Interfacial Engineering

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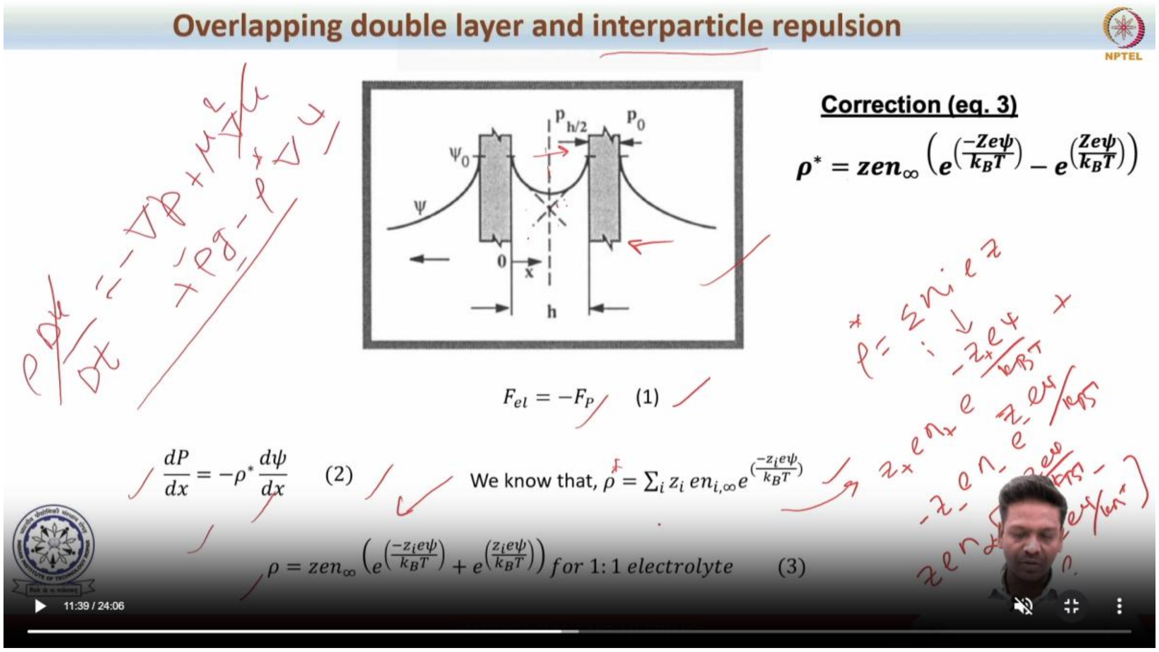
Lecture-35

Overlapping double-layer interaction

Repulsive double layer pressure or positive disjoining pressure due to EDL; variation of disjoining pressure with the distances between 2 planar surfaces in known electrolyte concentrations for varying surface potentials

Welcome back in this video lecture we are going to look at overlapping double layer interaction okay so we are going to consider if 2 charged surface interact with each other okay uh how they will uh you know interact right so let's say uh we have looked at the um uh the electrical double layer models uh say right from Helmholtz model uh Gouy Chapman and Gouy Chapman Stern model okay now let's say if uh we have 2 charged surfaces, right? So when they interact with each other, there can be electrostatic repulsion, right? Due to overlapping of double layer, right? Between the charged surfaces. We're going to look at these interaction in this video. Let's begin.

Time : 1.18mins



Yeah, so in this schematic, we have shown the overlapping double layer, okay? And I have menti1d inter-particle repulsion, but it can be inter-particle. Also, it can be repulsion between 2 objects, any given objects, okay? Right, so..

. So imagine you have the charged surface. Let's say you have 1 charged surface, right? Which is negatively charged. Okay.

And you have another charged surface or the similar charged surface. right? And both will develop the electrical double layer, right? Because of the, okay, diffuse, it can be due to diffuse counter ions or strongly bound counter ions or weakly bound counter ions, but there will be electrical double layer between these 2 objects. What if these 2 objects, when they come when they approach you know very close with each other there will be overlap right between the double layer okay and when they overlap there will be repulsion between the 2 that is because of the you know overlapping double layer okay of each object right right so that is exactly what we are looking at in this lecture okay right So we are going to develop an equation that is going to be, you know, electrostatic repulsion, right? What if, let's say we have electrostatic repulsion, right? How they will be varying as a function of the separation distance, right? That is exactly what we are going to look at now. Right, our starting point is going to be this equation. That is, we are going to say at equilibrium or when they are at a stationary, the force due to electric field and pressure force both will be equal okay but both will be counteracting forces right so 1 will be both will be acting in the opposite direction right so but at equilibrium we can say that the force due to electric field and force due to the pressure are going to be the same so this is our starting point but

This can be written as:

$$dP/dx = -\rho^* \, d\psi/dx \quad ...(1)$$

where:

P = pressure (osmotic pressure)

ψ = electric potential

ρ^* = local charge density

So this can also be expressed by equation 2. Alternatively, you can also obtain this equation using the Navier-Stokes equation for a special case. So, for special case we can also include the external force other external force like electric field although we have ignored magnetic field in this case right for brevity. So, you can consider both the external force that is the gravitational as well as electric field force as we have menti1d here right. And using this Navier-Stokes equation, because we are talking about the case where the equilibrium is attained, or both these plates are kept at a distance where they are stationary, So you can say that there is no fluid flow.

So any term associated with u, velocity can be neglected. And if we say that the body force, that is the gravitational force, compared to the force due to electric field, if it is far lesser than the force due to electric field, we can also ignore the gravitational force for this problem.

Then 1 would get the equation that is the: $-\nabla P = -\rho^* \nabla$....(2)

Again, further we want to simplify this problem by assuming that it is a 1-dimensional problem, which means that the variation of potential in the y direction and z direction is ignored. At the same time variation of pressure in y and z direction are not considered.

So by simplifying in this way, you can get the equation that is given in the equation number 2. That is this 1,

$$dP/dx = -\rho^* \, d\psi/dx \quad ...(\text{reaffirming Eq. 1})$$

So this is going to be our governing equation for this problem. So what is this pressure? So the pressure here that we menti1d is the osmotic pressure. So when they overlap with each other, so when this double layer overlap, what will happen is they actually, you know, prevent the flow of ions into this, you know, domain, right? Because when they overlap with each other, It actually, you know, prevent the flow of any ions within this domain, which means that they are making this volume, this space, right, inaccessible to ions, counter ions, such that they will not be able to freely move around.

For example, any counter ions here cannot move, okay, within this domain. a domain so that will cause some sort of imbalance right osmotic imbalance okay so what they will do they will try to access more area by compressing this you know the object right towards each other in that way the ions will get more accessible volume okay so this is called osmotic pressure right due to imbalance right so this pressure is acting in the this pressure creates a compressive force, right? Because they will be, the plates will be moved closer to each other. On the other hand, because of the double layer, electrical double layer, there will be repulsion between the 2. So this repulsive force will try to keep this plate away. So the force will also be experienced in the opposite direction.

1 hand, you have pressure force due to osmotic imbalance that will try to compress the plate. On the other hand, there will be electrostatic repulsion, which will try to keep the plates away from each other. So these 2 competing force, competitive forces are acting. So we are considering this scenario, right? Right. So if this is going to be our governing equation, how we can solve this equation further, okay? our approach is to get the electrostatic repulsive force right right so we know what is rho star rho star is defined in this way that is we know that rho star is nothing but ,

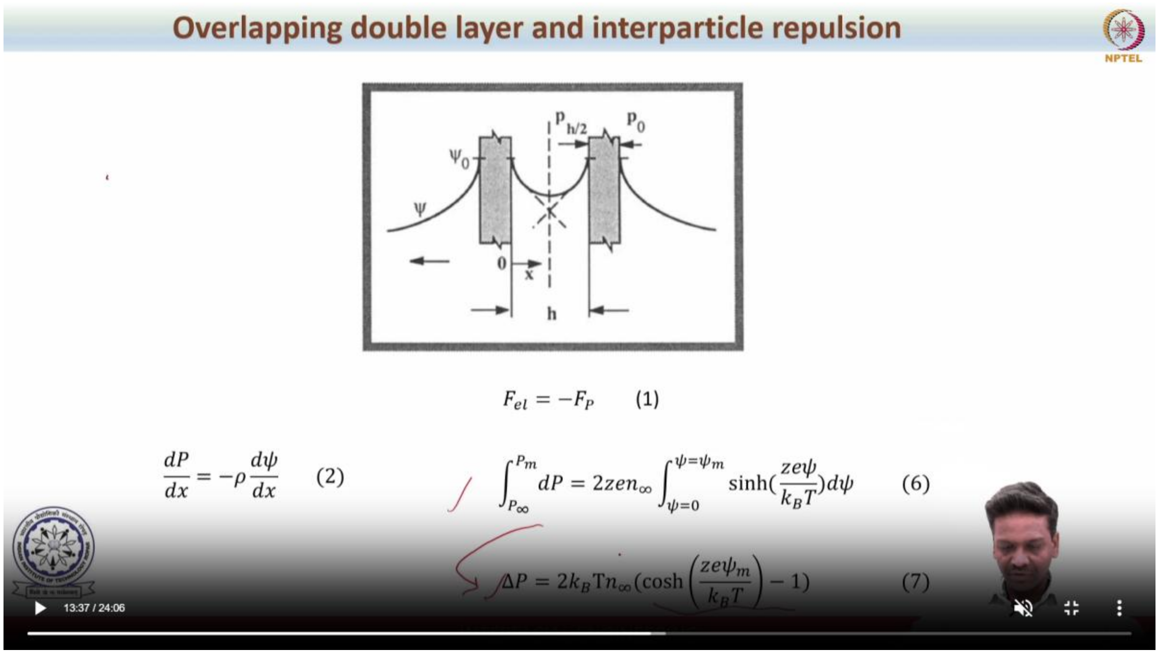
$$\rho^* = \Sigma n_i z_i e \quad ...(3)$$

We know ni that we already defined in the previous lecture.

$$n_i = n_i^o \exp(-z_i e \psi / k\_B T) \quad ...(4)$$

This is coming from the Boltzmann distribution function. So when you incorporate this into a row star, you get this equation.

Time : 11.56mins



Substituting into Eq. 3 for 1:1 electrolyte (e.g., NaCl):
$\rho^* = z e n_\infty [\exp(-z e \psi / k_B T) - \exp(z e \psi / k_B T)]$

This is already known to us, right? Let's say if I have to expand this equation for electrolyte, let's say 1:1.
So how do we expand this? That is exactly what we will look at.

So, if I expand this equation, I can express it as:
$Z^+ = (e^{(-Z * e * \Psi / k_B T)}) + Z^- = (e^{(Z * e * \Psi / k_B T)})$

Let us consider NaCl as an example. For the cation (Na^+), valence Z = +1, and for the anion (Cl^-), valence Z = -1. If we assume equal quantities:
$Z^+ = Z^- = Z$, and $N^+ = N^- = N_\infty$.

Substituting common terms:
$Z * e * N_\infty * (e^{(-Z * e * \Psi / k_B T)} - e^{(Z * e * \Psi / k_B T)})$

This simplifies for a 1:1 electrolyte, yielding the generalized equation (3).

Now, substitute this equation into ρ^*, noting that the term is already negative.
This yields:
$dP^2 = ...$

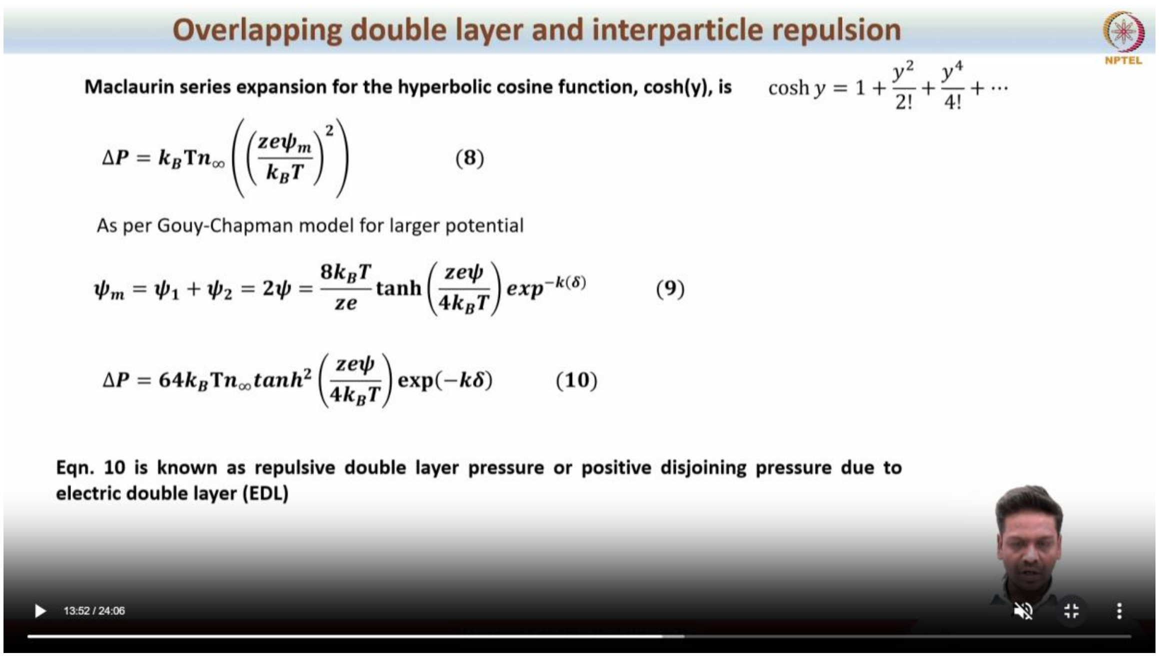
To integrate, use limits from infinity (pressure at infinity) to the midpoint (pressure P_{mid}):

∫ [limits: 0 to Ψ_m] dΨ = ...

After integration, the result transforms equation (6) into equation (7). For sinh(Ψ): Integration of sinh(Ψ) yields cosh(Ψ). Applying limits:
cosh(0) = 1.

Thus, the final result:
ΔP = ... (with z, e, k_B, and T terms simplified).

Time : 13.52mins



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Substituting common terms:
Z * e * N_∞ * (e^(-Z * e * Ψ / k_B T) - e^(Z * e * Ψ / k_B T))

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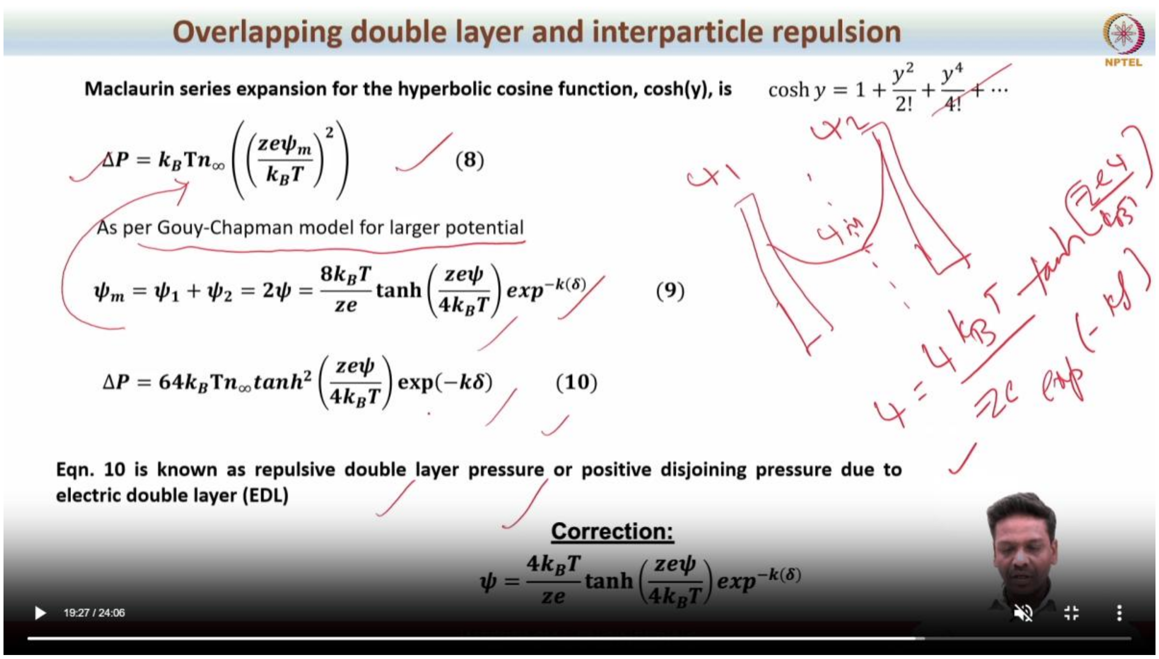
Thus, the final result:
ΔP = ... (with z, e, k_B, and T terms simplified).
Time :14.25mins



And now what we are going to do is we have this charged plate, right? Okay.

So 1 advantage of this, so you have 1, this is Ψ 1, let's say, right? And this is Ψ 2, okay? And when they overlap with each other, this is called midpoint, okay? This is called midpoint. Now, we know from the principle of superposition, at this point, okay, what is the potential at this point? We know Ψ 1, you know, the charge of the plate 1 is Ψ 1, and the surface charge of the plate is... sorry surface potential of plate 1 is Ψ 1 and surface potential of plate 2 is Ψ 2 but what is the potential at the midpoint right this comes from the super principle of superposition you know theorem that is so the ,

$\psi_m = \psi_1 + \psi_2$

so let's say you have this plate when the the electric you know force duty electric field acts on the other plate okay via this electrical double layer is nothing but the sum total of this potential acting on the plate one and potential acting on the plate two will be taken into consideration.

If $\psi_1 = \psi_2 = \psi$, then $\psi_m = \psi_1 + \psi_2 = 2\psi$

For higher potentials, Gouy-Chapman gives:

$\psi = (4\ kBT / z\ e) \tanh^{-1}(\psi_0 / 4\ kBT) \exp(-\kappa x)$

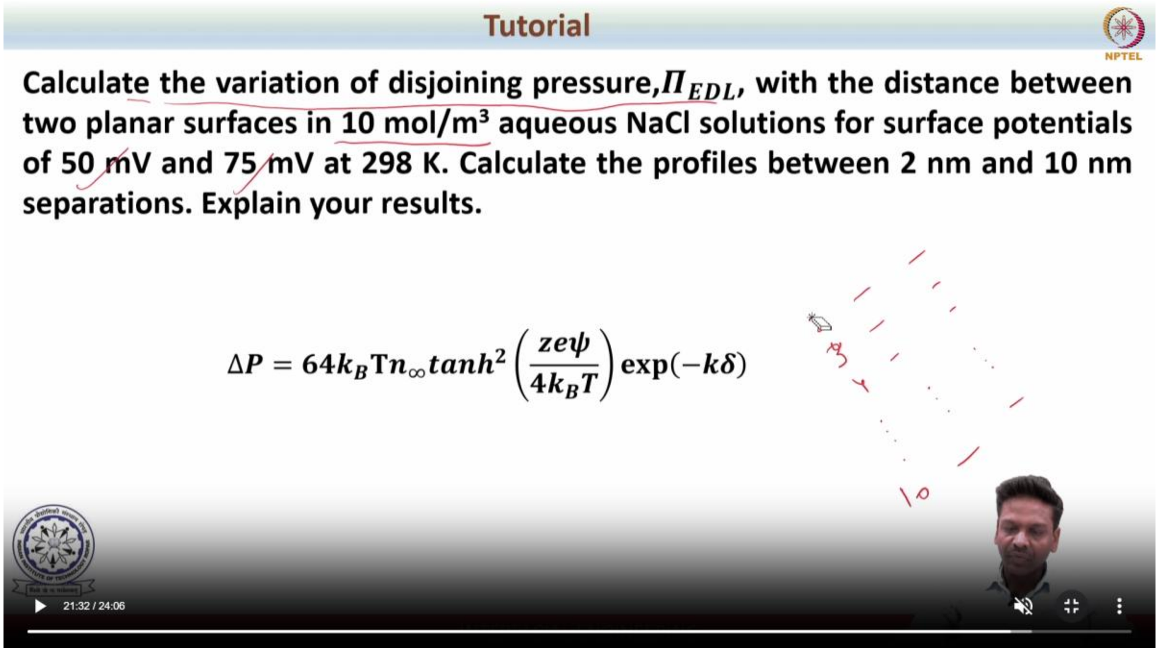
So, $\psi_m = (8\ kBT / z\ e) \tanh(z\ e\ \psi / 4\ kBT) \exp(-\kappa\delta)$ ...(9)

Substitute ψ_m into ΔP equation to get:

$\pi\_EDL = 64\ kBT\ N\infty \tanh^2(z\ e\ \psi / 4\ kBT) \exp(-2\kappa\delta)$ ...(10)

All right. So this is what we have. Okay. So this is nothing but double-layer pressure, repulsive double-layer pressure. or positive disjoining pressure due to the electrical double layer.

Time : 19.33mins



Here in this slide, we will look at a tutorial.

We aim to solve and obtain the profile of the disjoining pressure (π_EDL) between 2 nanometers and 10 nanometers of separation distance. This disjoining pressure represents the electrical double layer (EDL).

The scenario involves two planar surfaces in an aqueous NaCl solution. The concentration and ionic strength are provided. We analyze two cases:
1. Planar surfaces carrying a potential of 50 mV.
2. Planar surfaces carrying a potential of 75 mV.

Temperature remains constant in both cases.

Steps:
1. Develop a profile for separation distances (x-axis) ranging from 2 nm to 10 nm.
2. Plot π_EDL for both cases.

Equation and Parameters:
- π_EDL is a function of δ (separation distance).
- K (Debye length): Provided as the inverse of κ.
- Z (valence): Z = 1 (for monovalent ions like Na^+, Cl^-).
- Ψ (surface potential):
  - Case 1: 50 mV = 0.05 V.

  - Case 2: 75 mV = 0.075 V.
- N_∞ (bulk concentration): Derived from molarity multiplied by Avogadro's number.
  - Since the problem is given in moles per meter^3, no conversion to liters is needed.
- k_B T (thermal energy): Known constants for the Boltzmann constant and temperature.

Procedure:
- Calculate π_EDL using the provided values.
- For bulk concentration (N_∞), multiply molarity by Avogadro's number to get ions per cubic meter.
- Substitute the known values (Ψ = 0.05 for case 1, Ψ = 0.075 for case 2).
- Vary separation distances (δ) from 2 to 10 nm.

Plot:
- x-axis: Separation distance (nm).
- y-axis: Disjoining pressure (π_EDL).
- Blue line: Case 1 (50 mV).
- Orange line: Case 2 (75 mV).

This exercise can be implemented using MATLAB or Excel. By plotting, you can understand how the disjoining pressure varies with separation distance when the EDLs overlap.

We will continue in the next lecture. Thank you.