Colloids and Surface
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Lecture - 37
Structure of Electrical Double Layer

So, in today's lecture so we will start with discussing the summary of electrical double layer models followed by structure of double layer and then we will move on to think about what happens when there is overlap of the double layers? We will calculate what is the force? And the potential of interaction between the particles when there is overlap of the double layers. Then something called as a DLVO potential followed by how does the DLVO potential varies for different cases that is what we are going to do today.

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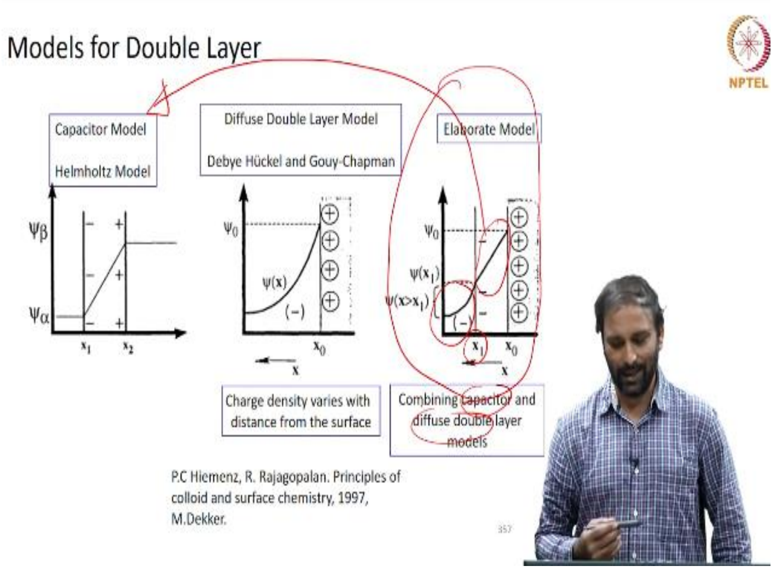

Models for Double Layer

Capacitor Model

Helmholtz Model

Diffuse Double Layer Model

Debye Hückel and Gouy-Chapman

Elaborate Model

Charge density varies with distance from the surface

Combining capacitor and diffuse double layer models

P.C Hiemenz, R. Rajagopalan. Principles of colloid and surface chemistry, 1997, M.Dekker.

So, what we have discussed in the model for double layers is that one of the simplest models was capacitor model or the Helmholtz double layer model in which it was assumed that if you have any charge surface in the immediate vicinity of the charge surface. You have a layer of counter ions, which are tightly bound to the charge surface and the way the potential varies with this distance it in a very much resembles this line that is there is a linear variation of the potential with distance in the double layer.

And the next model that we looked up was what are called as a class of model called a diffuse double layer model in that we have looked at Debye Huckel formulation and Gouy Chapman formulation in which it is assumed that the correct picture of the distribution of charges in the solution are considered. So the idea is that the fact that the counter ions and the co-ions that you have in the solution; you know they do have thermal energy.

And because of this thermal energy there is a more diffuse distribution of counterions in solution that is the charge density varies with distance from the surface. So, that gave us the fact that the potential psi goes as psi 0 exponent - kappa x or gamma = gamma 0 exponent - kappa x. That is what we are derived for the two diffused double layer models. However in one could also think about a more elaborate model in which you can combine both the aspects of the capacitor model and the diffused a double layer model.

And then we can say that look in the region very close to the charge surface, you still have a linear variation that is captured by the capacitor model and however it is at a distance x greater than x_1 you can have a diffuse double layer kind of model. So, one could combine both the capacitor model and the diffuse double layer model to come up with a better or a more elaborate model and because we know how the potential varies in the two regions. And one could think about exploiting this fact to come up with a more general description of the electrical double layer model and this is the situation which is more close to reality.

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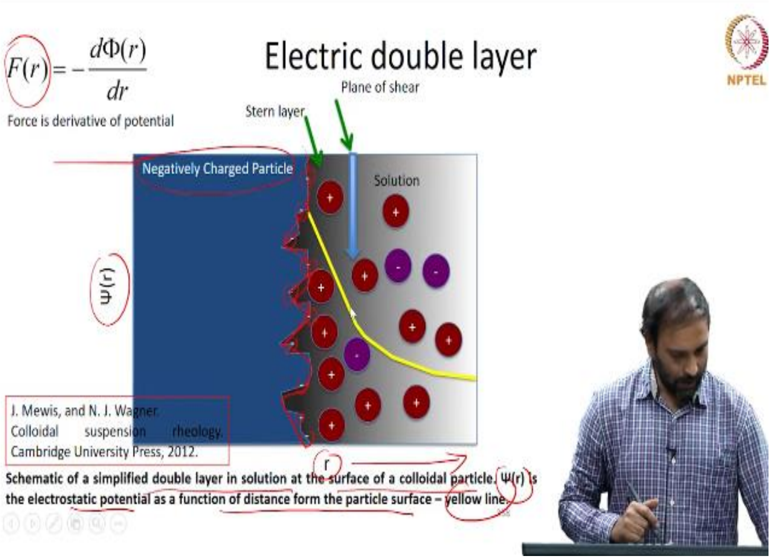

Electric double layer

$$F(r) = -\frac{d\Phi(r)}{dr}$$

Force is derivative of potential

J. Mewis, and N. J. Wagner. Colloidal suspension rheology. Cambridge University Press, 2012.

Schematic of a simplified double layer in solution at the surface of a colloidal particle. Ψ(r) is the electrostatic potential as a function of distance form the particle surface – yellow line.

So, we will talk a little bit more details about electrical double layer itself so, what is plotted is there is a picture here, a schematic in which what you have is a negatively charged particle and these are the negative charges that are represented on the particle surface and as you can see that you know it is a real surface. Therefore you see that there you know it kind of exhibits these undulations these.

So, this is because if you look at any particle at a nano scale is not homogeneous there could be some heterogeneities on the surface. So, that what this essentially depicts and so, what is plotted here is this is a potential and that is a separation distance r and of course we know that the force of you know interaction is related to the potential of interaction through this particular formula that is F of r is the negative gradient of the potential.

So, what you are seeing is a schematic of a simplified double layer model in solution at the surface of the colloidal particle that is colloidal particle that we are considering and at the surface how does the psi r vary with distances what is shown. So, psi r is the electrostatic potential and it is plotted as a function of distance from the particle surface that is this line and that is the yellow line that you know is marked here.

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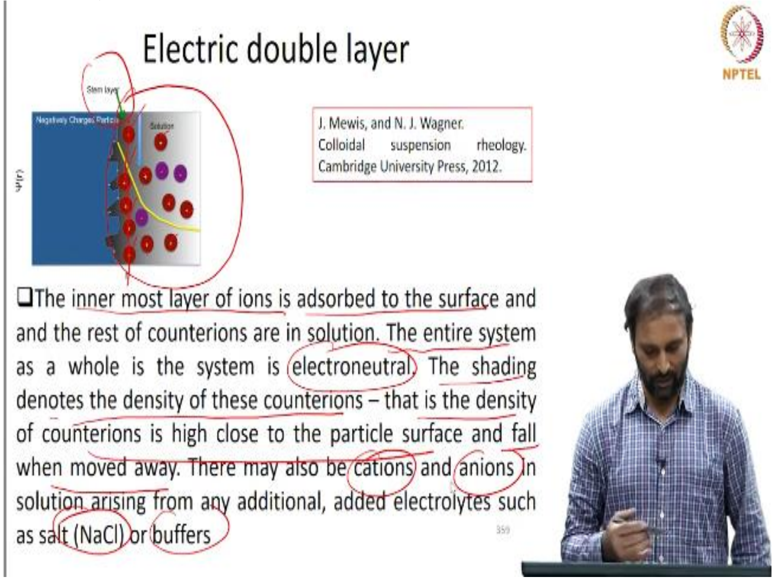

Electric double layer

J. Mewis, and N. J. Wagner.
Colloidal suspension rheology.
Cambridge University Press, 2012.

❑The inner most layer of ions is adsorbed to the surface and and the rest of counterions are in solution. The entire system as a whole is the system is electroneutral. The shading denotes the density of these counterions – that is the density of counterions is high close to the particle surface and fall when moved away. There may also be cations and anions in solution arising from any additional, added electrolytes such as salt (NaCl) or buffers

So, what is also marked here in this picture of electrical double layer is something called as a stern layer, the innermost layer of ions that is we are talking about now because the particle is negatively charged. So, these positive charges that you see these are the counter ions now in the immediate vicinity of the charge surface, the innermost layer of the ions is adsorbed to the surface and the rest of the counter ions are in the solutions.

That is the inner layer of ions, counter ions and of course, there are some other counter ions as well and the whole system, the entire system as a whole is electro neutral because they will be equal number of positive and negative charges in the solution. If you look at the region that is a solution region that is marked here, you see that the intensity of the shading decreases as you move away from the charge surface.

The shading denotes the density of the counter ions and the counterions concentration is high closer to the charge surface that is the density of the counterions is high close to the particle surface and it falls when we move away from the surface. Of course there could be additional cations and anions in solution that may arise because often what is done is to dispersion of charged particles will add some additional electrolyte or some buffers.

Because of which there could be additional cations and anions in the solution and of course they will also be distributed in a particular way in the solution and so this innermost layer of ions that is adsorbed close to the surface that the region that corresponds to this innermost layer of ions is what is called as a stern layer.

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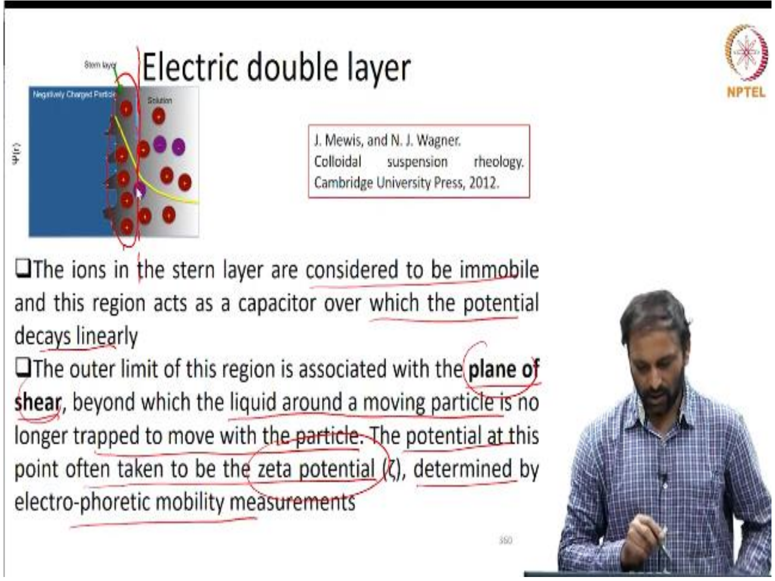

Electric double layer

J. Mewis, and N. J. Wagner.
Colloidal suspension rheology.
Cambridge University Press, 2012.

- The ions in the stern layer are considered to be immobile and this region acts as a capacitor over which the potential decays linearly
- The outer limit of this region is associated with the **plane of shear**, beyond which the liquid around a moving particle is no longer trapped to move with the particle. The potential at this point often taken to be the zeta potential (ζ), determined by electro-phoretic mobility measurements

So, the ions in the stern layer can be considered to be immobile that means for all practical purposes, they are adhered strongly onto the particle surface and therefore the this region essentially acts more like a capacitor over which the potential varies linearly with separation distance that is what is shown here. If you look at this, how this yellow line varies in this stern layer region there is a linear fall of potential with separation distance.

The outermost limit of the stern layer is associated with what is called as a plane of shear and so this essentially signifies that beyond this plane of shear that is I am going to draw a vertical line here so maybe here I am going to draw a dotted line that is the plane of shear beyond which the liquid around a moving particle is no longer trapped to move with the particle. So, if you look at the configuration of the charged particle and the solution next to it there is a stern layer where the counter ions are strongly bound charge surface.

And of course there will be also be some liquid as well in the stern layer. Now, when the particle moves whatever liquid that is trapped in the stern layer will also move along with a particle. However, beyond this boundary the liquid moving around a particle is no longer trapped to move with the particle. So, therefore, this boundary essentially tells you whether the liquid next to the particle is moving along with a particle or not moving with the particle.

The potential at this point is often considered to be the zeta potential and this is a zeta potential is a parameter of practical significance. Because depending upon the zeta potential of the particles in the dispersion you know, you can comment on the stability of colloidal particles in the solution and it is determined by a technique called electrophoteric mobility measurements which we will discuss in the in the next few classes.

So, just to sum up there is a stern layer in which the counterions are strongly bound to the particle surface and the outer limit of this stern layer is what is called as a plane of shear beyond which the liquid around the moving particle is no longer trapped to move with the particle that means, the liquid has the kinetic independence beyond the plane of shear. However, within the stern layer the liquid does not have kinetic independence because it moves along with a particle when the particle is set into motion.

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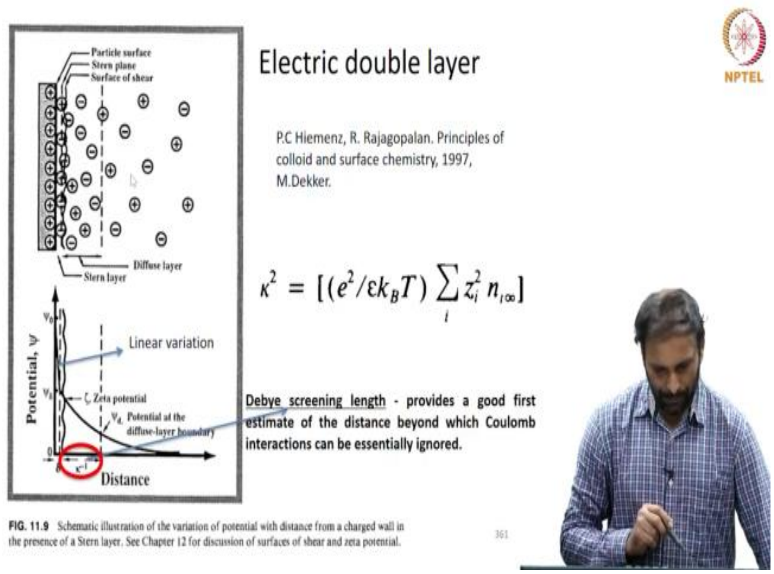

Electric double layer

P.C Hiemenz, R. Rajagopalan. Principles of colloid and surface chemistry, 1997, M.Dekker.

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

Debye screening length - provides a good first estimate of the distance beyond which Coulomb interactions can be essentially ignored.

FIG. 11.9 Schematic illustration of the variation of potential with distance from a charged wall in the presence of a Stern layer. See Chapter 12 for discussion of surfaces of shear and zeta potential.

So, that is again the similar picture depicted here so you have a positively charged particle surface and the stern layer very next to it and there is a plane of shear and of course if you look at there is a certain structure in which the counter ions and the co-ions are arranged in the solution that is what is called as a diffused layer. So, therefore if you look at the stern layer, the linear fall of potential is evident and in the diffuse double layer, the potential falls more like a exponential way.

And the potential at the surface is psi 0 and the potential at the plane of shear is the zeta potential and what is also marked as k inverse, which is the Debye screening length and at k inverse the potential typically is denoted as psi d that is the potential at the diffuse layer boundary and it turns out that this potential diffuse layer boundary is important because when the two particles start approaching each other.

When the potential is larger than when the potential at the overlap becomes larger than psi d that is when the repulsion between the particles become significant and this k inverse that is the Debye screening length, it provides a good first estimate of the distance beyond which the Coulomb interactions can be essentially ignored. That means if we are considering two particles in solution if the distance between the particles is larger than k inverse. So, we can ignore the electrical double layer interactions and one has to worry about the other kind of interaction that may be present in the system.

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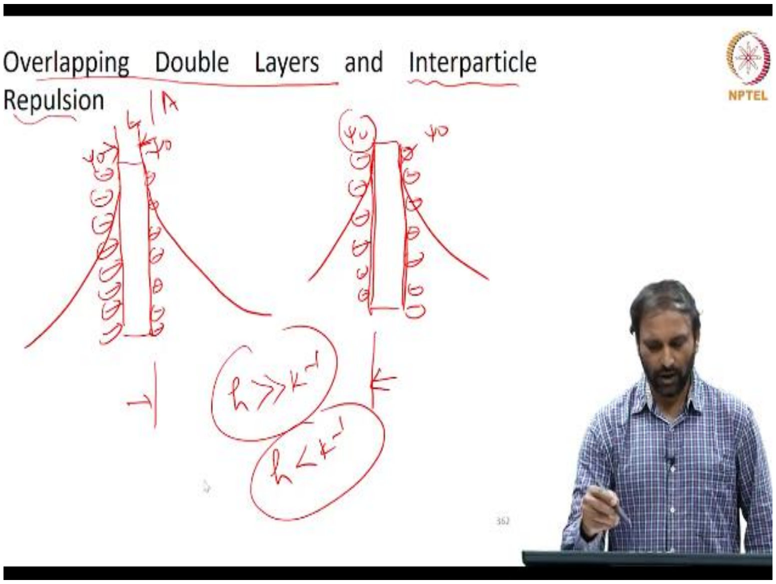

Overlapping Double Layers and Interparticle Repulsion

So, with that picture we will we would like to talk about overlap of electrical double layers and how does that manifest into inter particle repulsion. So, for that what we are going to do is we are going to consider two plates and say that both the inner you can think about them as infinite you know plates. So, in which both the surfaces of the particle are charged so, it is a substrate of some finite thickness t and they have an area A.

And now, so, we know that there will be some potential psi 0 associated with each of these surfaces and because we are assuming that both this surface and this surface are homogeneous in terms of surface chemistry the material you know they are made of therefore, we can assume that the potential of the surface on either side is essentially the same and of course we know how the potential varies with distance now because we have developed if we have developed expressions for how the potential varies with separation distance.

Now, if the distance between the plates that is h if it is greater than or far far greater than kappa inverse as I mentioned earlier though there would not be any overlap of electrical double layers therefore, in such cases the inter particle repulsion will not exist. So, what we are going to consider is the case where when h becomes less than kappa inverse that means when there is a overlap of the double layers. We will we would like to calculate what is the repulsion between the two particles?

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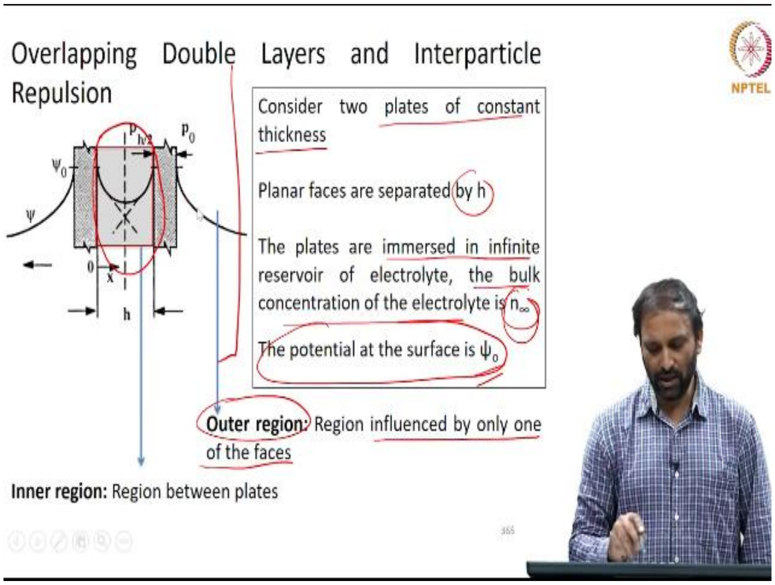

Overlapping Double Layers and Interparticle Repulsion

Consider two plates of constant thickness

Planar faces are separated by h

The plates are immersed in infinite reservoir of electrolyte, the bulk concentration of the electrolyte is n_∞

The potential at the surface is ψ_0

Outer region: Region influenced by only one of the faces

Inner region: Region between plates

So, therefore, the objective is to calculate the force per unit area or the pressure that operates on the two charged surfaces as a result of overlap of doubles layer. So, you have a schematic here this is a schematic of two plates that is a plate 1 and that is plate 2 and these are two plates of constant thickness and they are separated by a distance h that is the distance between the two plates and the plates are immersed in infinite reservoir of electrolyte that is the bulk concentration of the electrolyte is n infinity.

Because once so, you should imagine that so, these plates are immersed you know a bath of electrolyte and the concentration of the electrolyte is fixed and so essentially n infinity there is a concentration electrolyte in the bath is fixed and the potential at the surface is psi 0. So, whether you take the inner surface or the outer surface because they are chemically homogeneous. So, the potential of the surface is psi 0 and that in other words we can say that the charge density at the 2 surfaces is exactly the same.

So, now so, what is shown here is that so, there is a region that has between the two plates and there is a region outside. So, we are going to name two regions the outer region in this region the potential in this region is influenced by only one of the phases. So, that is the region outside the two plates that means so, that is the interior region, the inner region where the there is a region between the plates, where the potential in this gap is influenced by both the surfaces. However, in the outer region, the potential is influenced by only one of the phases.

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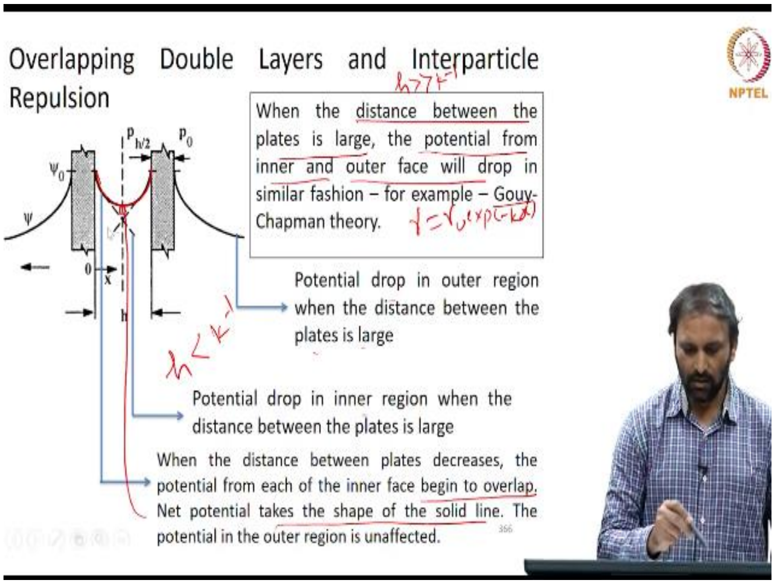

Overlapping Double Layers and Interparticle Repulsion

$h \gg \kappa^{-1}$

When the distance between the plates is large, the potential from inner and outer face will drop in similar fashion – for example – Gouy-Chapman theory. $\gamma = \gamma_0 \exp(-\kappa x)$

Potential drop in outer region when the distance between the plates is large

$h < \kappa^{-1}$

Potential drop in inner region when the distance between the plates is large

When the distance between plates decreases, the potential from each of the inner face begin to overlap. Net potential takes the shape of the solid line. The potential in the outer region is unaffected.

366

I have already made this point but I would like to go through it again when the distance between the plates is large and when I say large, we always talk about distances in terms of some characteristic length scales. So, in this case the distance h when I say it is larger it is larger than kappa inverse. The potential from the inner and the outer face will drop in a similar fashion that is when they are sufficiently far apart, whether you look at how the potential varies in the outer region from outer face or the inner face.

The potential would fall in a similar fashion and it could be Gouy Chapman way that is capital gamma = gamma 0 exponent – kappa x or it could be Debye Hackle way if we are considering the case of low potential. The potential drop in the outer region when the distance between the plates is large is given by the solid line. This line essentially captures how the potential falls with distance when the distance between the plates is larger.

Now so, there are some dashed lines in between so if you look at this line that is a dashed line this as well. The potential drop in the inner region when the distance between the place is large that means, when they are sufficiently far apart so, that the way the potential varies in the outer region is exactly same as the way the potential varies on the other face and that is captured by this dashed line and what you in the schematic is this line.

So, that is when this again is a potential variation, when the distance between the particles, start decreasing that means when the particles are sufficiently close such that now, h is less than kappa inverse. The potential from each of the inner face they begin to overlap the net potential takes the shape of a solid line that is shown here. However the potential in the outer region remains unaffected because in the outer region, the potential is only influenced by the outer face.

However, because of the overlap both the inner face of both the particle 1 and the particle 2 will influence how the potential varies within the gap and that is essentially captured by this solid line.