Modeling Transport Phenomena of Microparticles
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Lecture - 22
Detailed Routing (Part III)

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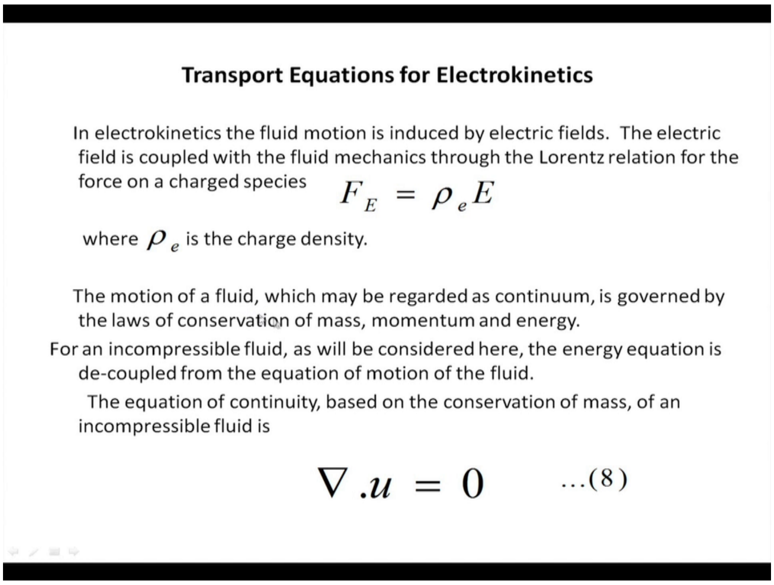

Transport Equations for Electrokinetics

In electrokinetics the fluid motion is induced by electric fields. The electric field is coupled with the fluid mechanics through the Lorentz relation for the force on a charged species $F_E = \rho_e E$

where ρ_e is the charge density.

The motion of a fluid, which may be regarded as continuum, is governed by the laws of conservation of mass, momentum and energy.

For an incompressible fluid, as will be considered here, the energy equation is de-coupled from the equation of motion of the fluid.

The equation of continuity, based on the conservation of mass, of an incompressible fluid is

$$\nabla .u = 0 \qquad \ldots(8)$$

Now the motion of fluid which we considered here is a Continuum are governed by the conservation principles. So as I think I has been already discussed on the fluid mechanics lectures, So the motion of fluid are we can develop based on the conservation of mass, Momentum and energy. Now energy equation based on the conservation principle of energy is decoupled for the incompressible fluid from the mass and Momentum.

So we here will be focusing on incompressible situation so you can avoid the discussion on the energy equation. So for incompressible fluid we have the equation of continuity that is based on the conservation principle as the Divergence of u = 0. u is the local fluid velocity vector, it is a vector at any point x, y, z .

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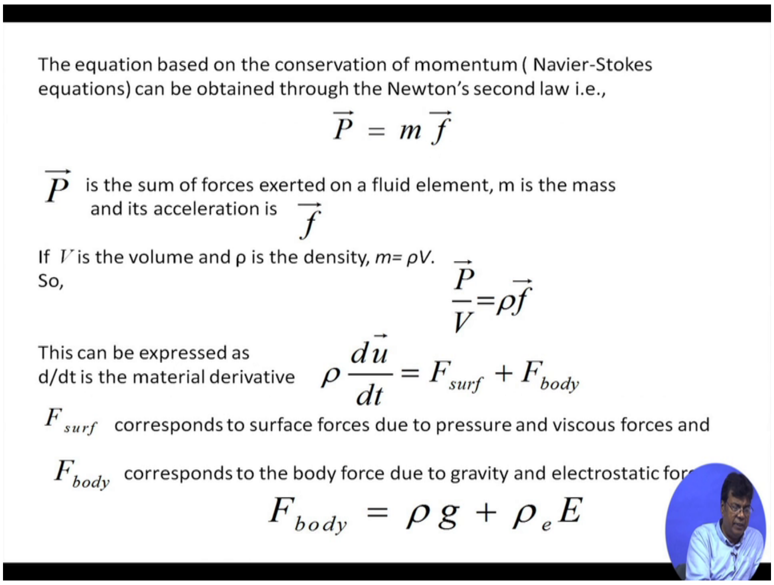

The equation based on the conservation of momentum (Navier-Stokes equations) can be obtained through the Newton's second law i.e.,

$$\vec{P} = m\vec{f}$$

$\vec{P}$ is the sum of forces exerted on a fluid element, m is the mass and its acceleration is $\vec{f}$

If V is the volume and ρ is the density, $m = \rho V$.
So,

$$\frac{\vec{P}}{V} = \rho\vec{f}$$

This can be expressed as
d/dt is the material derivative

$$\rho\frac{d\vec{u}}{dt} = F_{surf} + F_{body}$$

F_{surf} corresponds to surface forces due to pressure and viscous forces and

F_{body} corresponds to the body force due to gravity and electrostatic for

$$F_{body} = \rho g + \rho_e E$$

Say if it is Cartesian, so now the second equation which is called the equation of momentum, so this is based on the conservation of momentum principle, this is basically nothing but the Newton's second law which is P = m f, p is the sum of forces exerted on a fluid element, m is the mass and its acceleration is governed by f. So here is the V is the volume and Rho is the density, if I when the volume element we are considering so we can write this by this manner P by V = Rho f.

Now this can be if I considered a volume element within the fluid, so there will be a interacting force on the surface of the fluid element that is the what is referred as the pressure and also the viscous frictional force. So this way one can rewrite this equation in this form. The conservation of momentum equation now can be expressed in this way, where this du by dt is referred as a material derivative.

Now material derivative is not the exactly the total derivative, so that means here the every element is moving with the fluid itself.

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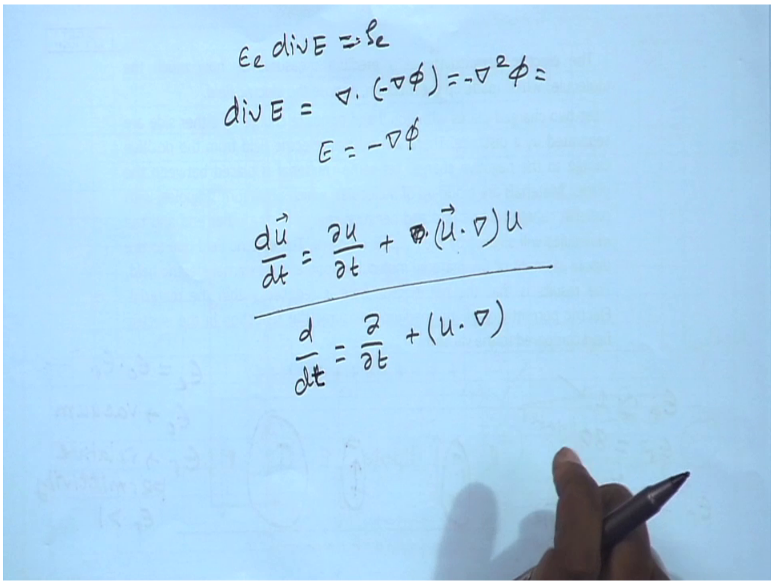

$$\epsilon_e \, \mathrm{div} E = \rho_e$$

$$\mathrm{div} E = \nabla \cdot (-\nabla \phi) = -\nabla^2 \phi =$$

$$E = -\nabla \phi$$

$$\frac{d\vec{u}}{dt} = \frac{\partial u}{\partial t} + (\vec{u} \cdot \nabla) u$$

$$\frac{d}{dt} = \frac{\partial}{\partial t} + (u \cdot \nabla)$$

So du dut is in this case we are the form as this is the way we define as a u is a vector so u dot Grad u, so this is referred as or this operator way if I write that is Del Del t + u Grad. So this gives the operator form. So the is also one can say the rate of change of momentum. So the forces surface force and body force, so the surface force corresponds to the pressure and viscous forces and body forces corresponds the body force due to gravity at that electrostatic force as we discussed over here.

So that means the body foods can be written as Rho g +Rho e E.

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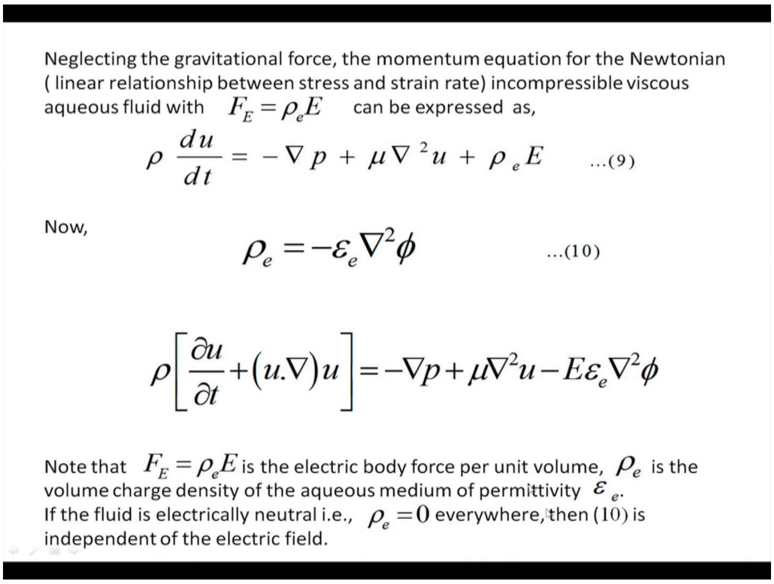

Neglecting the gravitational force, the momentum equation for the Newtonian (linear relationship between stress and strain rate) incompressible viscous aqueous fluid with $F_E = \rho_e E$ can be expressed as,

$$\rho \frac{du}{dt} = -\nabla p + \mu \nabla^2 u + \rho_e E \qquad \ldots(9)$$

Now,

$$\rho_e = -\varepsilon_e \nabla^2 \phi \qquad \ldots(10)$$

$$\rho\left[\frac{\partial u}{\partial t} + (u.\nabla)u\right] = -\nabla p + \mu \nabla^2 u - E\varepsilon_e \nabla^2 \phi$$

Note that $F_E = \rho_e E$ is the electric body force per unit volume, ρ_e is the volume charge density of the aqueous medium of permittivity ε_e.
If the fluid is electrically neutral i.e., $\rho_e = 0$ everywhere, then (10) is independent of the electric field.

Now if I neglect the gravitational force and only stick to the electrostatic force, so I can express the momentum equation in this form, where E is the pressure Mu is the viscosity dynamic viscosity of the fluid medium, so the momentum equation can be expressed in this manner Rho du dt = - Grad p + Mu Grad power 2 u + Pho e E. Now Rho e as we have already obtained from that Gauss law as that is that Poisson equation for electric potential Rho e is governed by this equation.

So if I substitute here so I get a situation now wrote the material derivative in this form Rho du dt plus this situation here p is we are denoted as the pressure. So this is due to the viscous drag or fictional force viscous frictional force. This is the term is got once to the charged density whatever is present, now if the fluid is electrically neutral electrically neutral means if Rho e is 0, everywhere so Rho e is the volume charge density of the aqueous medium, and Epsilon e is the permittivity.

Now if your situation where Rho e is zero everywhere within the fluid medium, so this is nothing but the equation of motion of a incompressible Newtonian fluid. Now another thing is that assumed you have made is that Newtonian fluid, that means there is a linear relation between the stress and strength rate are occurring. So we now develop the fluid governing equation for the fluid we in a aqueous fluid or ionized fluid.

So only extra term which is taking care is governed by here, So now which shows that this Phi and the Poisson equations whatever the situation we have developed are now coupled, so that means if it is not electrically neutral so we this equations are depending on each other.

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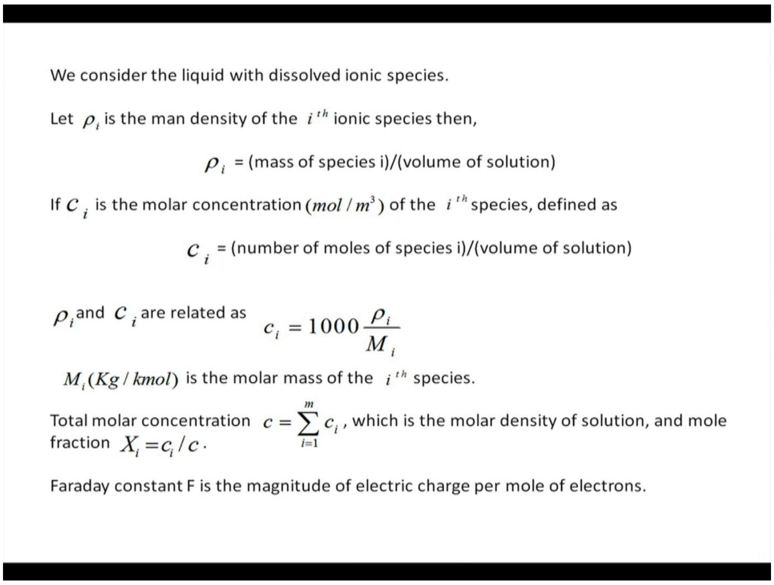

We consider the liquid with dissolved ionic species.

Let ρ_i is the man density of the i^{th} ionic species then,

$$\rho_i = \text{(mass of species i)/(volume of solution)}$$

If c_i is the molar concentration (mol/m^3) of the i^{th} species, defined as

$$c_i = \text{(number of moles of species i)/(volume of solution)}$$

ρ_i and c_i are related as $c_i = 1000 \dfrac{\rho_i}{M_i}$

$M_i (Kg/kmol)$ is the molar mass of the i^{th} species.

Total molar concentration $c = \sum_{i=1}^{m} c_i$, which is the molar density of solution, and mole fraction $X_i = c_i / c$.

Faraday constant F is the magnitude of electric charge per mole of electrons.

Now we have to know the as here I just mentioning that because of this moment of the Fluids and also the electric field and all.

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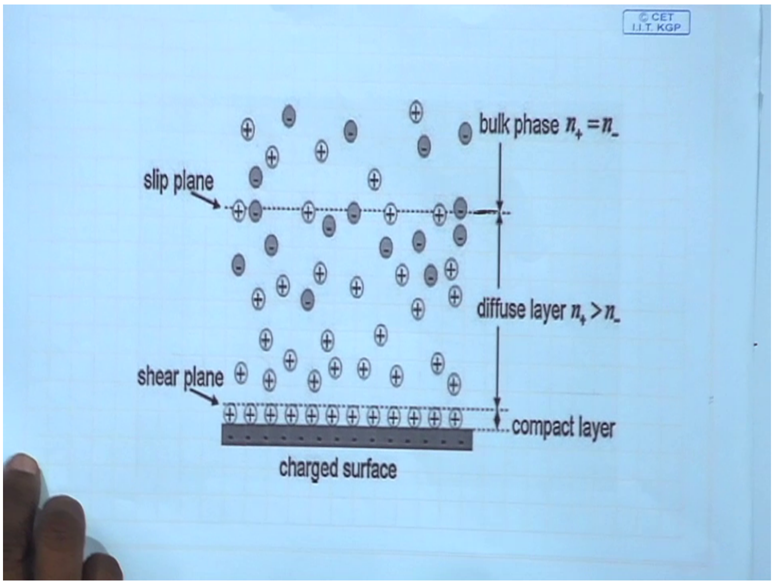

So if you just go back and have a look over here, so because of if you have a charged surface due to that there will be a movement of the ions positive will be attracted to the negative electrodes and negative will be moving to the positive electrodes. And there will be a moment of the ions so the concentration of the ions which is creating the charge density will be different within the domain itself within this domain. So you have a different concentration of the ions.

So now you need to know the distribution of the ions in order to get this equation correctly equation 10. So that means this equation 10 demands that we should have a expression for the Rho e which is governed by the distribution of ions okay. Now in order to do that, we first define some we measure the how we define the measure, how we measure the distribution of ion, so this is the we call the Rho i is a mean density of the ion ionic species.

We can considered several ionic species are dissolved the here we all considering at the miscible ions so that means there dissolved in liquid. So there at may be several components so one of any arbitrary component ith Component we defined as the mean mass density. Rho i is the mass density, c i is the molar concentration so the number of moles per volume and another important things which we require is the mole fraction.

So if the net concentration is governed by this way summation of this so this molar mole fraction of a particular ionic species is X i is the number of moles of the species per net amount of mole c i by c is measured the mole fraction of the ionic species.

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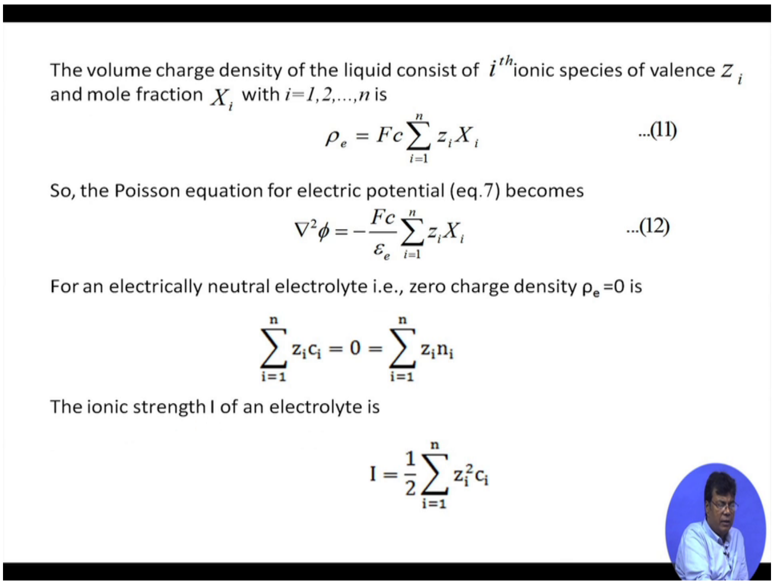

The volume charge density of the liquid consist of i^{th} ionic species of valence z_i and mole fraction X_i with $i=1,2,\ldots,n$ is

$$\rho_e = Fc\sum_{i=1}^{n} z_i X_i \qquad \ldots(11)$$

So, the Poisson equation for electric potential (eq.7) becomes

$$\nabla^2\phi = -\frac{Fc}{\varepsilon_e}\sum_{i=1}^{n} z_i X_i \qquad \ldots(12)$$

For an electrically neutral electrolyte i.e., zero charge density $\rho_e = 0$ is

$$\sum_{i=1}^{n} z_i c_i = 0 = \sum_{i=1}^{n} z_i n_i$$

The ionic strength I of an electrolyte is

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

Now charge density are governed by this equation this relation so charge density so each of these ionic species are creating a charge which is equal to Fc X i so Fc X i is basically the FC i and z i is the valence whether it is a positive or negative or the number of valence so this summation is the giving the charge density per unit volume of the ionized fluid so with that now the Poisson equation for electric field can be expressed by this equation okay.

Now if we have a situation where it is electrically neutral so that means the net charge density will be zero. So we will have z i c i or your sigma z i X i are 0 and in i we define n i is the number density so that is okay is governed by this way sum equation because it is zero homogeneous so that is why we can have the Sum equation and the ionic strength of an electrolyte is defined in this manner so if it is a so this is non zero even if it is a electrically neutral situation because is z i square.

So the net amount of this is the c i is the molar concentration so net amount of mole per all the ionic species per unit volume is easy ionic strength of the electrolyte.

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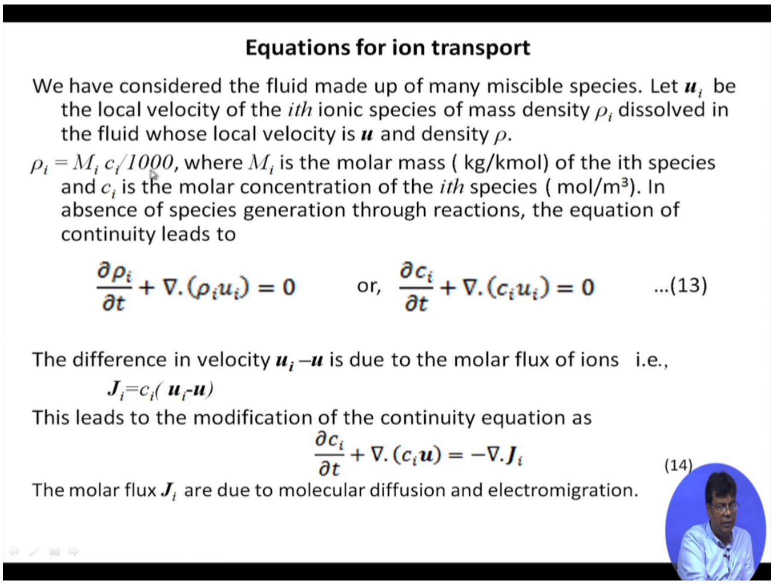

Equations for ion transport

We have considered the fluid made up of many miscible species. Let $\boldsymbol{u}_i$ be the local velocity of the ith ionic species of mass density ρ_i dissolved in the fluid whose local velocity is $\boldsymbol{u}$ and density ρ.

$\rho_i = M_i\, c_i/1000$, where M_i is the molar mass (kg/kmol) of the ith species and c_i is the molar concentration of the ith species (mol/m³). In absence of species generation through reactions, the equation of continuity leads to

$$\frac{\partial \rho_i}{\partial t} + \nabla.(\rho_i u_i) = 0 \qquad \text{or,} \quad \frac{\partial c_i}{\partial t} + \nabla.(c_i u_i) = 0 \qquad \text{...(13)}$$

The difference in velocity $\boldsymbol{u}_i - \boldsymbol{u}$ is due to the molar flux of ions i.e.,

$$\boldsymbol{J}_i = c_i(\boldsymbol{u}_i - \boldsymbol{u})$$

This leads to the modification of the continuity equation as

$$\frac{\partial c_i}{\partial t} + \nabla.(c_i \boldsymbol{u}) = -\nabla.\boldsymbol{J}_i \qquad (14)$$

The molar flux $\boldsymbol{J}_i$ are due to molecular diffusion and electromigration.

Now we are intended to derive the equation for ion transport now we are talking about the multicomponent fluid, so let a ionic species which has a velocity say u i and density mass density is governed by Rho i dissolved in a fluid medium whose local velocity is u and density is Rho. Now this mass density is also related can be related with the molar concentration by this relation because mole per meter cube.

So by this relations c i is the molar concentration of the ith ionic species. Now if there is no way to generate the ionic species that is in absence of any reaction show by the equation of continuity it will satisfy the equation of continuity each of the ionic species where Rho i is the mass density u i it is velocity so in terms of the molar concentration we can write this equation and this equation 13 form okay.

Now this u i may not be equal to the u because ionic species may have different velocities different ionic species may have different velocity other than the local fluid velocity there will be a difference u i – u, now you need to see what are the mechanism by which we have a difference now if I, we know the equation of continuity for the fluid is Divergence u is zero, so if I apply over here so you get it relation now I say that the J i is also revise the molar flux of ions is by this relation, so the if I apply over here Divergence u is zero.

So this equation 13 can be transferred to this form by virtue of continuity of the fluid Divergence u is zero so you get a relation govern by this way. Now J i are due to what are the mechanisms we can in absence of course here we have neglected the gravitational force and also the reactions and all so the mechanisms for this ionic flocks are the molecular diffusion and electro migration so now we have to get an expression for J i the molar flux of ions due to this mechanism.

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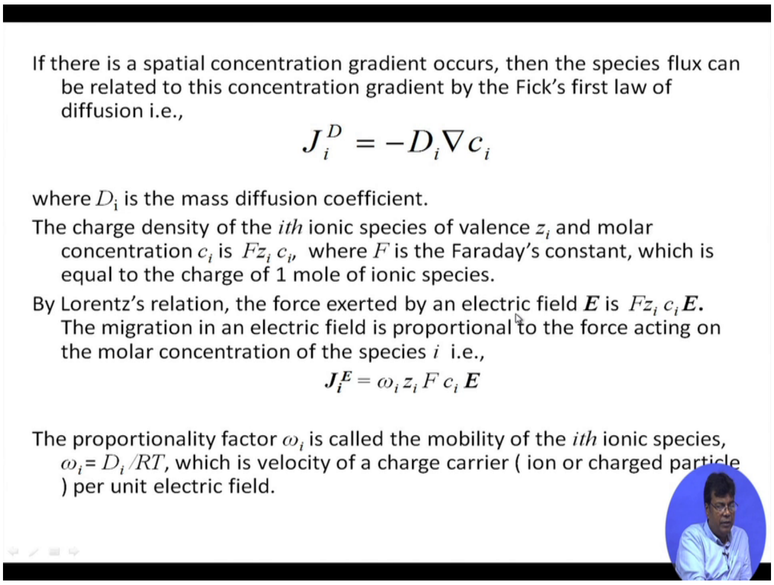

If there is a spatial concentration gradient occurs, then the species flux can be related to this concentration gradient by the Fick's first law of diffusion i.e.,

$$J_i^D = -D_i \nabla c_i$$

where D_i is the mass diffusion coefficient.

The charge density of the *ith* ionic species of valence z_i and molar concentration c_i is $Fz_i\, c_i$, where F is the Faraday's constant, which is equal to the charge of 1 mole of ionic species.

By Lorentz's relation, the force exerted by an electric field $\boldsymbol{E}$ is $Fz_i\, c_i \boldsymbol{E}$. The migration in an electric field is proportional to the force acting on the molar concentration of the species i i.e.,

$$\boldsymbol{J}_i^E = \omega_i z_i F c_i \boldsymbol{E}$$

The proportionality factor ω_i is called the mobility of the *ith* ionic species, $\omega_i = D_i / RT$, which is velocity of a charge carrier (ion or charged particle) per unit electric field.

Now molecular diffusion that is governed by the well known Fick's Law, Fick's First Law for that matter so Fick's Law means if there is a gradient that means there is, a in the space gradient in space of the distribution that means there is a difference in a difference in the concentration in special difference occurring, so this molecular diffusion flux is proportional to this gradient and this proportionality is referred as the diffusion coefficient D i so this is the flux due to the molecular diffusion okay.

Here it is negative because you may have the positive gradient or negative gradient, so depending on that the ionic species will move along the direction that is why you have a negative so D i is referred as a mass diffusion coefficients, now this is a thing here we have taken D i as a single value for the ith ionic species now it can differ say if you have to between two interacting with in two ionic species i and j, so it can have a dependence D i .

So here we avoid that one and we consider the D i is the diffusion coefficients for the ith ionic species now another thing is that when this ions are under electric field so each ions are carrying a charge so they will have a columbic attractive force and there will be a movement or ionic flux due to this electric field.

So that is the one we referred as the diffusion or the electro migration, so if c i is the molar flux the molar concentration of the ionic species so it has a charge density F z i c i E, F is again the Faraday constant and c i is the z i is the valence of that ionic species, so it will have a force F z i c i into E. So the due to migration of in an electric field of this you considering this is the charged volume charge so these ionic species will have a flux due to the presence of an electric field which is proportional to this net amount of charge.

So this proportionality constant is Omega i is called the mobility of the ith ionic species. Mobility is basically is the velocity per unit electric field that is the way is mobility is defined so we have to class of ionic flux generation one is due to the molecular diffusion and other is due to the electro migration of the ionic species so this Omega i can be written as D i by RT where R is the universal gas constant and T is the temperature D i is the division coefficient.

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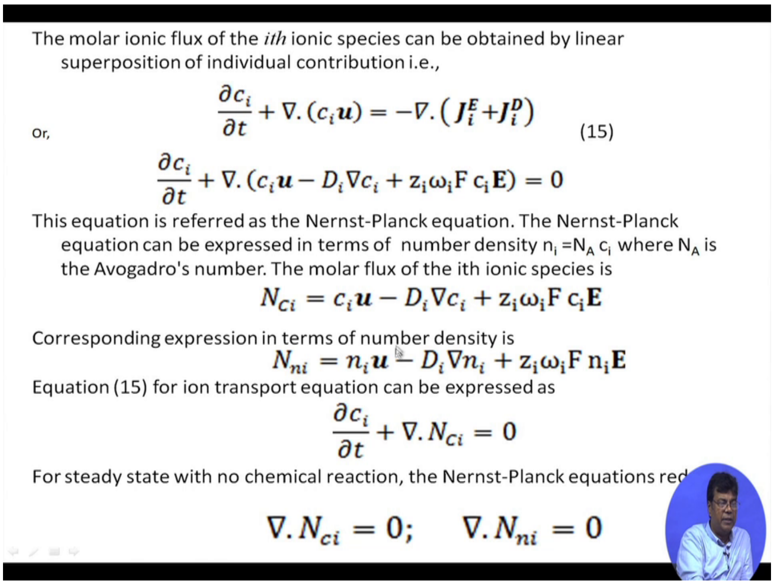

The molar ionic flux of the *ith* ionic species can be obtained by linear superposition of individual contribution i.e.,

$$\frac{\partial c_i}{\partial t} + \nabla.(c_i \boldsymbol{u}) = -\nabla.\left(\boldsymbol{J}_i^E + \boldsymbol{J}_i^D\right) \qquad (15)$$

Or,

$$\frac{\partial c_i}{\partial t} + \nabla.(c_i \boldsymbol{u} - D_i \nabla c_i + \mathrm{z_i} \omega_\mathrm{i} \mathrm{F}\, \mathrm{c_i} \mathbf{E}) = 0$$

This equation is referred as the Nernst-Planck equation. The Nernst-Planck equation can be expressed in terms of number density $n_i = N_A c_i$ where N_A is the Avogadro's number. The molar flux of the ith ionic species is

$$N_{ci} = c_i \boldsymbol{u} - D_i \nabla c_i + \mathrm{z_i} \omega_\mathrm{i} \mathrm{F}\, \mathrm{c_i} \mathbf{E}$$

Corresponding expression in terms of number density is

$$N_{ni} = n_i \boldsymbol{u} - D_i \nabla n_i + \mathrm{z_i} \omega_\mathrm{i} \mathrm{F}\, \mathrm{n_i} \mathbf{E}$$

Equation (15) for ion transport equation can be expressed as

$$\frac{\partial c_i}{\partial t} + \nabla. N_{Ci} = 0$$

For steady state with no chemical reaction, the Nernst-Planck equations red

$$\nabla. N_{ci} = 0; \qquad \nabla. N_{ni} = 0$$

With that we can write the equation what we have already derive the Valence equation or conservation of ionic flux we can write as this manner okay, so now we are here considering a linear superposition of the two components this is the two components is due to the electro migration and the diffusion so the charged transport equation now can be written in this manner so the total flux of the net flux at any point are governed by this is the fluid convection this is the diffusion molecular diffusion.

And other is the electro migration so if it is a neutral so this part would have been zero, so that means if it is a neutral solvent any other kind of solvent so this last term that means the molecular electro migration term is neglected so that is also referred as a mass transport equation, so this is a equation so we can now write the molar flux of the ith ionic species are by distillation c i u, u is the local fluid velocity.

And this is the molecular diffusion and the electro migration and if I write in terms of the number density of the ith ionic species, so this is governed by this relation. Now if I consider So this relation 15 can be written in this manner so if I consider a steady state situation so if it is a steady state situation, so either of this Divergence N ci or ni becomes zero, so this can be expressed of this form so Divergence N ci .

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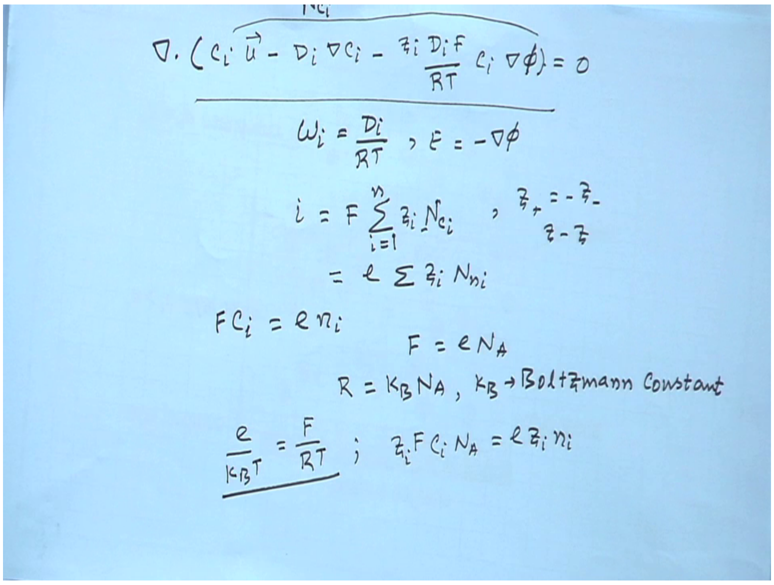

$$\nabla \cdot \big(\overbrace{c_i \vec{u} - D_i \nabla c_i - z_i \frac{D_i F}{RT} c_i \nabla \phi}^{N_{c_i}}\big) = 0$$

$\omega_i = \frac{D_i}{RT}$, $E = -\nabla \phi$

$i = F \sum_{i=1}^{n} z_i N_{c_i}$, $z_+ = -z_-$

$z - z$

$= e \sum z_i N_{n_i}$

$F c_i = e n_i$

$F = e N_A$

$R = K_B N_A$, $K_B \rightarrow$ Boltzmann Constant

$\frac{e}{K_B T} = \frac{F}{RT}$; $z_i F c_i N_A = e z_i n_i$

So that means you have a situation where ci u , ci u is the vector of course - D i Divergence c i - z i (D i F by RT) because Omega i is (F by RT) ci Grad Phi = 0, Phi how which notation I think is the notation so this is the in a steady situation this become the governing equation for the ionic transport Omega i we have already defined as Di by RT okay and E is – Grad Phi, so basically this is a think we are substituted over here now okay.

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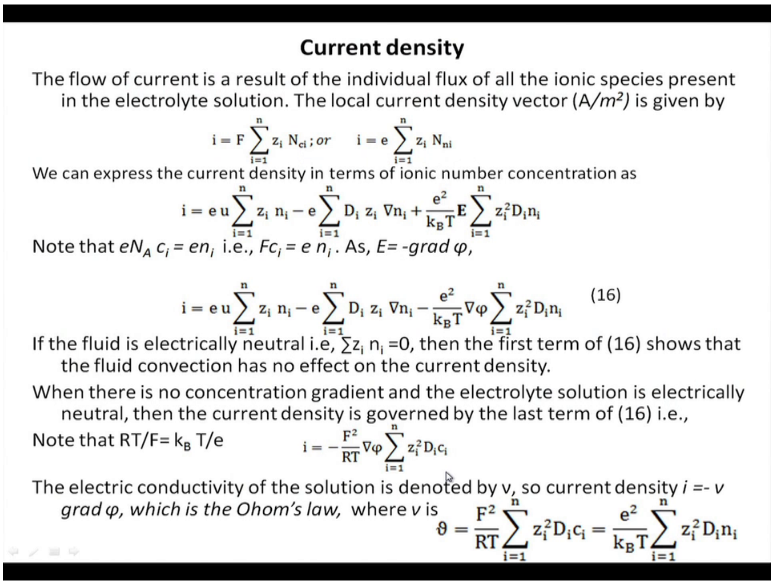

Current density

The flow of current is a result of the individual flux of all the ionic species present in the electrolyte solution. The local current density vector (A/*m*^{2}*)* is given by

$$\mathrm{i} = \mathrm{F}\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{z_i}\,\mathrm{N_{ci}}\,;\,or \qquad \mathrm{i} = \mathrm{e}\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{z_i}\,\mathrm{N_{ni}}$$

We can express the current density in terms of ionic number concentration as

$$\mathrm{i} = \mathrm{e\,u}\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{z_i\,n_i} - \mathrm{e}\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{D_i\,z_i\,\nabla n_i} + \frac{\mathrm{e}^2}{\mathrm{k_B T}}\mathbf{E}\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{z_i^2 D_i n_i}$$

Note that $eN_A\,c_i = en_i$ i.e., $Fc_i = e\,n_i$. As, *E= -grad* φ,

$$\mathrm{i} = \mathrm{e\,u}\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{z_i\,n_i} - \mathrm{e}\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{D_i\,z_i\,\nabla n_i} - \frac{\mathrm{e}^2}{\mathrm{k_B T}}\nabla\varphi\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{z_i^2 D_i n_i} \qquad (16)$$

If the fluid is electrically neutral i.e, $\sum z_i\, n_i = 0$, then the first term of (16) shows that the fluid convection has no effect on the current density.

When there is no concentration gradient and the electrolyte solution is electrically neutral, then the current density is governed by the last term of (16) i.e.,

Note that RT/F= k_B T/e

$$\mathrm{i} = -\frac{\mathrm{F}^2}{\mathrm{RT}}\nabla\varphi\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{z_i^2 D_i c_i}$$

The electric conductivity of the solution is denoted by v, so current density *i =- v grad* φ*, which is the Ohom's law,* where *v* is

$$\vartheta = \frac{\mathrm{F}^2}{\mathrm{RT}}\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{z_i^2 D_i c_i} = \frac{\mathrm{e}^2}{\mathrm{k_B T}}\sum_{\mathrm{i}=1}^{\mathrm{n}} \mathrm{z_i^2 D_i n_i}$$

Now we need to know because this ions are moving so there will be a current density will be developed, so ions are transporting by the equation has we have just derived so because of this movement of the ions you have a development of current so this current can be considered or we can measure the current density so that means the ampere per meter square local current density by this relation.

So the flux and what do you have is i equal to the Faraday constant and what yeah of course the valence and this all this flux so if you have n number of ionic species so here some over if it is a binary so you have z + and z – monovalent situation otherwise you may have a z, z electrolyte you may have arbitrary what to binary species and also this can be written as if I write in terms of number density function so this is z i in n i.

Now you substitute this is the relation is for the N c i so if I now substitute here or also you can say this is the because if I E multiply with E. So basically ci and ni are governed by this way so c i is can be written as this number density into e the elementary charge so that gives you the molar concentration. So F Ci so if I substitute in the flux of or numbers the way we can say this is the number density flux corresponding to number density flux.

If I substitute in this relation so the current density is covered by this equation, now e if I write in a Grad Phi form so we get a situation here has govern by this now here I have written e by KBT now this since we have we can note this relation F is basically e into N A okay and also R the gas constant that is the this is the Boltzmann constant K B N A . N A is the Avogadro's number and K B is the Boltzmann constant.

Now we have this situation that we have F= eNA so what we can write is e by KBT = F by RT okay, so because the charge density so net charge z i F C i N A is nothing but e z i n i okay. now n i we can write as which e n i, so in this way we can get an expression as e by KBT equal to F by RT now there is a thing is been written over here, now if the fluid is taken to be electrically neutral that means the net charge density zero.

So first term is out Sigma zi ni is zero which shows that the current density is independent of the fluid motion because fluid motion is involved only in this time so also now when there is no concentration gradient, so what we have the and these two terms if it is dropped so that means you have a situation where electrically neutral and also they know concentration gradient are developed in that case the current density can be written as F square RT.

So e now change n i, n i will be now in Fc i, so this F c i will come out so this is e by KBT is F by RT so this becomes F square by RT Grad Phi z i into d i c i. z i square, so we define the electric conductivity of the medium by this relation this Nu. So Nu is defined as the electric conductivity so what you find that this is basically the Ohm's law i= Nu – Nu Grad Phi, so the electric field is proportional current density is proportional to the applied electric field.

And this is the electric conductivity of the medium is governed by this way okay. Now this n i here solving the previous equation okay.

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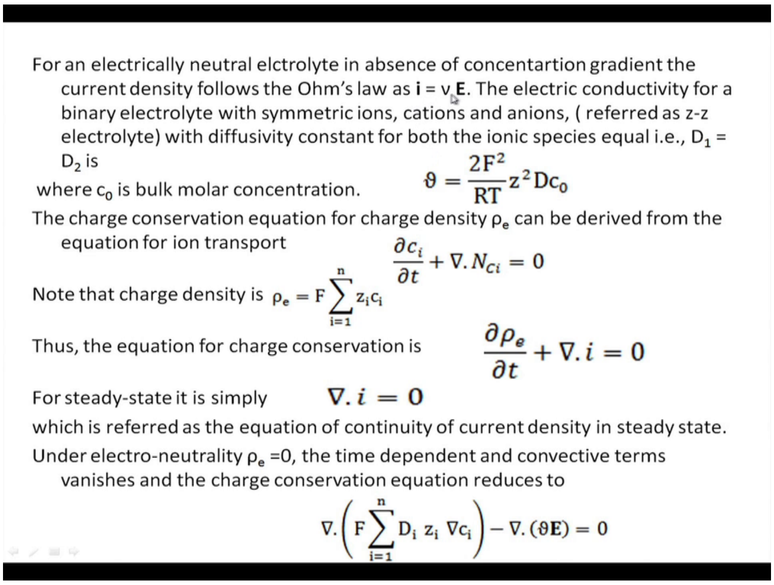

For an electrically neutral elctrolyte in absence of concentartion gradient the current density follows the Ohm's law as **i** = ν **E**. The electric conductivity for a binary electrolyte with symmetric ions, cations and anions, (referred as z-z electrolyte) with diffusivity constant for both the ionic species equal i.e., $D_1 = D_2$ is

$$\vartheta = \frac{2F^2}{RT} z^2 D c_0$$

where c_0 is bulk molar concentration.

The charge conservation equation for charge density ρ_e can be derived from the equation for ion transport

$$\frac{\partial c_i}{\partial t} + \nabla . N_{ci} = 0$$

Note that charge density is $\rho_e = F \sum_{i=1}^{n} z_i c_i$

Thus, the equation for charge conservation is

$$\frac{\partial \rho_e}{\partial t} + \nabla . i = 0$$

For steady-state it is simply $\nabla . i = 0$

which is referred as the equation of continuity of current density in steady state.

Under electro-neutrality ρ_e =0, the time dependent and convective terms vanishes and the charge conservation equation reduces to

$$\nabla . \left(F \sum_{i=1}^{n} D_i \; z_i \; \nabla c_i \right) - \nabla . (\vartheta \mathbf{E}) = 0$$

So this is the Ohm's law we can talk about if you have a z z electrolyte that is D1 = D2 so one can write Nu is governed by that relation can be simplified c 0 is a bulk molar concentration next one will talk about the other part later.