

Modeling Transport Phenomena of Microparticles
Prof. Somnath Bhattacharyya
Department of Mathematics
Indian Institute of Technology - Kharagpur

Lecture - 25
Electric Double Layer

Now we have derived the relation between the surface charge density and potential of through that we can establish a relation between the Zeta potential at the surface charge density.

(Refer Slide Time: 00:38)

Relation between σ_s and ψ -potential on the interface.

Poisson-Boltzmann equation for electric potential

$$\epsilon \epsilon_0 \frac{d^2 \psi}{dy^2} = 2 F C_0 \sinh\left(\frac{F\psi}{RT}\right), \quad \text{binary sym. Electrolyte } z_1 = -z_2 = 1$$

Debye-Hückel approximation, $\psi < RT/F$, we get

$$\frac{d^2 \psi}{dy^2} = \frac{2 C_0 F^2}{\epsilon \epsilon_0 RT} \psi = \frac{\psi}{\lambda^2}, \quad \lambda = \sqrt{\frac{\epsilon \epsilon_0 RT}{2 C_0 F^2}} = \frac{1}{\kappa}$$

$$\psi = A e^{\psi/\lambda} + B e^{-\psi/\lambda}$$

Let $-\frac{d\psi}{dy} \Big|_{\text{wall}} = \sigma_s / \epsilon \epsilon_0$ on $y=0$

and $\psi \rightarrow 0$ as $y \rightarrow \infty$.

$$\psi = \frac{\lambda \sigma_s}{\epsilon \epsilon_0} e^{-y/\lambda}$$

So a relation between Sigma s and Zeta potential on the interface, now the Poisson Boltzmann equation which we have already derived that means what we have to give a little bit of revising the previous assumption that in the Poisson Boltzmann equation for the electric field what I did is we have assumed that the ions are distorted by the Boltzmann distribution, that means the equilibrium condition, that means there is no normal flux on the charged across the charged surface.

So you have a charged surface say x so there is no normal flux of the ions across this charged surface, so why and also the fluid convection is assumed to be zero, so is that what we have already derived is the Poisson Boltzmann equation for electric field, for electric potential is given by $d^2 \psi / dx^2$ okay dy^2 in this case because here we have taken the y is the normal direction this is equal to $2 F C_0 \sinh(F \psi / RT)$.

So here we are backwards taken this binary electrolyte symmetrical, electrolyte are monovalent also so that means $Z_1 = -Z_2 = 1$ but of course we can take as this also valid if you have Z_1 equal to, it can be also $Z_2 = Z$ so that's kind of $Z Z$ electrolyte situation so here there will be a Z will appear in this situation for the sake of simplicity, we have taken the monovalent situation.

So if I apply the Debye-Huckel approximation, so that means what we are assumed is that the Φ is less than RT by F so with the Debye-Huckel approximation will get the $d^2 \Phi / dy^2 = 2 C_0 F^2 / RT \Phi$, so there something ϵ will be there ρ_e because this is ϵ there is a ϵ will be divided, so this is the net charge density, if I divide one so now if I define the which is already introduce the Debye layer thickness λ^2 .

Where λ^2 as you remember λ equal to which we have define already $\epsilon RT / 2 C_0 F^2$ square root over, this is also the square is also referred as $1/\kappa$ which is the inverse for the Debye length, so it that way one can write the solution is equal to $Ae^{x/\lambda} + Be^{-x/\lambda}$, now if we have a situation that Φ is tending zero.

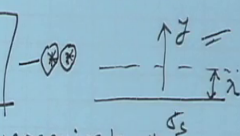
Let $d\Phi/dy$ on $y = 0$, is given by on the wall is given to be σ_s / ϵ and on sorry this is y on $y = 0$ and Φ is the equilibrium potential is tending to 0, y is infinity, in that case so the solution, so if we do the A is straight away 0 and b comes to be if I take the derivative and also the solution become $\Phi = \lambda \sigma_s / \epsilon e^{-y/\lambda}$.

(Refer Slide Time: 07:15)

© CET
I.I.T. KGP

$$\phi = \frac{\lambda \sigma_s}{\epsilon \epsilon_0} e^{-y/\lambda} \quad (*)$$

If $\phi = \zeta$ on $y=0$

$$\zeta = \frac{\lambda \sigma_s}{\epsilon \epsilon_0}$$


The Debye length λ is the screening length of the surface charge σ_s .

If $\lambda \ll 1$, thin Debye length, at a fixed σ_s the surface potential is low. This relation is for flat surface under the Debye-Huckel approximation for binary symmetric electrolyte.

So Phi comes to be Lambda Sigma s, okay lets go the next page, So Phi becomes Lambda Sigma s by Epsilon e e to power - y by Lambda, where Sigma s is the surface charge density, now if Phi = Zeta on y = 0, so what I can write is a relation you can establish that Zeta is surface potential is Lambda Sigma s by Epsilon e, okay.

So this shows that this is the relation what we can talk about the between the surface charge density and the Zeta potential okay, now here on interesting thing is that the this equation this relation if I talk about so Lambda is the Debye layer, Debye length thickness, so if you have a surface which has got a charge density Sigma s, so you have a layer say this is the length of this layer estimated Lambda which is we call the EDL thickness.

So beyond which the effect of the Sigma is tending to zero, so that is Phi is becoming very negligible when y become Lambda, so the Debye length write that Debye length Lambda is the screening length of the surface charge Sigma s, of course here this the equation star is based on the assumption that we are taking a monovalent.

Monovalent is not going to make any difference but binary symmetric electrolyte and also what we have considered is that the Debye-Huckel approximation that means surface charge or surface potential is quite low. Now one deduction from this relation if we call relation double star, so from the double star is the relation between Zeta and Lambda what I can see that If Lambda is low, Lambda less than one or that is the case Lambda is quite low.

Lambda for thin Debye length this Zeta is low at a fixed Sigma s, the surface potential is low so that means it is screened. Now one point will be remembered that this relation is for a flat surface, we have considered a flat surface because we have taken the Poisson Boltzmann equation in only one direction that uses of the direction y so this is valid for a flat surface.

The Debye-Huckel approximation with for binary symmetric electrolyte, so obviously what we can see conclude from here that there is a definite length beyond which these Sigma s is not visible, so if I go far away from the wall, far away from the distance Lambda, so Sigma s has zero effect beyond this and also you have the Zeta potential or the surface potential as Sigma s is related it by this way.

So Lambda is low, 6 Sigma s is your Zeta potential is low, so this is the way one can characterized Debye layer. Now I will show the slides where the Gouy-Chapman model is discussed the slides over here, so no one can assume the Debye layer forming on the surface, charge surface over which there is a rapid change in the ion distribution.

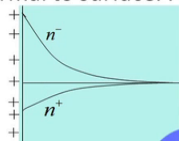
(Refer Slide Time: 13:13)

Gouy-Chapman Model


Gouy and Chapman were the first to consider the thermal motion of ions near a charged surface. They considered a diffuse double layer forms on a charged surface embedded in a dielectric liquid medium. In the diffuse double layer, counterions (i.e. ions of opposite charge to the surface) are attracted to the surface and co-ions repelled by it.

The distribution of ions are governed by the Boltzmann distribution i.e., flux of ions is zero along the direction normal to surface. For binary electrolyte,

$$c_i = c_i^0 \exp\left(-\frac{z_i F \phi}{RT}\right)$$



The electric potential is governed by the Poisson-Boltzmann equation

$$\nabla^2 \phi = \frac{2F c_0}{\epsilon_e} \sinh\left(\frac{F \phi}{RT}\right)$$


And so this is the one which a proposed by the Gouy and Chapman, considered that the thin layer over which the electric potential within this layer is governed by this Poisson-Boltzmann equation and the ion distributions are governed by the equilibrium Boltzmann distribution, so that means in the assumption is that the no penetration or no flux of ions on the vertical direction across the Debye layer is assumed to be zero.

And so the diffused over layer or is also referred as the electric double layer which forms on a charged surface embedded and dielectric medium, in induced double, the counter ions so here we referred the counter ions, the answer of opposite charge of the surface are attracted to the surface and co-ions repelled by the surface itself by it. Distribution of ions are governed by the Boltzmann distribution of that is flux of ion is zero

And the along at the direction normal to the surface for binary electrolyte, so this is the way one can describe the Gouy-Chapman model okay. So now we are in a position to formulate the Electroosmotic flow over a charged surface so in the beginning we have already described that when you have a charged surface.

(Refer Slide Time: 15:08)

Electroosmotic flow in a slit micro-channels

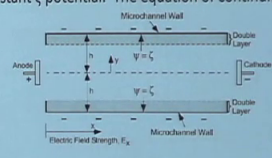
We consider the flow in a straight gap formed by two infinitely long parallel plates separated by a distance $2h$. Such a flow configuration is referred as the slit channel. We consider a parallel flow under an external electric field applied parallel to x-axis, the axis of the channel. The driving mechanism is the electric field, so the external pressure gradient can be neglected.

The surfaces of the channel are at constant ζ -potential. The equation of continuity is $\frac{\partial u}{\partial x} = 0$

Thus, $u = u(y)$. The momentum equation gives $\mu \frac{d^2 u}{dy^2} = \rho_e \frac{\partial \phi}{\partial x}$

Where μ is the viscosity of the fluid, ρ_e is the charge density and ϕ is the electric potential.

The electric potential at any point (x, y) arise due to the superposition of the applied electric field and the induced electric field produced by the surface charges i.e., $\phi = \phi_0 - E_0 x$. The equation for electric field is $\nabla^2 \phi = -\rho_e / \epsilon_e$ or, $\frac{d^2 \phi}{dy^2} = -\frac{\rho_e}{\epsilon_e}$



So when you have a charged surface over which embedded in electrolyte, say if we consider this situation so and electrolyte is filling two charged surface which are infinitely long let us assume and this configuration is referred as the slit micro channel. So slit micro channel formation, so that means you have two parallel plates of constant surface charge density or constant surface potential $\Phi = \zeta$.

So this is $\Phi = \zeta$ and this is $\Phi =$ say some values, so maybe both are charged for both are same charge or maybe different charge and a dielectric medium is filling the interior, so this also called the slit micro channel. Now we considered a liquid flow within that, now we have assumed a parallel flow so that is flow is only along the X direction, along which the electric field is applied say electric field is E_0 is applied.

And we call this is as the x axis and perpendicular to that we referred as a y axis show normal to the direction is the y-axis know the situation we are considering is a fully developed situation, so that when the gradient like $\text{Del Del } x$ that is alongside the radiation this direction can be treated to be negligible, which is the condition for the fully developed situation. Now you see the continuity equation of continuity equation we find that $\text{Del } u \text{ Del } x = 0$.

So this implies that you have only u is a function of y okay, so that means the momentum equation if I now drop the pressure term is dropped because here there is no external pressure gradient so dp/dx , so it should have been a $\text{Del } x$ which you have taken as zero because no external pressure gradient is imposed, so flow is only driving mechanism is the electric field so flow is driven only by the electric field.

And we are considering this is x and this is y direction, so we have the momentum equation, x momentum equation or Moment equation for along the X direction is governed by this equation, this is basically viscous diffusion is balanced why the electric body force. So this represents a valance of the electric body force stop with the viscosity diffusion ρe is the charge density and Φ the electric potential.

Now electric potential are governed by two mechanism one is we have considered an applied electric field is zero and other because of this electric field ions there will be a moment, at this moment of the ions will induce a electric field with that is caused by the surface charge of the wall, surface Zeta potential so that means there two component of electric field.

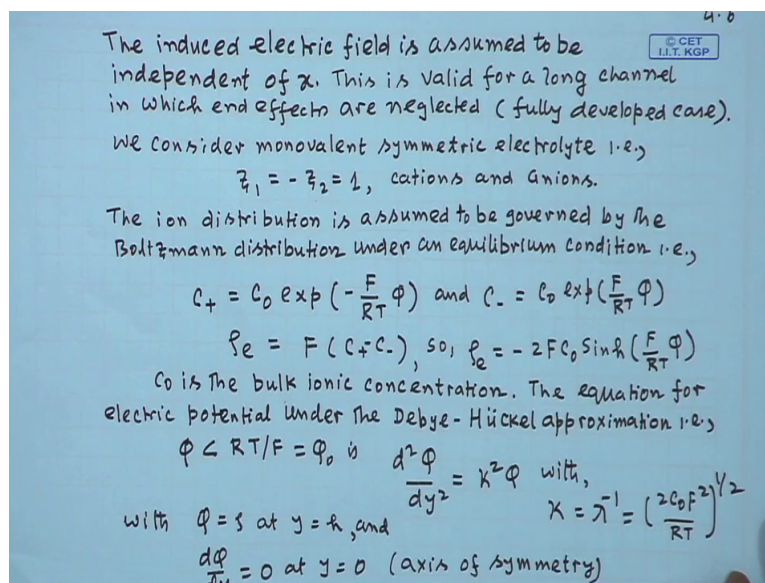
One because of the external electric field is E_0 which we have taken as along the X direction and other is induced electric field induced by the surface charge, so we assume is superposition of these two electric field, so that will it take for $\Phi = \Phi - E_0 x$, the electric potential due to the electric field along the X direction is E_0 . So we get the net electric potential capital Φ we are defining.

This $\Phi = \Phi - E_0 x$, so this part that is the electric field which is induced by the wall charges or now to be solved no electric field at any point I satisfy the Boltzmann that is called it is not Boltzmann the equation, this is the Poisson equation, we are not so far Boltzmann equation, this is not the Poisson-Boltzmann equation, this is simply Poisson equations.

Poisson equation it satisfies the which comes out to be $d^2 \Phi dy^2 =$ this way here, we have taken a fully developed EOF, fully developed situation so that means all the gradients with respect to X are the variation of the variables x, u Phi are neglected along the X direction. So this Laplace Equation then $\Delta^2 \Phi dy^2$ can we go down to $d^2 \Phi dy^2 = - \rho_e / \epsilon$

Now the induced electric field we have assumed to be if I say the induced electric field is assumed to be independent of x and this is valid I can write this way for a fully developed case.

(Refer Slide Time: 21:20)



Now considered the valid for a fully developed, is now considered the monovalent symmetric electrolyte that is a situation $Z_1 = - Z_2 = 1$, so that means the electrolyte are containing cations and anions, so the ion distribution assumed to be governed by the Boltzmann distribution under an equilibrium condition.

Again ion distributions are considered in such a way that the no normal flux and distribution of ions are independent of the fluid convection, so we can write the distribution of ions as C^+ that is a positive ions and C^- ions by this way, so that means a certain point if I get the electric potential Phi, so through that Phi one can obtain the ion distribution C^+ and C^- given by this way.

So once I know the distribution of ions at any point show the charge density ρ_e is Faraday constant into the net ion concentration, so this molar flux, molar concentration of ions, so

that means this ρ_e becomes the 2 $FC_0 \sin$ hyperbolic F by $RT \Phi$ where C_0 is the bulk ionic concentration. Now bulk ionic concentration is governed by the C_0 the equation for electric potential under the Debye-Huckel approximation can be written as I have already done $d^2 \Phi / dy^2 = k^2 \Phi$, with k is λ^{-1} , $2C_0 F$ square by RT by length.

So we impose the condition, we consider the origin and that is the x -axis is along the centre line of the channel and we considered a axis of symmetry so that means this axis of symmetry is valid provided we have both the walls of the same Zeta potential. So this is the condition $d\Phi / dy = 0$, at $y = 0$ that is along the axis of symmetry. Symmetry assumption is valid about the walls of the same Zeta potential.

With that if I can solve this equation so what I get is:

(Refer Slide Time: 24:05)

$\Phi = A e^{ky} + B e^{-ky}$
 ~~$A - B = 0$ as $y = 0, \Phi = \zeta$~~
 $A e^{kh} - B e^{-kh} = 0$ as $\frac{d\Phi}{dy} = 0$ at $y = 0$
 $A = B$
 again, $\Phi = \zeta$ for $y = h$, so,
 $\zeta = A e^{kh} + B e^{-kh}$
 $A = B = \frac{\zeta}{2 \cosh(kh)}$
 so, $\Phi = \frac{\zeta \cosh(ky)}{\cosh(kh)}$, electric potential at any point in the slit channel.

$\Phi = A e^{\text{to power } Kappa y} + B e^{\text{to power } - Kappa y}$, we have done already and so $A - B = 0$, as no zero this is equal to Zeta, as $y = 0$, $\Phi = \text{Zeta}$, and what we have is $A e^{\text{power } Kappa h} - B e^{\text{power } - Kappa h} = 0$, this is zero but this is a I have written wrongly because so this is a let us write better way this is $d\Phi / dy = 0$ and $y = 0$ under this conditions, so we get this so that means this implies that $A = B$.

Again what you have is $\Phi = \text{Zeta}$ for $y = h$, so what we have so $\text{Zeta} = A e^{\text{power } Kappa h} + B e^{\text{power } - Kappa h}$, so this gives $A = B = \text{Zeta} / 2 \text{Cos hyperbolic } Kappa h$, so now if I substitute so this gives, so Φ which is the equation, so this becomes $\text{Zeta} \text{ Cos hyperbolic } Kappa y / \text{Cos hyperbolic } Kappa h$ so this is the electric potential.

Electric potential at any point in the slit channel, this is a potential distribution at any point of the slit channel, so now we need to find out the velocity of which is defined as the Electroosmotic velocity or EOF velocity from the valance of the charge and electric body force at the frictional track, so that will continue in the next lecture.