Colloids and Surfaces
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Lecture - 38
Force of Repulsion between Interacting Surface

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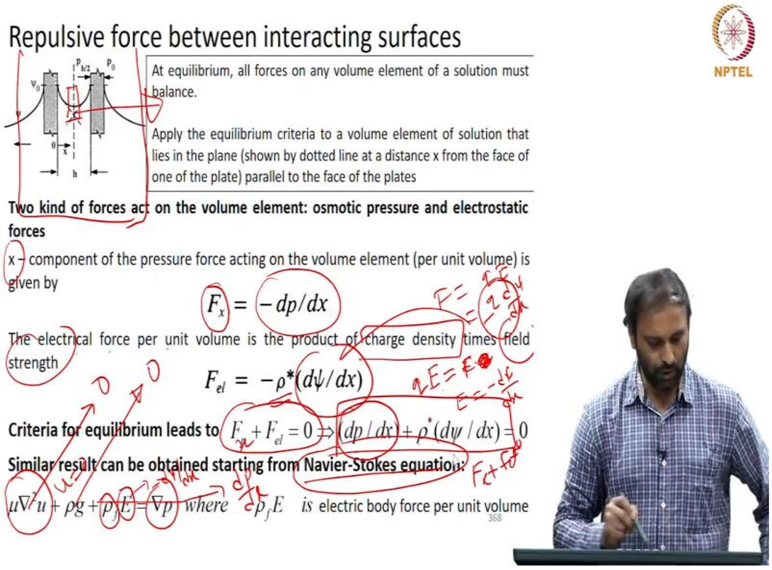

Repulsive force between interacting surfaces

At equilibrium, all forces on any volume element of a solution must balance.

Apply the equilibrium criteria to a volume element of solution that lies in the plane (shown by dotted line at a distance x from the face of one of the plate) parallel to the face of the plates

Two kind of forces act on the volume element: osmotic pressure and electrostatic forces

x – component of the pressure force acting on the volume element (per unit volume) is given by

$$F_x = -dp/dx$$

The electrical force per unit volume is the product of charge density times field strength

$$F_{el} = -\rho^*(d\psi/dx)$$

Criteria for equilibrium leads to $F_x + F_{el} = 0 \Rightarrow (dp/dx) + \rho^*(d\psi/dx) = 0$

Similar result can be obtained starting from Navier-Stokes equation:

$\mu\nabla^2 u + \rho g + \rho_f E = \nabla p$ where $\rho_f E$ is electric body force per unit volume

So, now of course you have some fluid in between the plates, because you know these two plates are immersed in a bath of electrolyte there is fluid you know in the outer region as well as inner region. And if we assume that the plates are in equilibrium what you could do is you can consider you can think about doing a force balance so, you can consider a volume element of fluid that is parallel to the face of the plates that are considered.

And you could do a force balance it turns out that there are two forces that are acting on the volume element first is what is called as osmotic pressure force. And this arises because if you look at the region within the two plates there is certain concentration of electrolyte and because of the fact that there is a concentration of you know the counter ions close to the surface is higher. So, the concentration in this region would be very different from the concentration in a region that is in the region outside the gap.

That is the concentration of the if I am going to think about the concentration of the electrolyte in the region as C_1 and if I say that the concentration of the electrolyte in the region outside the plates is C_2, this C_1 would be greater than C_2 because of the fact that the gaps are low and the if you look at the number density of ions the in the gap would be larger compared to what you have in the region outside.

Because of which because of this difference in the concentration of ions in the region between the plates and that outside there is going to be an osmotic pressure force term that is going to be important. And the second force will arise because of the fact that you have particles that are charged. And because of this there is going to be an electrostatic force that will also come into the picture.

So, what we are going to do is we are going to consider the x component of the two forces the x component of the automatic pressure force is given by - dp / dx that is because we are only considering a 1 dimensional case of how the force varies with distance in the x direction. And F x is given by - dp / dx and the electrical force per unit volume is given by the product of charge density times the field strength.

That again comes from the electrostatic concept that electric field E is force times q and E again is - d psi / dx sorry this is F times q so, this F is E times q and therefore I can write F as q times E that is q times - d psi / dx and there is a minus sign here. So, therefore one could write the electric force per unit volume that is acting on a fluid element that is considered is given by the charge density rho star times the gradient in the potential and because the plates are in equilibrium the summation of all the forces should be equal to 0.

That is F_p in this case $F_x + F_{el}$ should be equal to 0 therefore dp / dx + rho star times d psi / dx is going to be 0 you can arrive at a similar expression for the force balance if you start with Navier Stokes equation as well. And this is the term that comes if you have flow in the solution. However because we are talking about a case where you have particles immersed you know infinite bath of electrolyte and there is no bulk flow the velocity u is going to be 0 therefore this term is going to be 0.

And we are going to assume that the gravitational effects are not important therefore that term again would be 0 and you have the charge density here times E that is the strength of the electric field and that we know it is - d psi / dx and you have delta p here and because we are only worrying about the pressure gradient in the x direction therefore this del p essentially would be dp / dx.

So, whether you identify the different forces acting on the volume element and then do a force balance or you start with Navier Stokes equation and then cancel out or neglect the term that are not relevant you end up with the same expression that this $F_x + F_{el} = 0$.

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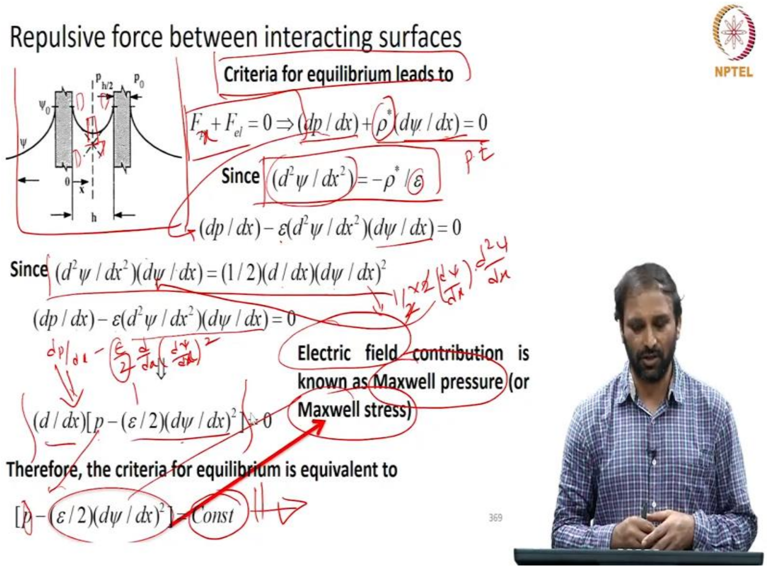

Repulsive force between interacting surfaces

Criteria for equilibrium leads to

$$F_x + F_{el} = 0 \Rightarrow (dp/dx) + \rho^*(d\psi/dx) = 0$$

Since $(d^2\psi/dx^2) = -\rho^*/\varepsilon$

$$(dp/dx) - \varepsilon(d^2\psi/dx^2)(d\psi/dx) = 0$$

Since $(d^2\psi/dx^2)(d\psi/dx) = (1/2)(d/dx)(d\psi/dx)^2$

$$(dp/dx) - \varepsilon(d^2\psi/dx^2)(d\psi/dx) = 0$$

$$dp/dx - \left(\frac{\varepsilon}{2}\right)\frac{d}{dx}\left(\frac{d\psi}{dx}\right)^2$$

$$(d/dx)[p - (\varepsilon/2)(d\psi/dx)^2] = 0$$

Electric field contribution is known as Maxwell pressure (or Maxwell stress)

Therefore, the criteria for equilibrium is equivalent to

$$[p - (\varepsilon/2)(d\psi/dx)^2] = Const$$

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So, therefore the criteria for the equilibrium is $F_x + F_{el} = 0$. Therefore dp / dx + rho star times d psi / dx = 0 and we know this from the Poisson equation; the Poisson equation 1 dimension is d square psi / d x square = - rho star / epsilon. So, I can instead of rho star I can replace so, that is the dp / dx term instead of rho star I can replace that with epsilon times d psi / dx and d square psi / dx square times d psi / dx.

Since, we know that d square psi / dx square times d psi / dx = 1/2 d / dx of d psi / dx whole square so, if I simplify this what I get is 1 over 2 times d / dx of d psi / dx whole square is 2 times d psi / dx times d square psi / dx square this, this gets cancelled we essentially end up with the same term. So, therefore dp / dx - epsilon times d square psi / dx square times d psi / dx I can write this as dp / dx - epsilon / 2 times d / dx of d psi / dx whole square.

So, if I take d / dx is common so, therefore this becomes p - epsilon / 2 times d psi / dx whole square = 0. Now, if I integrate this so what I end up with this p that is this - epsilon / 2 d psi / dx whole square is equal to constant. And therefore the criteria for equilibrium now becomes p - epsilon / 2 d psi / dx whole square is equal to constant and now if you look at this expression this is the contribution that comes from the osmotic pressure and this is a contribution that comes from the electric field.

So, what this expression is it tells you is that if you look at not only for the volume element like say at the central location if you look at volume element at any location this equation would be satisfied because of the fact that we are assuming that the entire system is in equilibrium and the electric field contribution to the pressure is what is called the Maxwell pressure or the Maxwell stress which comes into picture.

Whenever you have flow or maybe a flow coupled with electric field effects in the solution or any case where you have pressure contribution comes from things like osmotic pressure or flow and then there is a coupled effect along with the electric field present in the system.

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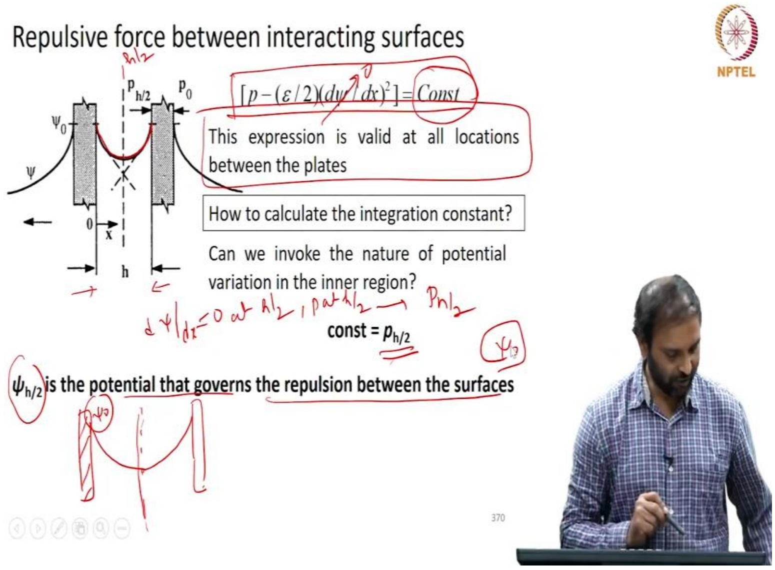

Repulsive force between interacting surfaces

$[p-(\varepsilon/2)(d\psi/dx)^2] = Const$

This expression is valid at all locations between the plates

How to calculate the integration constant?

Can we invoke the nature of potential variation in the inner region?

$d\psi/dx = 0$ at $h/2$, p at $h/2 \rightarrow p_{h/2}$

const = $p_{h/2}$

$\psi_{h/2}$ is the potential that governs the repulsion between the surfaces

So, therefore this expression that we have derived which is the condition for equilibrium is valid at all location within the plates. So, of course we will be interested to find out what is the integration constant one of the way to think about obtaining the integration constant is to look at how does this potential because of the overlap varies with the distance. So, if you look at this I can say that at the midpoint so if h is the distance between the plates.

And that is the dashed line that is drawn that is the mid plane that is at the distance h / 2 at the midpoint you can say that d psi / dx = 0 at h / 2 and pressure at h / 2 is $p_{h/2}$. So, therefore if I substitute these conditions this term becomes 0 therefore constant essentially becomes p at h / 2. Now, if you look at the overlapping electrical double layers so, even though the surface potential is psi 0.

When the overlap occurs, let us say that this is the potential with respect to one plate and say that this is the potential with respect to other plates. So, the repulsion between the particle does not depend on what is psi 0 however what is the potential at the overlap therefore psi h / 2 is the potential that governs the repulsion between the surfaces not psi 0.

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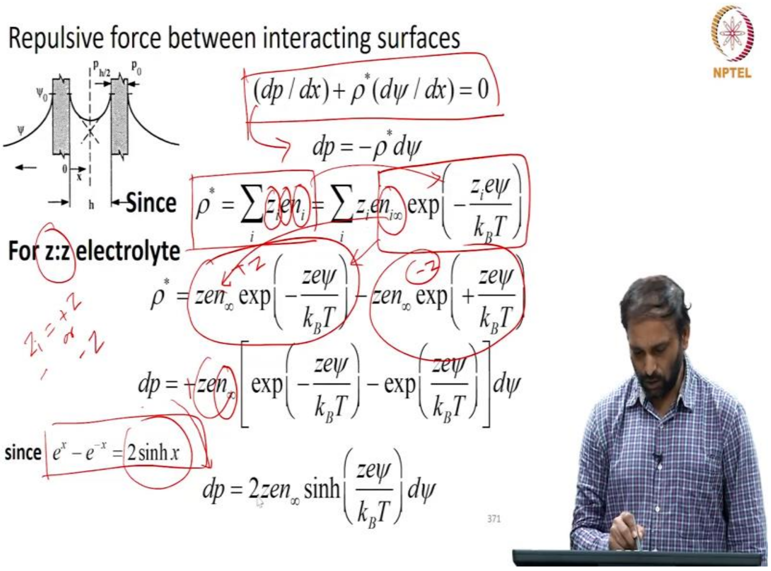

Repulsive force between interacting surfaces

$$(dp/dx) + \rho^*(d\psi/dx) = 0$$

$$dp = -\rho^* d\psi$$

Since $\rho^* = \sum_i z_i e n_i = \sum_i z_i e n_{i\infty} \exp\left(-\frac{z_i e\psi}{k_B T}\right)$

For z:z electrolyte

$z_i = +z$ or $-z$

$$\rho^* = zen_\infty \exp\left(-\frac{ze\psi}{k_B T}\right) - zen_\infty \exp\left(+\frac{ze\psi}{k_B T}\right)$$

+z

-z

$$dp = -zen_\infty\left[\exp\left(-\frac{ze\psi}{k_B T}\right) - \exp\left(\frac{ze\psi}{k_B T}\right)\right]d\psi$$

since $e^x - e^{-x} = 2\sinh x$

$$dp = 2zen_\infty \sinh\left(\frac{ze\psi}{k_B T}\right)d\psi$$

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So, therefore now we would like to express the potential you know the so, what we will do is we will again do some simplifications. So, that is the force balance and therefore I can write recast this as dp = - rho star multiplied by d psi and we know that the charge density in solution can be written as summation i z_i e times n_i. So, all that we are doing is we are summing up the charge contribution because of different types of ions in solution.

So, z_i is the valency and e is the charge on the electron and n_i is the concentration of the i th type of ions in solution. So, I can bring in the Boltzmann factor so, z_i e times the Boltzmann factor that is rho star and when you have z is to z electrolyte is a z_i takes the value of + z or - z therefore I can expand this term I can write 2 terms one for the + z case and the other one for the - z case. Therefore dp becomes - z e n infinity times.

And now note that n_i infinity I am replacing that as n infinity itself because the concentration of both the cations and the anions is exactly same. And I can denote that as n infinity. So, therefore I can take this out that is a common factor. So, you have exponent minus is z e psi / k_BT sorry z e n infinity times exponent – z e psi/ k_B T - exponent of z e psi / k_B T. So, that is what you end up with. And we can use the fact that exponent x - exponent - x is 2 sin hyperbolic x therefore I could write this as dp. So, I think there is a mistake here. So that is should be positive. Therefore dp is = 2 times z e n infinity times sine hyperbolic z e psi/k_B T times d psi.

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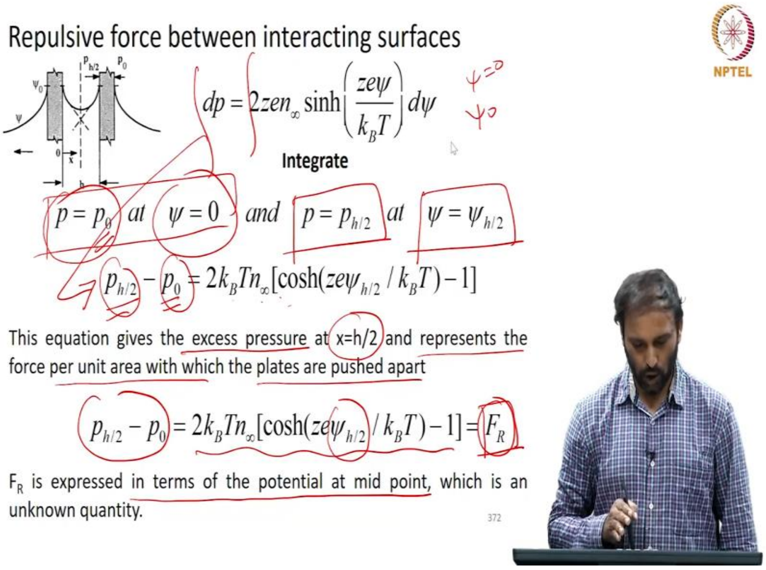

Repulsive force between interacting surfaces

$$dp = 2zen_\infty \sinh\left(\frac{ze\psi}{k_BT}\right) d\psi$$

Integrate

$p = p_0$ at $\psi = 0$ and $p = p_{h/2}$ at $\psi = \psi_{h/2}$

$$p_{h/2} - p_0 = 2k_BTn_\infty[\cosh(ze\psi_{h/2}/k_BT) - 1]$$

This equation gives the excess pressure at x=h/2 and represents the force per unit area with which the plates are pushed apart

$$(p_{h/2} - p_0) = 2k_BTn_\infty[\cosh(ze\psi_{h/2}/k_BT) - 1] = F_R$$

F_R is expressed in terms of the potential at mid point, which is an unknown quantity.

I could integrate this and use the boundary condition that at a in the so, when we consider that the potential is at a very large separation at a very large distance from the surface we know that the potential would be 0 that is size equal to 0 and at that location we say that the osmotic pressure which is proportional to the concentration of ions that you have at that location is p_0. And at h / 2 the potential is psi h / 2 and correspondingly the osmotic pressure p is p at h / 2.

Therefore once I integrate and then substitute these conditions end up with $p_{h/2}$ - p_0 = 2 times k_BT n infinity and you have a cos hyperbolic z e psi h / 2 / k_B T - 1. So, this expression essentially gives the excess pressure that is p h / 2- p 0; p 0 is the osmotic pressure when were psi is 0 and the difference between p at h / 2 - p_0 essentially gives you what is the excess pressure at x = h / 2.

And it represents the force per unit area with which is the plates are pushed apart because of the overlap therefore $p_{h/2}$ - p essentially is F_R that is the force of repulsion and that is the force of repulsion per unit area and that is what given by this. So, therefore what we are trying to do here is that if you look at this expression F_R which is a force of repulsion it is expressed in terms of the potential at the midpoint that is it is expressed in terms of psi at h / 2 that is the potential at the midpoint between the 2 plates and of course this is an unknown quantity what we know is psi 0 however psi at h / 2 is not known.

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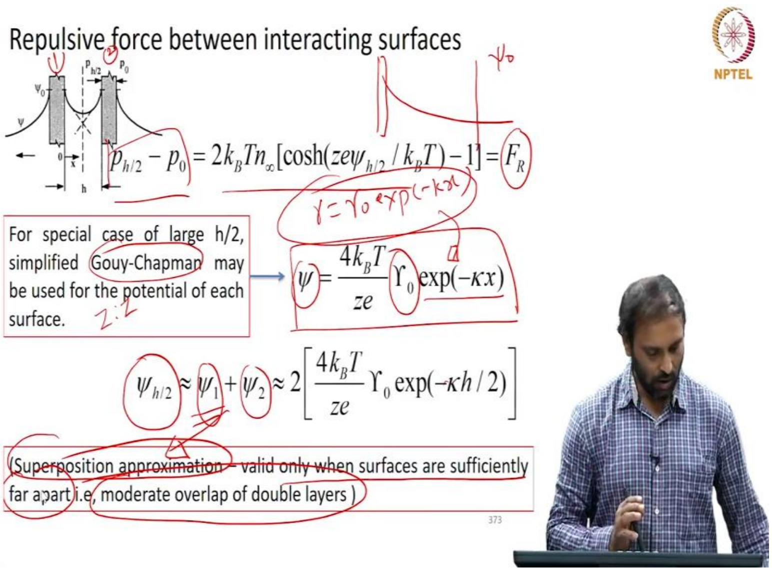

Repulsive force between interacting surfaces

$$p_{h/2} - p_0 = 2k_BTn_\infty[\cosh(ze\psi_{h/2}/k_BT) - 1] = F_R$$

$$\gamma = \gamma_0 \exp(-\kappa x)$$

For special case of large h/2, simplified Gouy-Chapman may be used for the potential of each surface. Z:Z

$$\psi = \frac{4k_BT}{ze}\Upsilon_0 \exp(-\kappa x)$$

$$\psi_{h/2} \approx \psi_1 + \psi_2 \approx 2\left[\frac{4k_BT}{ze}\Upsilon_0 \exp(-\kappa h/2)\right]$$

(Superposition approximation – valid only when surfaces are sufficiently far apart i.e, moderate overlap of double layers)

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And you can do some approximations to find out to evaluate what is psi at h / 2. So, that is the excess pressure F_R. Now, we did think about some special case of Gouy Chapman expression which is applicable for z is to z type of electrolyte for any surface potential. So, now if you look at this expression we derived this for a case where the potential has fallen to a low value that means we are talking about a distance at a distance that is sufficiently.

So, we are talking about the case where we are looking at a distance, a very large distance from the charge surface such that the potential is fallen to a low value. So in such a case we can simplify a gamma = gamma 0 exponent - kappa x as psi = 4k_B T / z e gamma 0 times exponent of - kx. So, what we are going to do so, because we have two plates plate 1 and player 2.

So, therefore there is going to be psi 1 that is contribution that comes from the plate 1 and psi 2 there is a contribution that comes from the psi 2. So, we are going to say that psi at h / 2 is summation of psi 1 + psi 2 therefore psi h /2 becomes 2 times 4k_B T / ze gamma 0 exponent of -kappa h/2. So, this particular approximation is what is called as a superposition approximation which is valid only when the surfaces are sufficiently far apart.

That is what I mentioned that the Gouy Chapman theory was simplified to give this expression which is applicable for any psi 0 the psi 0 could be very high. However which is valid only when the surfaces are sufficiently far apart that is we are considering a case where the overlap of the double layers is moderate.

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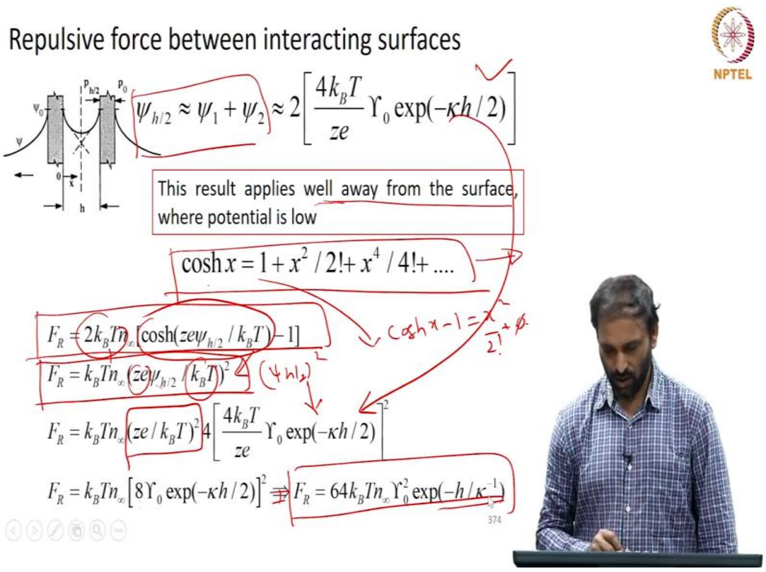

Repulsive force between interacting surfaces

$$\psi_{h/2} \approx \psi_1 + \psi_2 \approx 2\left[\frac{4k_BT}{ze}\Upsilon_0 \exp(-\kappa h/2)\right]$$

This result applies well away from the surface, where potential is low

$$\cosh x = 1 + x^2/2! + x^4/4! + \ldots$$

$$\cosh x - 1 = \frac{x^2}{2!} + \emptyset$$

$$F_R = 2k_BTn_\infty[\cosh(ze\psi_{h/2}/k_BT) - 1]$$

$$F_R = k_BTn_\infty(ze\psi_{h/2}/k_BT)^2 \quad (\psi_{h/2})^2$$

$$F_R = k_BTn_\infty(ze/k_BT)^2 4\left[\frac{4k_BT}{ze}\Upsilon_0 \exp(-\kappa h/2)\right]^2$$

$$F_R = k_BTn_\infty\left[8\Upsilon_0 \exp(-\kappa h/2)\right]^2 \Rightarrow F_R = 64k_BTn_\infty\Upsilon_0^2 \exp(-h/\kappa^{-1})$$

So, therefore psi h/2 we have derived that and so, this result that we have used it applies well; away from the surface where the potential is low. So, and we can of course consider the fact that the cos hyperbolic that you have here. So, if you look at the expression for the excess force I have a cos hyperbolic term and you know I can consider a series expansion of the cos hyperbolic term.

And the excess pressure now I can write this in terms of I can neglect the higher order terms and therefore so, instead of cos hyperbolic what I can do is I have 2 times k_BT this term instead of cos hyperbolic h / 2 / 2 k_BT - 1 what I will do is I can take this it is cos hyperbolic x – 1 = x square / 2 factorial and I am going to neglect the higher order terms therefore so, I can write this as this divided by 2 therefore this, this gets cancelled.

So, I essentially end up with this expression. So, therefore F_R which is the force of repulsion goes as k_BT times n infinity is z e psi at h / 2 / k_BT whole square. So, I can take z e / k_BT outside and I have psi h / 2 square here I can replace for psi h / 2 I can replace this expression now therefore F_R that is the force of repulsion essentially becomes k_BT n infinity. So, I have 8 gamma 0 exponent of – k h/2 whole square that means the force of repulsion essentially becomes F_R = 64 k_B T n infinity gamma 0 square exponent of - h / k inverse.