

Modeling Transport Phenomena of Microparticles
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Lecture - 28
Non-Linear EOF, Overlapping Debye Layer

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Electrical conductivity

$$\bar{\sigma} = \frac{F^2}{RT} \sum z_i^2 D_i c_i^0$$

if, $D_1 = D_2 = D$ in a binary symmetric electrolyte with $z_1 = -z_2 = 1$.

$$\bar{\sigma} = \frac{2F^2}{RT} D c_0$$

We define $\bar{\sigma} = \frac{F^2}{RT} \sum z_i^2 \frac{1}{2h} \int_{-h}^h c_i dy$ as the average conductivity. as $u = \frac{E_0 \epsilon_0 (\phi - \zeta)}{\mu}$

$$I = 2h \bar{\sigma} - \frac{E_0 \epsilon_0^2}{\mu} \int_{-h}^h (\phi - \zeta) \frac{d^2 \phi}{dy^2} dy \quad \left| \begin{array}{l} \rho_e = F \sum z_i c_i \\ = -\epsilon_e \frac{d^2 \phi}{dy^2} \end{array} \right.$$

Integrating by parts

$$\int_{-h}^h (\phi - \zeta) \frac{d^2 \phi}{dy^2} dy = -(\phi - \zeta) \frac{d\phi}{dy} \Big|_{-h}^h - \int_{-h}^h 1 \cdot \left(\frac{d\phi}{dy} \right)^2 dy$$

$$= - \int_{-h}^h \left(\frac{d\phi}{dy} \right)^2 dy$$

Okay, so we have this I so if this now integrate this one this is nothing to integrate of course if I integrate by parts so this terms integrating by parts we get - h to h Phi - zeta d2Phi dy2 dy equal to case as okay let me write the full way d Phi dy and - h to h, - h to h 1 into d Phi dy whole square dy, so this is zero because Phi is 0 in both + h and in - h so this is nothing but this is zero so what I get is - h to h d Phi dy whole square dy now d Phi dy whole square Phi known in Cos hyperbolic terms.

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$$\begin{aligned}
&= -\frac{\zeta^2 \kappa^2}{\cosh^2(\kappa h)} \int_{-h}^h \sinh^2(\kappa y) dy \\
&= -\frac{\zeta^2 \kappa^2}{\cosh^2(\kappa h)} \left[\frac{\sinh(2\kappa h)}{2\kappa} - h \right] \\
\text{So, } I &= E_0 \left[2h\bar{\nu} + \frac{\zeta^2}{\mu h} \cdot \left\{ \frac{\sinh(2/\epsilon)}{2/\epsilon} - 1 \right\} \right] \\
\text{Where, } \epsilon &= \lambda/h = \frac{1}{\kappa h}, \text{ if } \lambda \ll h \text{ implies } \epsilon \rightarrow 0 \\
I &= 2h E_0 \bar{\nu} \quad \text{When EDL is thin } \bar{\nu} = \bar{\nu} \\
I &= 2h E_0 \frac{F^2}{RT} D_0, \text{ for an electrically neutral bulk fluid.} \\
&\quad D_1 = D_2 = D, \quad \sum z_i n_i = 0 \\
I_0 &= 2 C_0 D F/h, \text{ Note } \phi_0 = RT/F \\
\text{And } (\phi_0/h) &\text{ is the scale for electric field. } \bar{\nu} = \frac{1}{I_0} \cdot E_0 (q_0/h) = \frac{\bar{\nu}}{2h}.
\end{aligned}$$

So, this becomes an integration if I substitute the Φ κ y \cosh hyperbolic κh , so this becomes $-h$ to h \sinh hyperbolic square κy dy this not κ defined as κ . Because κ is a in words of the EDL thickness. Okay, so if I now simplify this one so this is going $-\zeta^2 \kappa^2$ square by \cosh hyperbolic κh , if you do the little simplification this will come as \sinh hyperbolic $2 \kappa h$ by 2κ $- h$.

So I becomes is E_0 into $2 h \bar{\nu}$ average conductivity plus. There is a $+$ so this $+$ ζ^2 square by μh into write this is \sinh hyperbolic 2 by ϵ , if I now introduce ϵ which is nothing but 1 by κh by 2 by $\epsilon - 1$ by $\epsilon^2 \cosh$ hyperbolic ϵ . Okay, where ϵ just introduced a $\epsilon = \lambda/h$ so that means in other words this is one by κh . So if I have the λ to be very thin.

So, ϵ tends to zero. Okay, so that is λ tends to λ many, many times less than h implies ϵ tends to zero. So in this situation what we will have? From here that this term will reduce to one and what we get is I , nothing but if instead of that is let us write if so in that case what we get is to I is $2 h E_0 \bar{\nu}$ and also the $\bar{\nu}$ what we have define before so is also if I have the when EDL is thin.

So this $\bar{\nu}$ is also something like ν already have defined that so, this I becomes $2 h E_0 F$ square by $RT D$ into $2 C_0$ because there are any concentration can $2 C_0$ as $2 C_0 \sum z_i$ so this

is under for an electrically neutral situation case or that this the electrically neutral bulk fluid or on the code fluid. So that is normally the case if you have Λ is many, many times less than each so this is the way the slip model free slip model which we have introduced previously calculate the average current density.

So average current density per unit with an also with height if I now divide by $2h$ so that we can say constant value. Now if I define if here there are several simplification we have taken that the diffusivity constants are taken to be same for both as so and also we have taken into consideration that $z_i n_i = 0$. Because of the electro-neutrality know if I considered a characteristic current density, I_0 if I defined by this manner $2C_0 D F$ by h is characteristic current density.

So now here we note to that Φ_0 is RT by F . The thermal potential at that is become the scale forth is E_0 the electric field so then I_0 is the characteristic current density and Φ_0 by h is the scale for electro-neutral field. So if I introduce this so what we find this I is scaled I that become 1 by I_0 into E_0 by Φ_0 by h . So this is becoming the I by $2h$.

So we get it situation for under the electro-neutral condition here of course we have assumed that the molecular diffusion coefficients are identical for both the ions, so this is about the situation, where we have considered the current density and electric field and velocity and all where the answer taken to be symmetrical and governed by the equilibrium situation and also and another important thing. We have assumed is that they were considered the binary electrolyte.

So that symmetric binary electrolyte know if it is not a symmetric binary electrolyte so they are asymmetric is.

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Asymmetric electrolyte

- So far we have restricted our attention on electrokinetics of binary symmetric z-z electrolyte. However, electrolyte can have asymmetric ions. In that case the ionic strength of the electrolyte

$$I = \frac{1}{2} \sum_{i=1}^n z_i^2 c_i$$

is not same as the total molar concentration c_0 . We define a parameter $\beta = c_0/I$.

So here we are restricted our attention on electrokinetics of binary symmetric Z-Z electrolyte. However electrolyte can have asymmetric ions. In that case the ionic strength or not exactly equal to the C_0 . So this becomes a complicated situation and we cannot have a Poisson Boltzmann model. Poisson Boltzmann equation will not appear.

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Nernst-Planck Model for EOF in a slit channel.

Parallel flow (i.e., $u = u(y)$, $v = 0$)

Momentum equation

$$\mu \frac{d^2 u}{dy^2} = \rho_e \frac{\partial \phi}{\partial x}$$

as, $\phi = -E_0 x + \phi(y)$.

$$\mu \frac{d^2 u}{dy^2} = -E_0 F \sum_i z_i c_i \quad \text{--- (a)}$$

The transport equation of the i^{th} ionic species is

$$\frac{\partial}{\partial y} \left(\frac{\partial c_i}{\partial y} + z_i \frac{F}{RT} c_i \frac{\partial \phi}{\partial y} \right) = 0 \quad \text{--- (b), } i = 1, 2, \dots$$

So our next topic is to construct the Nernst-Planck model for EOF in a slit channel. We still considering the simple geometry, simple configuration. So that means you have the situation like this way you have an electric field and this is along x-axis, along the direction of the axis we have considered and both the walls are taken to be same Zeta potential. Of course, we can switch

to some other case also that means we can have a different Zeta potential that is not a that change switch over is not a very big amount of trouble will cause so we are considering a parallel flow.

Of course that is U is a function of Y and V is zero. So what you have here the momentum equation is $\mu \frac{d^2u}{dy^2} = \rho_e \text{Del } \Phi \text{ Del } x$ so that means is a valance of the viscous diffusion and electric body force. Now Φ as we have already stated this is a $E_0 X + \Phi(y)$ which is the as this because y of considering a fully developed situation so and also we have taken a symmetric electrolyte. Not yet, symmetric electrolyte.

So this is the induced potential so is that what you can write is $\mu \frac{d^2u}{dy^2} = -E_0 F \sum z_i c_i$. The $\rho_e \text{Del } \Phi \text{ Del } x$ is this $-E_0$. Now F is simplicity, no simplicity will come later on. So the transport equation for the i th ionic species is can be written because again fully developed. So all the gradient with respect to X is zero, so $\text{Del } c_i \text{ Del } y + z_i F \text{Del } \Phi \text{ Del } y = 0$.

So this is one equation say a, this equation b and also the this is I equal to whatever situation you are considering because in the Boltzmann distribution we are not restricting like Boltzmann distribution. So also this is Poisson Boltzmann equation. We must have the symmetry electrolyte consideration.

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Parallel flow (i.e., $u = u(y), v = 0$)
 Momentum equation

$$\mu \frac{d^2u}{dy^2} = \rho_e \frac{\partial \phi}{\partial x}$$
 as, $\phi = -E_0 x + \phi(y)$

$$\mu \frac{d^2u}{dy^2} = -E_0 F \sum_i z_i c_i \quad \text{---(a)}$$
 The transport equation of the i th ionic species is

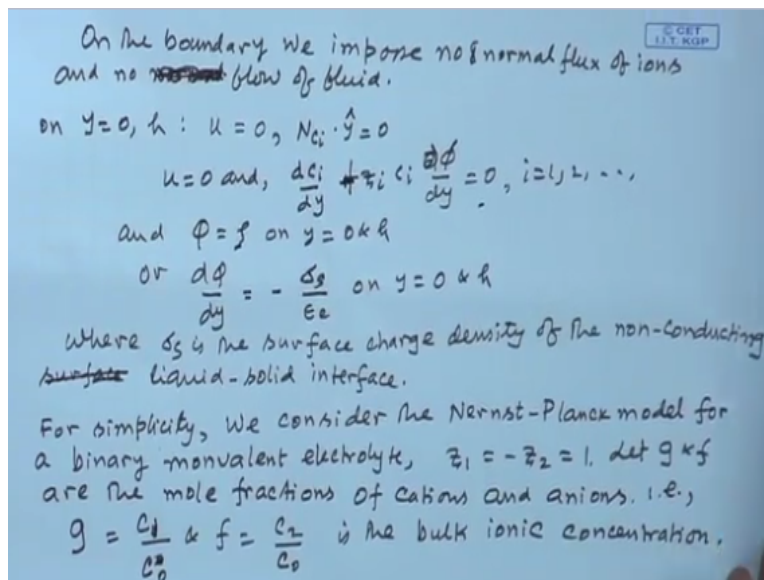
$$\frac{\partial}{\partial y} \left(\frac{\partial c_i}{\partial y} + z_i \frac{F}{RT} c_i \frac{\partial \phi}{\partial y} \right) = 0 \quad \text{---(b), } i = 1, 2, \dots$$
 supplemented by the equation for the electric potential

$$\frac{d^2\phi}{dy^2} = -\frac{1}{\epsilon_e} F \sum z_i c_i \quad \text{---(c)}$$

And this supplemented by the equation for electric field or the electric potential. This can be written as $\nabla^2 \phi = -\frac{1}{\epsilon_0} \sum z_i c_i$. So these equations basically are known to us. Now how we impose the boundary condition so basically we need to solve this state of equations for if we do not go by the assumption that c_i are governed by the Boltzmann equation and the number of ionic species are symmetric and binary so that kind of assumption if you are not imposing.

So any kind of situations $i = 1$ to n , so you have a situation like this way. Now so these are the equation a, b, c, so these equations of order number of ionic species so they are coupled. What we can see is that we can solve it individually, so one solution is depending on the other. So we have to impose the boundary conditions of the boundary what conditions we can imposed on the boundary.

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So we impose no & normal flux of ions and no normal flow of fluid, in other words the boundaries are assumed to be ion penetrable and rigid so if we assume this kind of situations. So what we get here that on the boundary we can have a situation has on $y = 0$ and if I take the other one is h , so you have the $u = 0$, because u is the velocity slit here is the no slit. So fluid velocity we impose no & normal flux of ions and no fluid flow, flow of fluid.

So no normal flow is zero and also it to the viscous flow the condition that no flow of fluid. So, $u = 0$ and $N_{ci} \cdot y$ here is a vector, so this is equal to zero. So this gives you $u = 0$ and the other conditions what we have is $d c_i dy + z_i c_i$, - I guess $d \Phi dy = 0$, there will be +, there - over, there should be plus I guess, so there will be plus so this is the for $I =$ whatever 1, 2, etc., and you have $\Phi = \zeta$ on $y = 0$ and h or you can have the condition of charge density that is $d \Phi dy = - \sigma_s / \epsilon_0$ on $y = 0$ & h .

Where σ_s is the surface charge density of the non-conducting surface of which or non-conducting liquid surface interface. If it is the perfectly conducting so in that case we can impose condition as $\Phi = \zeta$, ζ can be prescribed so on this rigid surface itself, so these are the boundary conditions one has to impose for Φ this is the conditions for c_i this is the condition for the velocity, so this boundary conditions are complete. Because we have a second order alternative Differential Equation and we have the governing boundary conditions.

So this set of equations along with this boundary condition cannot be solved in analytics fashion obviously and also things becomes complicated if you have the number of ionic species are species are increased okay and this boundary conditions can also be little simplified that means since we are taking this is a zero and U is zero so one can assume a Boltzmann distribution on the surface itself, only assume the Boltzmann distribution along the surface.

Now let us considered for Simplicity a situation where we consider the Nernst-Planck model for a binary, let us take monovalent electrolyte so in other words you have $Z_1 = - Z_2 = 1$ and let g and f the mole fraction of cations and anions. What is g and f that is $g = C_1 / C_0$ and $f = C_2 / C_0$, C_0 is the bulk ionic concentration. So in terms of the mole fractions g and f if defined this way.

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$$\frac{d^2 u}{dy^2} = -(\kappa h)^2 (g - f)$$

$$\frac{d}{dy} \left(\frac{dg}{dy} + g \frac{d\phi}{dy} \right) = 0 \times \frac{d}{dy} \left(\frac{df}{dy} - f \frac{d\phi}{dy} \right) = 0,$$

$$\frac{d^2 \phi}{dy^2} = -(\kappa h)^2 (g - f)$$

Here u is scaled by $U_0 = \frac{\epsilon_0 \epsilon_0 \phi_0}{\mu}$, the ϕ is scaled ϕ_0
 ($= RT/F$), y is scaled by h . and
 $\kappa = \kappa^{-1} = \left(\frac{2F^2 C_0}{\epsilon_0 \epsilon_0 RT} \right)^{1/2} = \left(\frac{F^2 \sum z_i^2 C_i}{\epsilon_0 \epsilon_0 RT} \right)^{1/2}$

Equation for u and ϕ are identical.

$y=0, h: u=0, \frac{dg}{dy} + g \frac{d\phi}{dy} = 0, \frac{df}{dy} - g \frac{d\phi}{dy} = 0$ and $\phi = \psi$ or
 $\frac{d\phi}{dy} = -\psi / \epsilon_0$.

So you can rewrite the equations whatever we have derived the governing equations can be expressed as $d^2u/dy^2 = -\kappa^2 h^2 (g - f)$ and $d/dy (dg/dy + g d\phi/dy) = 0$ and $d/dy (df/dy - f d\phi/dy) = 0$ and along with the electric potential equation that is $d^2\phi/dy^2 = -\kappa^2 h^2 (g - f)$, here what I did is we have taken the u , here u is scaled by u_0 and κ was introduced.

So κ is in this case is since we are taking a symmetric binary electrolyte so this will be the ionic concentration is C_0 . So but if it is not a symmetric electrolyte so will have the ionic concentration is different from C_0 . So U_0 we have taken as $\epsilon_0 \epsilon_0 \phi_0 / \mu$. So basically this is a small κ velocity with surface potential as ϕ_0 . So this is the thing is considered to be a velocity scale here u scaled by ϕ_0 , the electric potential ϕ is scaled by ϕ_0 . ϕ_0 which is nothing but RT/F .

The thermal potential scale and y is scaled by h and the κ which is nothing but the inverse of Debye length is $2F^2 C_0 / \epsilon_0 \epsilon_0 RT$. Now if it is not a binary electrolyte in general κ is I would say so this is toward half to $F^2 \sum z_i^2 C_i / \epsilon_0 \epsilon_0 RT$ to the power half. Now in this case if you have a symmetric binary electrolyte so we can have this one is equal to $2 C_0$ but otherwise there will be a parameter has to be introduced.

As we have discussed before the ionic concentration may not be the same as C_0 , so another thing is that from here that the equation for Φ , equation for u and Φ are identical, but however their boundary conditions are not same, so these equations for u and Φ identical and also we have the boundary conditions we can write has $y = 0, h$ we have $u = 0$ $dg/dy + g d\Phi/dy = 0$, if $dy - g d\Phi/dy = 0$.

And the conditions for Φ , so $\Phi = \zeta$ or $d\Phi/dy$ or you may have this one $d\Phi/dy = -\sigma_s / \epsilon$, so one need to solve this couple set of equations by some numerical technique. Okay so will carry to the next lecture thank you.