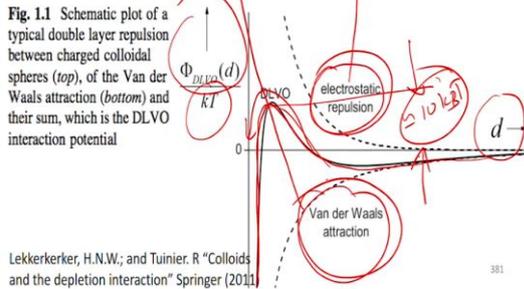
Lekkerkerker, H.N.W.; and Tuinier. R "Colloids and the depletion interaction" Springer (2011)

And this fact that the total interaction energy is the summation of the Vander Waals forces and the electrical double layer forces is what is called as a DLVO theory which is named after Derjaguin Landau, Verwey and Overbeek and this theory was put forward to explain the stability of charge stabilized colloidal dispersions. So, and what you see here is a plot of how the DLVO will potential or the total potential in a charged stabilised suspension scaled with thermal energy how does that vary as a function of separation distance.

So, you have repulsive contribution that comes from the electrical double layer effect and the Van der Waals contribution that comes from the Van der Waals the attractive term in the expression and the continuous line that is drawn here is the DLVO interaction and so, because you have electrical double layer repulsion and Van der Waals attraction, which are of opposing tendencies.

So, whenever you add up this term, you are going to have a maxima and depending upon the extent of this maxima what is the so, what is the energy that is required to overcome this barrier. So, that attractive interactions become dominant this is what is called as a energy barrier for aggregation. So, typically, when this energy barrier is of the order of several tens of k_BT one could say that such colloidal dispersions of charge stabilized particles are stable to aggregation and one could manipulate the strength of this energy barrier by manipulating by playing with several conditions which we are going to discuss in a while.

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Colloidal interactions – charged suspensions

The contribution of individual interactions to total potential depends on – particle geometry, surface charge, concentration of electrolyte, chemical composition of the particle, etc...
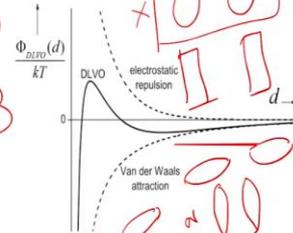
For planar surfaces:

$$\Phi_{net} = \underbrace{64 k_B T n_\infty \kappa^{-1} \Upsilon_0^2 \exp(-\kappa d)}_{\Phi_{Electrostatic}} - \underbrace{(A/12\pi) d^{-2}}_{\Phi_{vdW}}$$

$$\kappa^2 = [(e^2/\varepsilon k_B T) \sum_i z_i^2 n_{i\infty}]$$

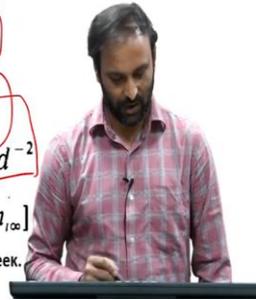The DLVO theory is named after Derjaguin and Landau, Verwey and Overbeek.

So, the contribution of individual interactions that means the contribution of the electrostatic interactions of electrical double layer interactions and Van der Waals interactions to the total potential depends on the particle geometry whether we were working with spherical particles or planar surfaces or you know elliptical particles so, it depends on the particle geometry and when the particles are you know, not isotropic that is non spherical, any case other than this, it turns out that what is also important is the orientation effect.

That means, whether in the case of ellipsoids if are the particles when they approach are they oriented in this particular fashion or are they oriented in the tip fashion or are they oriented tip to the side. So, therefore, depending upon the orientation of the particles the individual contribution could vary. The individual contribution also depends on the surface charge, what is the charge density on the particle surface the concentration of the electrolyte in the solution and the chemical composition of the particles and many other factors as well.

So, for a planar surface, we have derived this expression for how the potential varies with separation distance and this expression again we have derived in module 2. That comes from the Vander Waals forces where kappa is given by e square divided epsilon k_BT summation i z_i square and n_i infinity.

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Manipulation of colloidal interactions in charged suspensions

For particles of given geometry (planar surfaces)

$$\Phi_{net} = 64 k_B T n_\infty \kappa^{-1} \Upsilon_0^2 \exp(-\kappa d) - (A/12\pi)d^{-2}$$

$$\kappa^2 = [(e^2/\varepsilon k_B T) \sum_i z_i^2 n_{i\infty}]$$

Temperature

Permittivity

Chemical Composition of particles (Hamaker Constant)

Surface charge

Concentration of Electrolyte

The DLVO theory is named after Derjaguin and Landau, Verwey and Overbeek.

So, now, if you take particles refer a particular geometry or a given geometry in this case if you look at planar surfaces, if you look at the phi net or the phi total or phi DLVO you can say that the total potential depends on several parameters for example, temperature because you have you know the temperature term in the electrical double layer repulsion therefore, one could play with the temperature of the solution and then modulate the total potential.

It depends on the permittivity as well. So, if you have kappa inverse here and kappa inverse depends on again temperature as well as permittivity. So, therefore, you can disperse particles in fluid of different permittivity and then manipulate the total potential the chemical composition of the particles also is important because the chemical composition dictates what is the Hamaker constant of the particle under consideration. And the surface charge whether the charge density is high, low which will directly affect what is the electrical double layer repulsion and finally, the concentration of electrolyte as well.
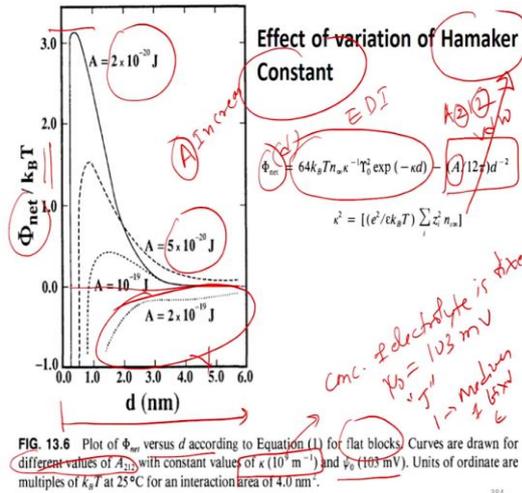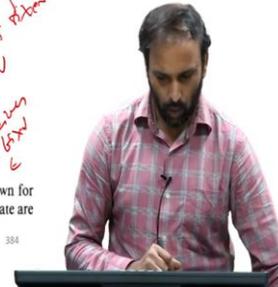
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FIG. 13.6 Plot of Φ_{net} versus d according to Equation (1) for flat blocks. Curves are drawn for different values of A_{212} with constant values of κ (10^9 m^{-1}) and ψ_0 (103 mV). Units of ordinate are multiples of $k_B T$ at 25 °C for an interaction area of 4.0 nm^2.

So, we look at particular case and look at how each of these parameters are going to affect so, what we are going to look at is essentially plotting this expression what we are going to do is we will consider a case of planar surfaces. So, for which the total potential is given by this expression and we will look at the effect of first the effect of variation of Hamaker constant. So, what we will do here is that we take a particular case.

So, we are going to plot phi net which is scaled with k_B T and we are going to plot phi net is the function of separation distance d of course, these expression is for flat blocks or the planar surfaces. And these plots that you see here, they are actually drawn for different values of A_{212} that means, this is A_{212} that is, this is the blocks of similar chemical composition to they are interacting via medium 1.

So, therefore, and they are plotted for a constant value of k that is k is 10 power 9 meter inverse that means, the concentration of electrolyte is fixed concentration of is fixed and they are also plotted for a case where psi not is equal to 103 millivolts. And of course, the temperature is also fixed and the medium 1 is medium 1 that is a medium of fixed epsilon. So, therefore, if you look at the contribution of the electrical double layer and the Van der Waals forces.
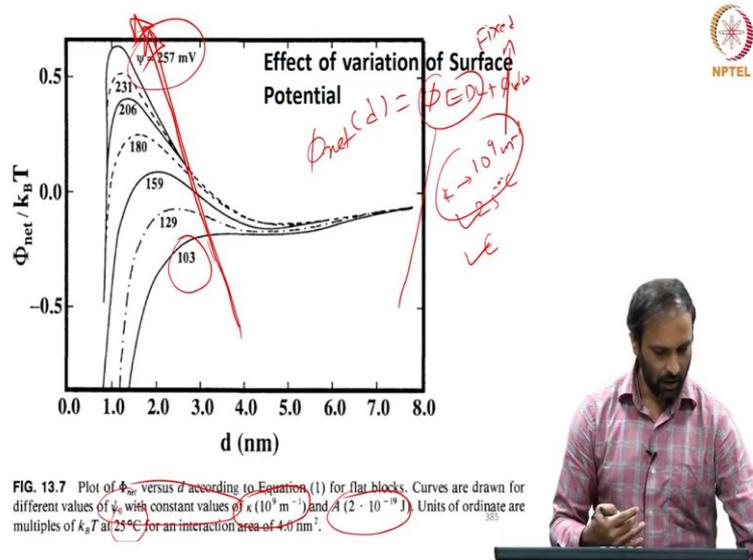
What is kept constant in this plot is that the electrical double layer interactions are kept constant and the only contribution that has been you know varied is what is the Van der Waals contribution. So, therefore, what you will see is that so, this is the dotted line that you

see if is for the case where A is 2 into 10 power - 19 joules and this is for 10 power - 19 and this is a 5 into 10 power - 20 and this is for 2 into 10 power - 20 joules.

Therefore, as you move in this direction Hamaker constant A increases. Now, when A increases that means to say that for a fixed electrical double layer interaction when A is increasing what happens is the Van der Waals contribution becomes more and more dominant as A increases therefore, there is some energy barrier for aggregation of the order of 3 k_BT when A is 2 into 10 power - 20 joules.

However, when the value of A increases to 2 into 10 power - 19 joules that is 1 order of magnitude you know increase you can see that the overall interaction is always attractive if you look at this case the if I draw this line we can see that the overall interaction in that case is always attractive that means for given separation distance that we have considered the total interaction is always attractive. Therefore, this method gives you a way of manipulating the overall interaction between the colloidal particles by varying the Hamaker constant of the material being considered.

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FIG. 13.7 Plot of Φ_{net} versus d according to Equation (1) for flat blocks. Curves are drawn for different values of ψ_o with constant values of κ (10^9 m^{-1}) and A ($2 \cdot 10^{-19}$ J). Units of ordinate are multiples of $k_B T$ at 25°C for an interaction area of 4.0 nm^2.

So, now, what we can do is we can consider a case where again you have phi net d is phi electrical double layer + phi Van der Walls. So, what is done in this case is A nought is fixed there because A nought is fixed the Van der Waals term is fixed that means, the variation of Van der Waals force of attraction with distance is fixed and also fixed is the concentration of the electrolyte kappa is 10 power 9 meter inverse.

And the temperature is also fixed 25 degrees centigrade and the medium is also fixed therefore, epsilon is fixed. So, if you look at electrical double layer interaction when the temperature medium and kappa is also fixed phi electrical double layer depends on what is the surface potential. So, the so, in this particular case what is varied in the surface potential is varied and it is varied over a wide range all the way from 103 milli volts to 257 milli volts.

Therefore, you are increasing the surface potential in this particular fashion. So, therefore, with increasing the potential, so, what will happen is as expected, the electrical double layer interactions will become more and more dominant therefore, if you look at the repulsive contribution would increase as you systematically increase the electrical double layer contraction.

Therefore, for a fixed Van der Waals force of interaction and for a given salt concentration you can manipulate phi net or the total interactions between charge stabilized collides by manipulating the surface potential and with the increase in the surface potential the magnitude of repulsion would increase.

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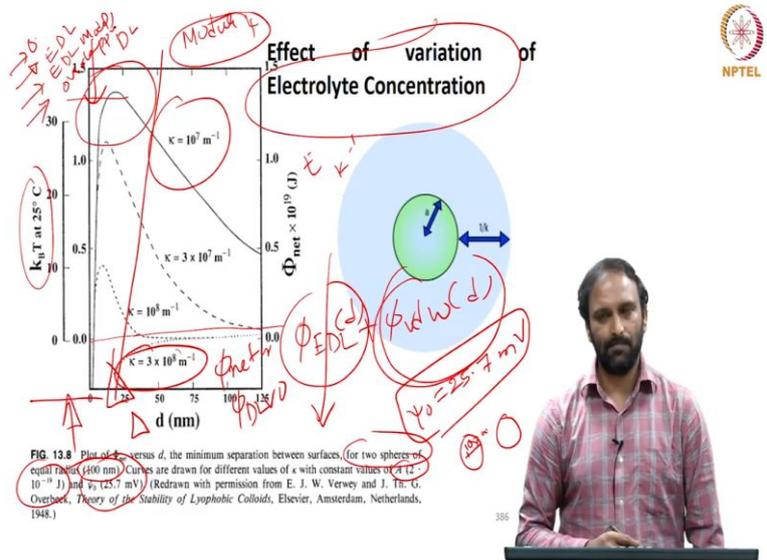
So, the third way of manipulating the total interaction potential is by varying the electrolyte concentration. So, in this case phi electrical double layer + phi Van der walls that is phi net or phi DLVO and again the Van der Waals contribution is kept constant here because A is fixed at 10 per - 10 millivolts and psi nought is fixed that is the surface potential is fixed at 25.7 million volts.

That is the limit of the aah low potential case. And so, in this particular case, what you have is this is drawn for two spherical particles of radius 100 nanometre that means, we are considering two spherical particles whose radius is 100 nanometres and we are looking at the variation of total potential as a function of separation distance and what has changed here is if you look at the plot there is different values of k that is mentioned.

The different values of kappa and that is achieved by adding different concentration of electrolyte into the system. So, if you move in this way kappa the value of kappa is increasing therefore, if you move this particular way kappa inverse is increasing the fact that the kappa inverse is increasing that means, if you increase in this if you go in this concentration the concentration of electrolyte decreases kappa is increasing.

So, the concentration of the electrolyte decreases when the concentration of electrolyte decreases that means, we are if you look at the total contribution to the interactions, so, the repulsive interactions are becoming more and more dominant because the electrolyte concentration is decreasing in this particular way. So, therefore, the system such as this so, therefore, just to conclude a system such as this will have a higher concentration of electrolyte.

Higher concentration of electrolyte therefore, what will happen is the electrical double layer contribution to the total potential is weaker however, if you look at a case like this the kappa inverse is larger that means the electrolyte concentration is lower in this case therefore, the electrical double layer contribution becomes significant and therefore, the overall interactions if you look at there is energy barrier that comes into picture.

Because, if you look at this scale, this is k_BT at 25 degrees centigrade. So, therefore, there exists a energy barrier for the particles to aggregate and that happens when the concentration of electrolyte is lower. However, if you increase electrolyte concentration the Van der Waals force such become dominant and the overall interactions if we look it up, it is positive. So, with that we come to the end of module 4.

Where we have been able to look at a system of charged particles so, we started with looking at the origin of surface charge. Then, we looked at the concept of electrical double layers then we discussed electrical double layer models. So, followed by, we looked at overlapping

double layers and followed by that we talked about the colloidal interactions in a charge stabilized dispersions, namely the DLVO theory so that that would be it in this module.