Modeling Transport Phenomena of Microparticles

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Lecture - 21
Detailed Routing (Part III)

So today will talk about the Electrokinetic transport in Microfluidics.

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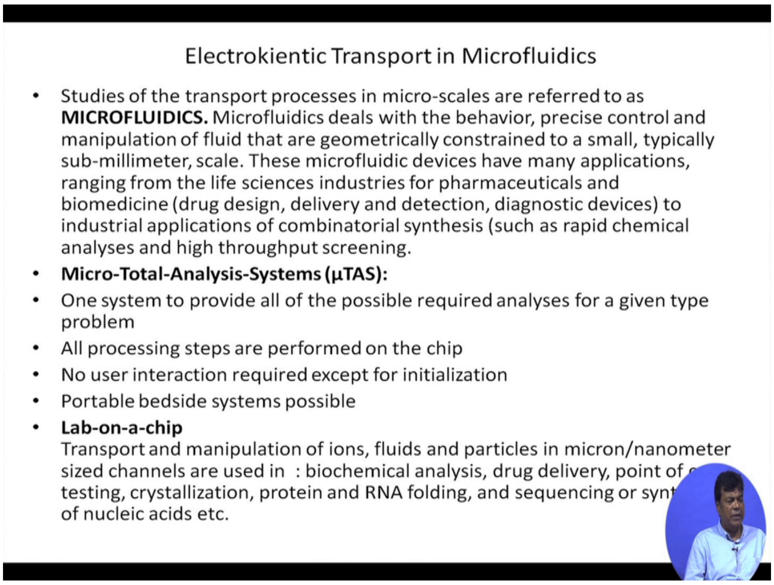

Electrokientic Transport in Microfluidics

- Studies of the transport processes in micro-scales are referred to as **MICROFLUIDICS.** Microfluidics deals with the behavior, precise control and manipulation of fluid that are geometrically constrained to a small, typically sub-millimeter, scale. These microfluidic devices have many applications, ranging from the life sciences industries for pharmaceuticals and biomedicine (drug design, delivery and detection, diagnostic devices) to industrial applications of combinatorial synthesis (such as rapid chemical analyses and high throughput screening.
- **Micro-Total-Analysis-Systems (µTAS):**
- One system to provide all of the possible required analyses for a given type problem
- All processing steps are performed on the chip
- No user interaction required except for initialization
- Portable bedside systems possible
- **Lab-on-a-chip**
  Transport and manipulation of ions, fluids and particles in micron/nanometer sized channels are used in : biochemical analysis, drug delivery, point of testing, crystallization, protein and RNA folding, and sequencing or syn of nucleic acids etc.

So basically what will be doing is on mathematical modeling for this Electrokinetic transport? Which arise in Microfluidics devices? Now how we can say that, the studies of transport process in micro-scales are referred to as Microfluidics. Microfluidics deals with behavior, precise control and manipulation of fluid that are geometrical constrained to a small typically, sub-millimeter scale. These microfluidic devices have many applications, so which we will, we can see some of the things I have written over here.

So mostly it is the advantages that it is portable and it require very tiny amount of samples and also, it has the capability of controlling the transport phenomena to our requirement. Because it can be driven by a say for example the Electrokinetic mechanism and all these things. Now what is the nanometer or micrometer?

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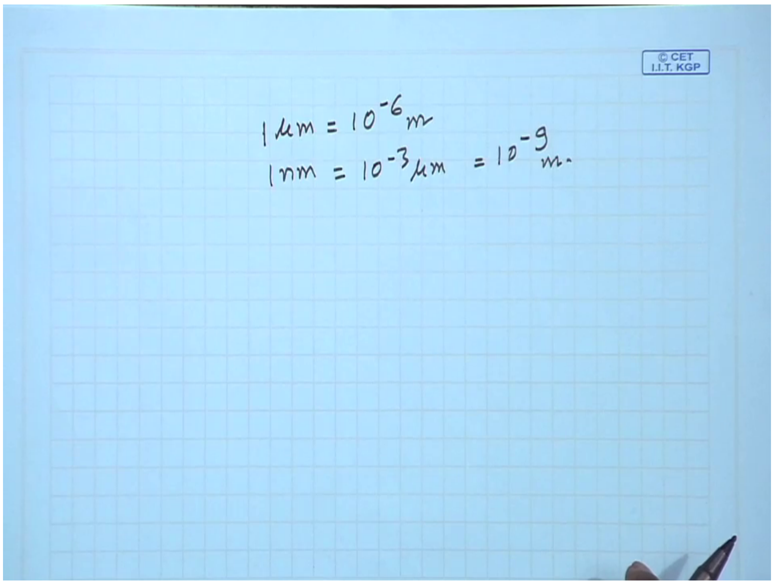

$1\,\mu m = 10^{-6}\, m$

$1\, nm = 10^{-3}\,\mu m = 10^{-9}\, m.$

So First let us know about this, So One micrometer we define as 10 to the power -6 meter and one nanometer is as 10 to the power -3 micrometer. So one nanometer is basically 10 to the power -9 meter. So obviously this show that is a very small length scale we will be talking about, Now when it comes to the small length scale so difficulty arise is that the surface area become enormous. Surface area will dominate the situations compared to the volume area, so that is one characteristics of Microfluidics.

So that means the surface dominate the phenomena are very important over here. Say for example the surface roughness, if any is a molecular dimensions roughness, If you Armstrong or the surface tension forces, and most important thing what you will be talking, referring here is, The surface charge densities and all those things. So that creates an important situation in the analyzing the microfluidic transportation transport in Microfluidics.

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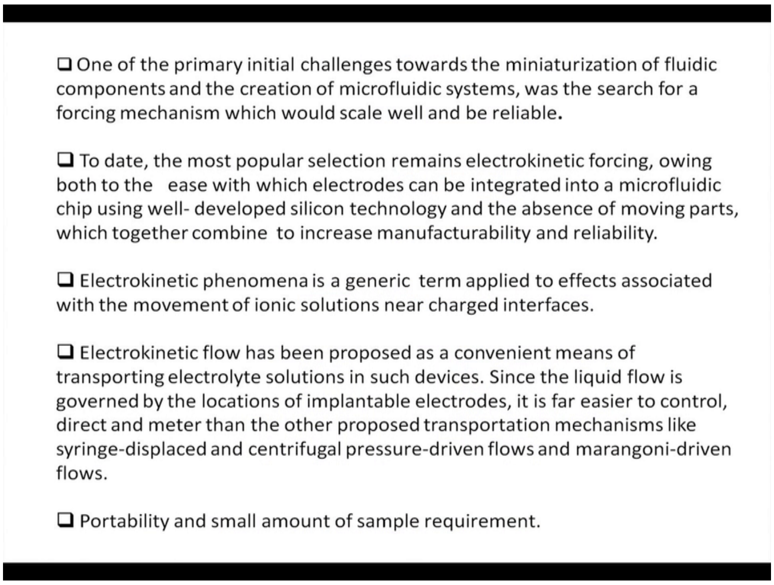

❑ One of the primary initial challenges towards the miniaturization of fluidic components and the creation of microfluidic systems, was the search for a forcing mechanism which would scale well and be reliable.

❑ To date, the most popular selection remains electrokinetic forcing, owing both to the ease with which electrodes can be integrated into a microfluidic chip using well- developed silicon technology and the absence of moving parts, which together combine to increase manufacturability and reliability.

❑ Electrokinetic phenomena is a generic term applied to effects associated with the movement of ionic solutions near charged interfaces.

❑ Electrokinetic flow has been proposed as a convenient means of transporting electrolyte solutions in such devices. Since the liquid flow is governed by the locations of implantable electrodes, it is far easier to control, direct and meter than the other proposed transportation mechanisms like syringe-displaced and centrifugal pressure-driven flows and marangoni-driven flows.

❑ Portability and small amount of sample requirement.

Now one of the primary initial challenges towards miniaturization of fluidic components, And the creation of microfluidic system was the search for a forcing mechanism. So what should be the mechanism? Because if you required to pump say a fluid a small syringe of a few millimeter and all. So how much enormous space is required to be applied in order to have a volume flow through a thinner channel or thin tubes situation capillary on concern.

Now so the pressure when it comes to the micro-scale it becomes enormous and it is impossible, what is the driving mechanism? So most popular driving mechanism is the Electrokinetic forcing. So because Electrokinetics forcing is has a advantage is that, it is very easy to control, you can place the electrodes in way wherever you require how much voltage drop to be created.

And also one can manipulate direction can be changed; it can be several sophisticated way one can handle the Electrokinetic mechanism. Now so that is why Electrokinetic flow has been proposed is a convenient means of transporting electrolyte solution in such devices. Since the liquid flow is governed by the locations of implantable electrodes, it is far easier to control.

And as I said so this kind of things is described here and also this important thing is that, a small amount of sample is enough to analyze in this Lab-on-a-chips or Microfluidic devices.

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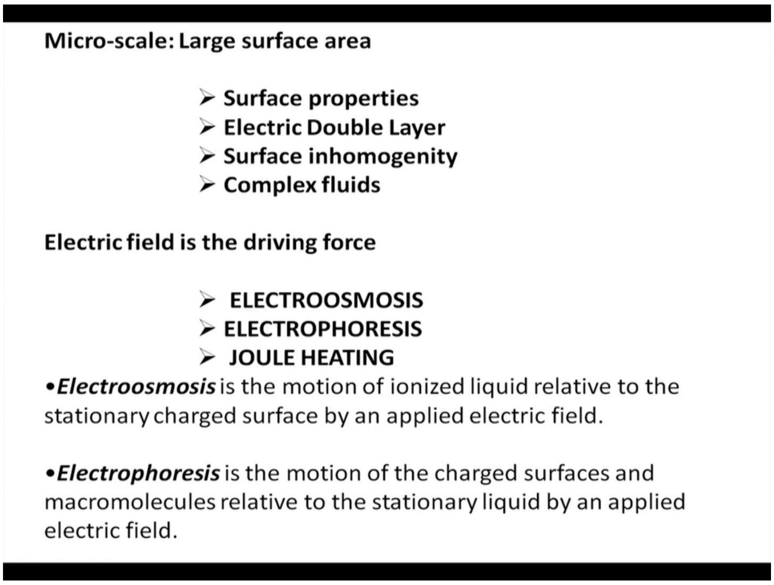

Micro-scale: Large surface area

- **Surface properties**
- **Electric Double Layer**
- **Surface inhomogenity**
- **Complex fluids**

Electric field is the driving force

- **ELECTROOSMOSIS**
- **ELECTROPHORESIS**
- **JOULE HEATING**

•***Electroosmosis*** is the motion of ionized liquid relative to the stationary charged surface by an applied electric field.

•***Electrophoresis*** is the motion of the charged surfaces and macromolecules relative to the stationary liquid by an applied electric field.

Now as I mentioned before, So this micro-scale what happen is a large surface area, so Surface Properties are dominating in such kind of transport phenomena. Then one of the surface induced phenomena is the creation of Electric Double Layer, then Surface Inhomogeneity. You can have different material in the surface compositions and also say roughness of even a molecular dimension is also can a change the scenario.

And also in microfluidics will deal with the complex Fluids means is a mixture of suspension of colloid particles, sub particles. So this kind of microparticles so that becomes a Complex Fluids and also this since we are talking about the Aqueous Media or Ionized Fluids. So it will have the multicomponent fluid is a Miscible Fluids. So that is why we can say this in this situation it will complex fluid.

Now this electric field driving forces are two kind of situation three kind of phenomena arises is the Electroosmosis, Electrophoresis and also the Joule Heating because of the movement of the irons there will be a heat generation and that that is Joule Heating We will talk later on about this Electroosmosis is basically is the motion of Ionized liquid with relative to the stationary charge surface by an applied electric field.

And Electrophoresis is the motion of the charged surface and macromolecules relative to the stationery liquid by an applied electric field.

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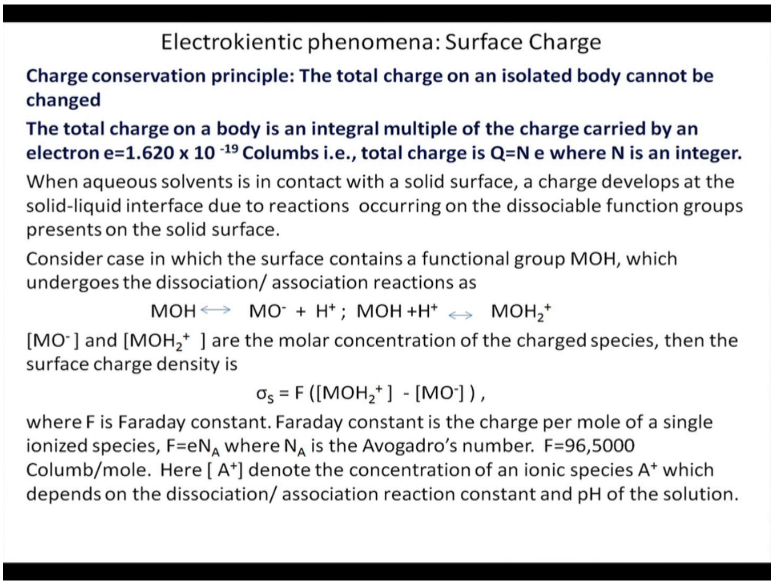

Electrokientic phenomena: Surface Charge

Charge conservation principle: The total charge on an isolated body cannot be changed

The total charge on a body is an integral multiple of the charge carried by an electron $e=1.620 \times 10^{-19}$ Columbs i.e., total charge is $Q=N e$ where N is an integer.

When aqueous solvents is in contact with a solid surface, a charge develops at the solid-liquid interface due to reactions occurring on the dissociable function groups presents on the solid surface.

Consider case in which the surface contains a functional group MOH, which undergoes the dissociation/ association reactions as

$$MOH \longleftrightarrow MO^- + H^+ ; \; MOH + H^+ \longleftrightarrow MOH_2^+$$

$[MO^-]$ and $[MOH_2^+]$ are the molar concentration of the charged species, then the surface charge density is

$$\sigma_S = F([MOH_2^+] - [MO^-]) ,$$

where F is Faraday constant. Faraday constant is the charge per mole of a single ionized species, $F=eN_A$ where N_A is the Avogadro's number. F=96,5000 Columb/mole. Here $[A^+]$ denote the concentration of an ionic species A^+ which depends on the dissociation/ association reaction constant and pH of the solution.

Now how the surface charge develops? Now here, now will be talking about the few things about the electrostatic phenomena. Now this electrostatics phenomena are governed by this few principles, one is the charge conservation principle, the total charge of an isolated body cannot be changed. Then another important principal is the total charge on a body is an integral multiple of the charge carried by an electron that is also referred as the elementary charge given by this, total charge will be some Q into Ne, and Where N is an integer so it cannot have a kind of fraction or something.

Now what happen is that, when aqueous solvents or ionized fluids is in contact with a solid surface, a charge develops static charge will develop at the interface between the liquid and fluid interface due to the, Now these are occurred because of the adsorption dissociation reaction has governed by this equation, Say in example cited over here so this reaction say if the solid liquid interface is have a functional group is MOH, it consists of a functional group is MOH so in presence of the H + ions and it will create this kind of Hans MO - and MOH 2 + .

Now this H + ions are related to the pH of the electrolyte and also the ionic concentration of the electrolyte also can influence. Now the rate of reactions and all the that depends on the reaction constants. So all the details I have omitted over here, so any book basic electrokinetics book and we will discuss about this kind of reactions. So basically what we want to show from here the how this charge is produced at the interface.

So this association dissociation reactions so what we have is a generation of negative ions and positive ion, so if we denote this as the concentration molar concentration of the charged species then surface charge density is net amount of concentration of positive and negative ions. So this is the way it is written Sigma S where F is the Faraday constant, Faraday constant is basically e into NA, NA is the number of molecules and e is a electron charge.

So this is N A is Avogadro's number so Faraday constant is the charge for mole of a single ionized species. So this is it a net concentration, so it is in 2F that is the way it is defined as the charge density, Because it is about volume so per unit area so Sigma S is the here is the surface charge density. So we have denoted hear A + the concentration of ionic species, A by this bracket [ ] so obviously this depends on the reaction constant and pH of the solution, so this give an idea that how is surface charge develops.

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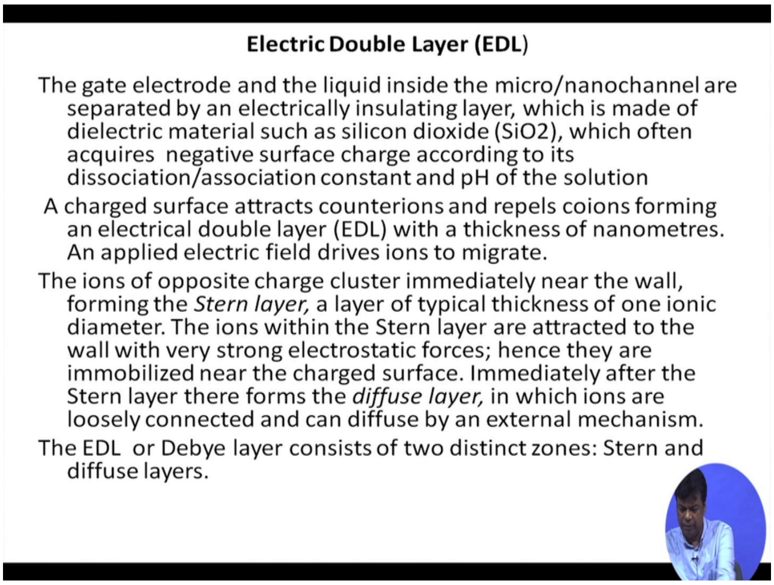

Electric Double Layer (EDL)

The gate electrode and the liquid inside the micro/nanochannel are separated by an electrically insulating layer, which is made of dielectric material such as silicon dioxide (SiO2), which often acquires negative surface charge according to its dissociation/association constant and pH of the solution

A charged surface attracts counterions and repels coions forming an electrical double layer (EDL) with a thickness of nanometres. An applied electric field drives ions to migrate.

The ions of opposite charge cluster immediately near the wall, forming the *Stern layer,* a layer of typical thickness of one ionic diameter. The ions within the Stern layer are attracted to the wall with very strong electrostatic forces; hence they are immobilized near the charged surface. Immediately after the Stern layer there forms the *diffuse layer,* in which ions are loosely connected and can diffuse by an external mechanism.

The EDL or Debye layer consists of two distinct zones: Stern and diffuse layers.

Now what will happen is that, when there is a so negative amount anomaly this electrodes or the channel interface are normally made up of SiO2 silicon dioxide kind of material so this will generate a vessel create a negative charge on the surface. Okay so this negative surface charge what will do is it will attract positive surface charge positive ions from the deliver sorry not deliver.

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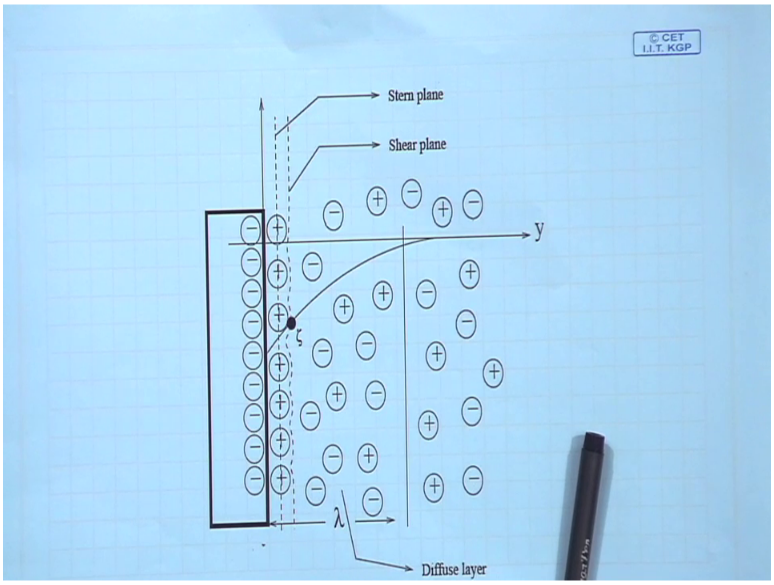

So, Now if I show in this figure, so this is the surface charge develops which is negative and it will attract positive ions from the aqueous media, so there will be a situation like this, so then this positive electron negative ions and in that process. There will be a layer near the surface where there will be a more number of unbalanced charged ions and compared to the bulk or core region.

Now this layer can be divided into two. One is very close to the surface that is the one is referred as the Stern layer and this is dimension of this length of this is of molecular dimension few Armstrong, and there is another layer above which is a diffuse layer where the ions are loosely attracted loosely connected so it can mobile okay.

So this is referred as the diffuse layer, so in total this is referred as the electric double layer or Devilier, Devile is the scientist who first discuss about this, so this total is referred as the Devilier. Another important thing is that the potential drop from the surface to the edger of this Devilier is also called the slip plane, so is referred Zeta potential okay. As it is drawn over here now what will happen is that since the ions are mobile over here save some external mechanism is applied.

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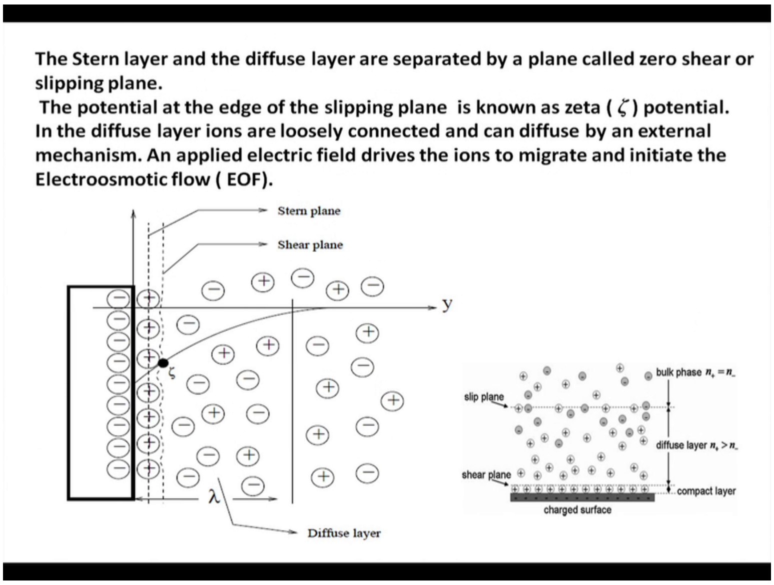

The Stern layer and the diffuse layer are separated by a plane called zero shear or slipping plane.

The potential at the edge of the slipping plane is known as zeta (ζ) potential.

In the diffuse layer ions are loosely connected and can diffuse by an external mechanism. An applied electric field drives the ions to migrate and initiate the Electroosmotic flow (EOF).

So if there is an external mechanism applied so okay, whatever was here so then what will happen? this positive ions will get attracted to the negative electrodes, say so if I apply say if I take a cathode anode here and there is a cathode here so that is called this is anode this is cathode. Now so this is the Devilier, so now if there is a voltage electric field is applied that is creating a voltage drop.

So this in the Devilier whatever the surplus positive ions it will be attracted towards the negative electrodes and when it will be have a Coulomb attractive force so and in that process it will generate a flow over within this. Because it will drag it is inside the liquid media, so it will drag the fluid along with them and there will be a flow generation.

So this is basically is the principle of Electroosmotic flow in a say capillary or channel regions so under a electric field, so here we are the driving mechanism under an electric field and basic principle is the formation of the Devilier at the charged surface okay.

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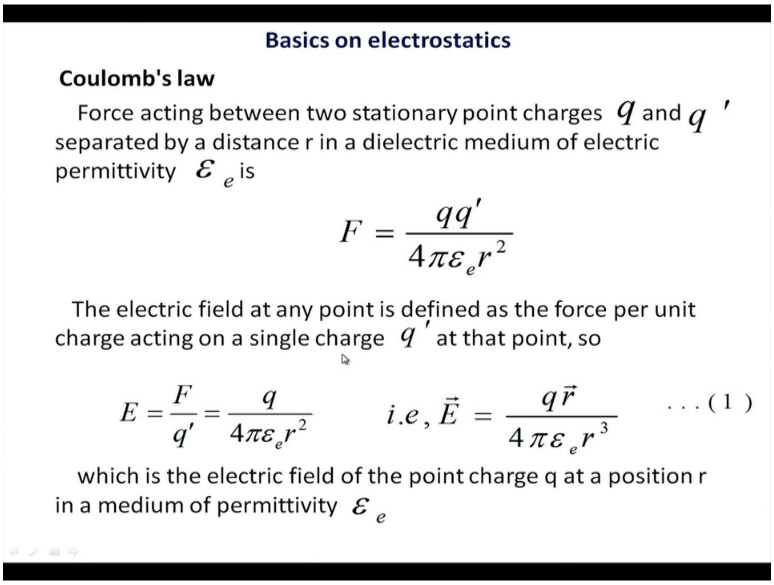

Basics on electrostatics

Coulomb's law

Force acting between two stationary point charges q and q' separated by a distance r in a dielectric medium of electric permittivity ε_e is

$$F = \frac{qq'}{4\pi\varepsilon_e r^2}$$

The electric field at any point is defined as the force per unit charge acting on a single charge q' at that point, so

$$E = \frac{F}{q'} = \frac{q}{4\pi\varepsilon_e r^2} \qquad i.e, \vec{E} = \frac{q\vec{r}}{4\pi\varepsilon_e r^3} \qquad \ldots(1)$$

which is the electric field of the point charge q at a position r in a medium of permittivity ε_e

Now so we are intended to do the modeling of this kind of situations, so before that we have to understand the electrostatic Terminology and the how we quantify the effects of charges and other things, So first we talk about the Coulomb's law so suppose there are two point charges q and q dash are placed at a distance permission distance say by r and in a medium which have a permittivity Epsilon e.

Then the force acting interacting force between this q and q dash is governed by this equation this is called Coulomb's law. Okay r is the separation distance now it define the electric field at any point as the force per unit charge on that works at this, if I consider the q is not at a origin so the electric field we can write as this force per unit charge and given by this, which I can consider in vector form if r vector r by this one this equation one.

So now this is Epsilon e is defined as the permittivity of the medium now before we talk about the permittivity, so now permittivity roughly we can say is the resistance created by the medium to the electric field. So if it is in vacuum so we would have had the electric field and if there is a medium in between the space on which the charges are placed so that has created a resistance which is measured by the permittivity.

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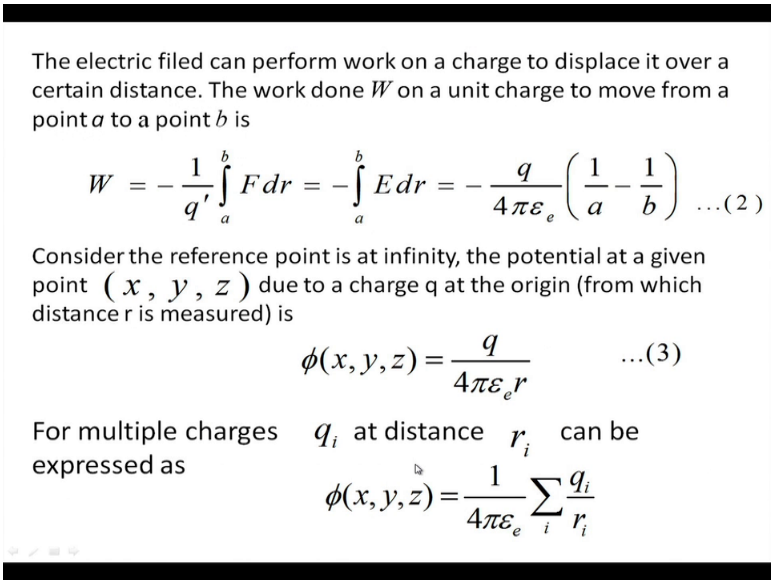

The electric filed can perform work on a charge to displace it over a certain distance. The work done W on a unit charge to move from a point a to a point b is

$$W = -\frac{1}{q'}\int_a^b F\,dr = -\int_a^b E\,dr = -\frac{q}{4\pi\varepsilon_e}\left(\frac{1}{a}-\frac{1}{b}\right) \quad \ldots(2)$$

Consider the reference point is at infinity, the potential at a given point (x, y, z) due to a charge q at the origin (from which distance r is measured) is

$$\phi(x,y,z) = \frac{q}{4\pi\varepsilon_e r} \qquad \ldots(3)$$

For multiple charges q_i at distance r_i can be expressed as

$$\phi(x,y,z) = \frac{1}{4\pi\varepsilon_e}\sum_i \frac{q_i}{r_i}$$

Now this force can work, so can perform work so the work W if I say in dragging a unit charge from point A to point B so that can be written as F dot dr Basically here it should be if we write in a vector format it is F dot dr so this is equal to a lot E dot dr should so what I get is why integration is this term equation 2.

Now if I consider that the point is at infinity so and then I define this is the potential electrostatic potential x, y, z in the work from dragging the point charge from infinity to a point x, y, z so one around electric field due to a charge q is placed at the origin is given by this. So these we call as a electric potential created by the electric field by define this way.

Now if there are number of point charges at different positions ri if I call the position vectors and q i are the number of point charges so then the electric potential combined one will be in the same principle we can write is this way in fact we can generalized to the Coulomb's law for finding the force a summation of all this Columbic Inverse Square Law Firm.

And we get a charge electric potential covered by this equation and other important thing from here is the work done by the electric interacting force electric force is independent of the path joining between the two points A and B so it is a material of how you connect the two points A and B so that means this is a conservative field.

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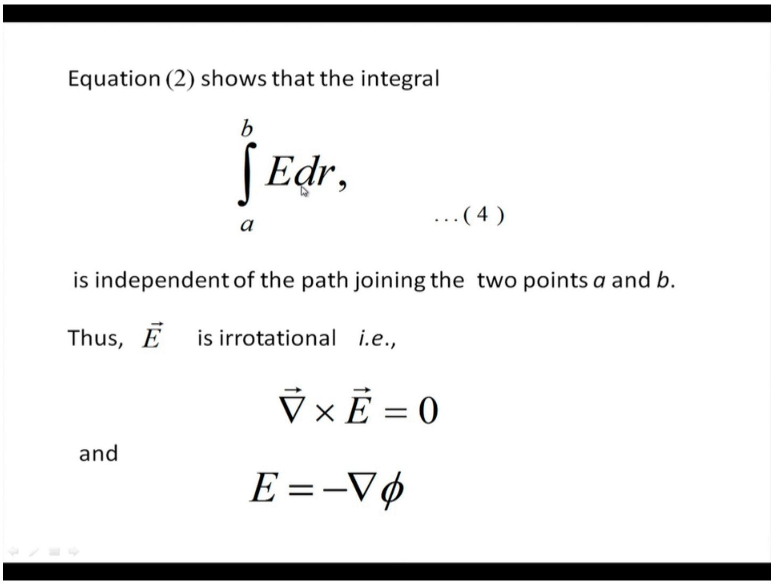

Equation (2) shows that the integral

$$\int_a^b E dr, \qquad \ldots(4)$$

is independent of the path joining the two points *a* and *b*.

Thus, $\vec{E}$ is irrotational *i.e.*,

$$\vec{\nabla} \times \vec{E} = 0$$

and

$$E = -\nabla \phi$$

Conservative field means we can write that this is equal to – Grad Phi is a scalar quantity and also which shows that it is a irrotational that means call of the electric field E at any point is zero so this suggests that we can associate a scalar quantity Phi which we have already defined as a gradient of Phi we can referred as the electric field and this is a minus because that if I represent in terms of work so that – appears. So in every point on the space we have always that electric field is irrotational.

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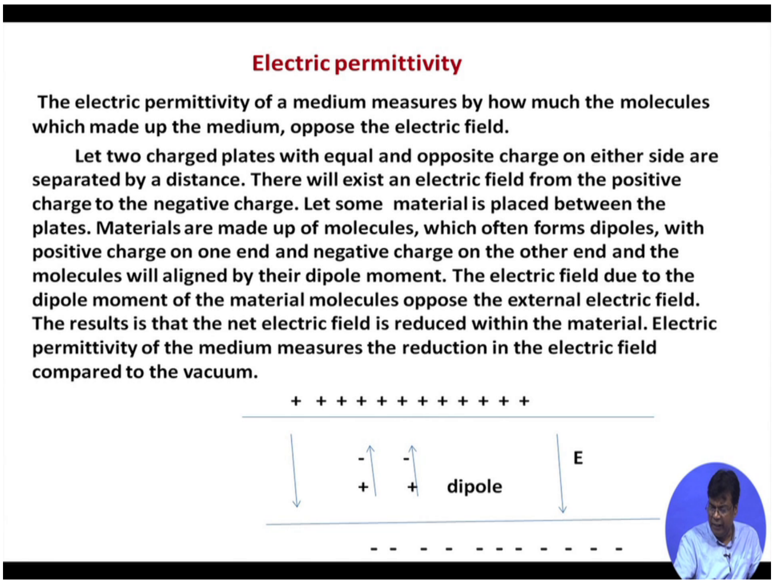

Electric permittivity

The electric permittivity of a medium measures by how much the molecules which made up the medium, oppose the electric field.

Let two charged plates with equal and opposite charge on either side are separated by a distance. There will exist an electric field from the positive charge to the negative charge. Let some material is placed between the plates. Materials are made up of molecules, which often forms dipoles, with positive charge on one end and negative charge on the other end and the molecules will aligned by their dipole moment. The electric field due to the dipole moment of the material molecules oppose the external electric field. The results is that the net electric field is reduced within the material. Electric permittivity of the medium measures the reduction in the electric field compared to the vacuum.

Now permittivity how you define the electric permittivity, Now electric permittivity is a case;

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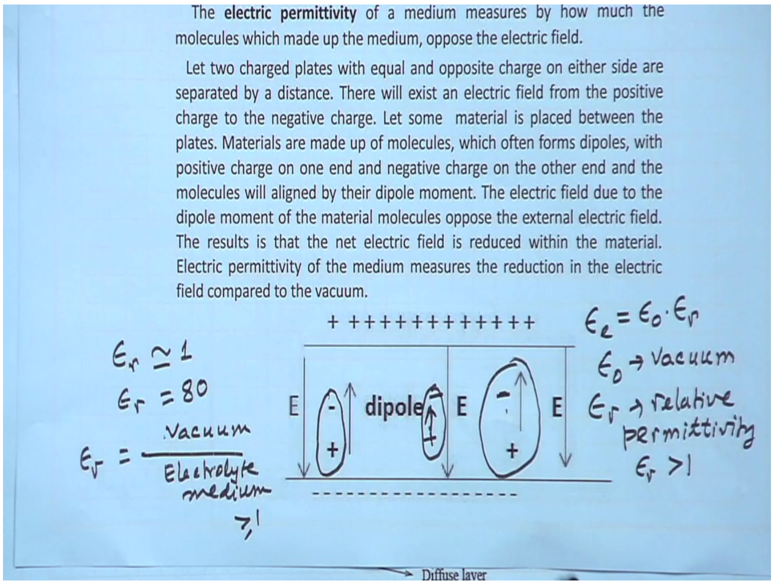

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So when you have a medium over here, say suppose you have two charged plates positively charged and negatively charged and there is a medium and so there will be electric field will be generated this mediums is composed of some water or something. So that will from a dipole to oppose the medium is made up of molecules of course so they will form it, each molecule will form a dipole to oppose the electric field.

So that means we will have a situation as this kind of things minus plus they will arrange themselves so there will be a electric field induced by this dipoles which opposes the electric field developed by this charges okay. Now so obviously the electric field generated by this charges are not the same so and it depends on what type of medium you are considering so normally this permittivity is represented as Epsilon 0. Epsilon r Epsilon 0 is the permittivity of vacuum.

And this Epsilon r greater than 1 and Epsilon r can be defined as the force when a two charges one charges are placed in vacuum so whatever the force that two point charges experienced and now if I place this point charges in the medium so whatever the force they acquired so that is what is written over here.

So the same separation distance so that is the thing is referred as the electric permittivity so obviously electric permittivity is always will be greater than equal to one so for gas here we can have the permittivity as one for water this is the permittivity is generally taken so that means that vacuum electric permittivity should be multiplied with the ratio of which is dimensionless.

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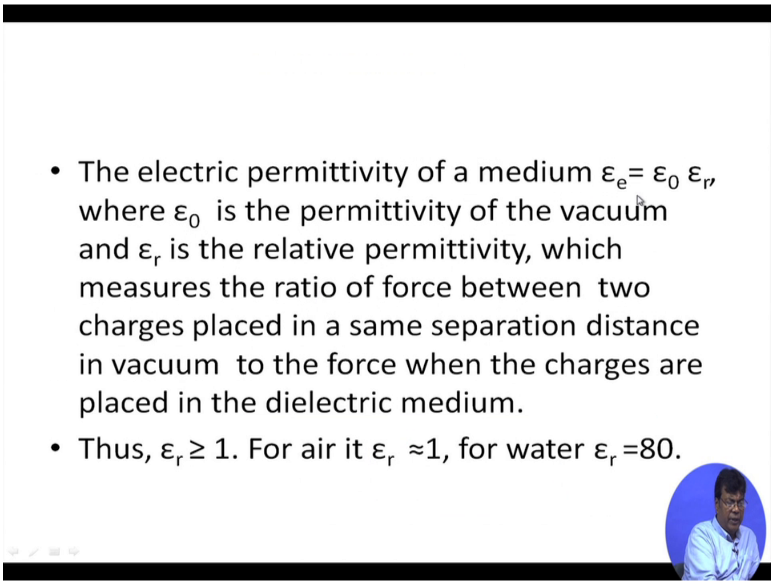

- The electric permittivity of a medium $\varepsilon_e = \varepsilon_0\ \varepsilon_r$, where ε_0 is the permittivity of the vacuum and ε_r is the relative permittivity, which measures the ratio of force between two charges placed in a same separation distance in vacuum to the force when the charges are placed in the dielectric medium.
- Thus, $\varepsilon_r \geq 1$. For air it $\varepsilon_r \approx 1$, for water $\varepsilon_r = 80$.

Now what I was just talking about so this is the thing is written in words over here so this is the way we define the permittivity so obviously it shows that the electric field whatever is developed in a region in a medium will be lowered compared to the electric field developed in the vacuum.

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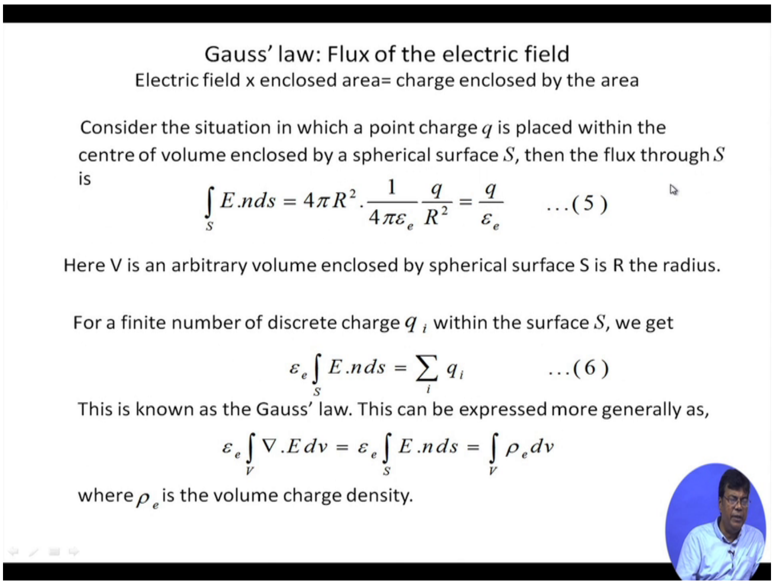

Gauss' law: Flux of the electric field

Electric field x enclosed area= charge enclosed by the area

Consider the situation in which a point charge q is placed within the centre of volume enclosed by a spherical surface S, then the flux through S is

$$\int_S E.nds = 4\pi R^2 . \frac{1}{4\pi\varepsilon_e}\frac{q}{R^2} = \frac{q}{\varepsilon_e} \qquad \ldots(5)$$

Here V is an arbitrary volume enclosed by spherical surface S is R the radius.

For a finite number of discrete charge q_i within the surface S, we get

$$\varepsilon_e \int_S E.nds = \sum_i q_i \qquad \ldots(6)$$

This is known as the Gauss' law. This can be expressed more generally as,

$$\varepsilon_e \int_V \nabla .E dv = \varepsilon_e \int_S E.nds = \int_V \rho_e dv$$

where ρ_e is the volume charge density.

Now what do you need to have a situation to get a equation for the electric field now one of the law is the Gauss law which gives the electric field into enclosure. This is basically the way one can be defined as low as a charge enclosed by the area you have a church point charges Q which is at some point Origins so latest construct a sphere volume be enclosed by surface S of radius R.

So now we meet their flocks of the electric field and electric field will be generated by the point charge so their flocks of the electric field will be measured by the surface integral. E dot nds, okay n is the outward normal to the surface okay. So n will considered as outward normal to the surface so E dot nds is measured over the whole surface area is measured the flux so that the electric field define already.

So this is the surface area because he is equal to Capital also you get the flux as Q by Epsilon E so now this is integration now if you have number of charges apart from this Q so that can be we can generalize this thing as the Sigma of qi now if we apply the Gauss divergence theorem. That means we Convert the surface integral to volume integral so what we get is this situation that is how we convert to go in the surface integral to the following integral given by this way.

So that is he now there is the divergence of E dv equal to know this is the integrated over the whole fall you so this Rho is called the volume charge density so this gives you know what we have here sorry I should have son them here itself now we here choose obituary volume. And enclosing the charged so and the Rho E is the volume charge density whatever the net amount of charge within the volume.

So that is because it is integrated has a volume integral, so V is obituary this is happening for any choice of which so we can write this as this form – Epsilon e into Phi = Rho e because if I write the divergence of equal to.

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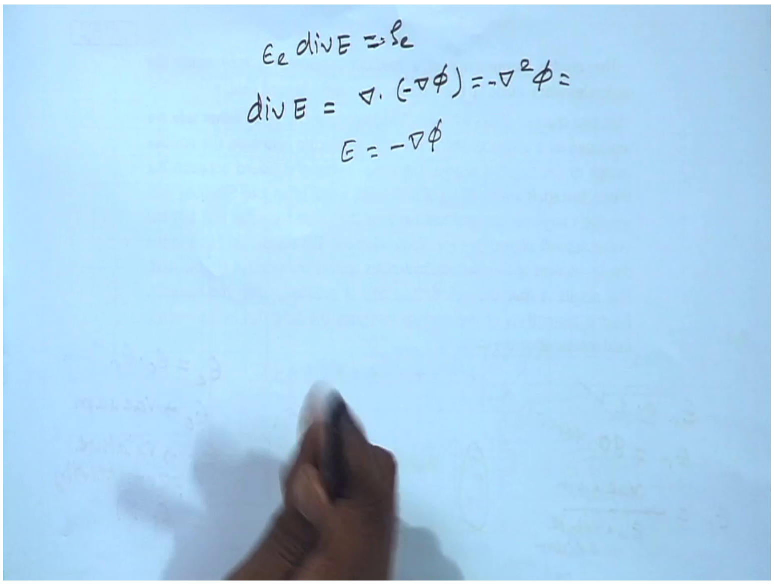

$$\epsilon_e \, \mathrm{div}\, E \Rightarrow \rho_e$$

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

$$E = -\nabla\phi$$

Basically this is great Phi already have define what is the we have already is Rho e what was there Rho e Epsilon, there was an over here Epsilon. So now what we have is Del = Phi, and there is a minus, minus will be here because this is e = - Grad Phi, so if you get this relation so what you find is that Del to Phi = - Rho e by Epsilon e is permittivity of the medium so we get relation for the electro electric potential with volume charge density.

This equation is referred as the Poisson equation, this is a Poisson equation of non homogeneous equation and this is Poisson equation and this governs the electric potential this Poisson equation for the electric field.

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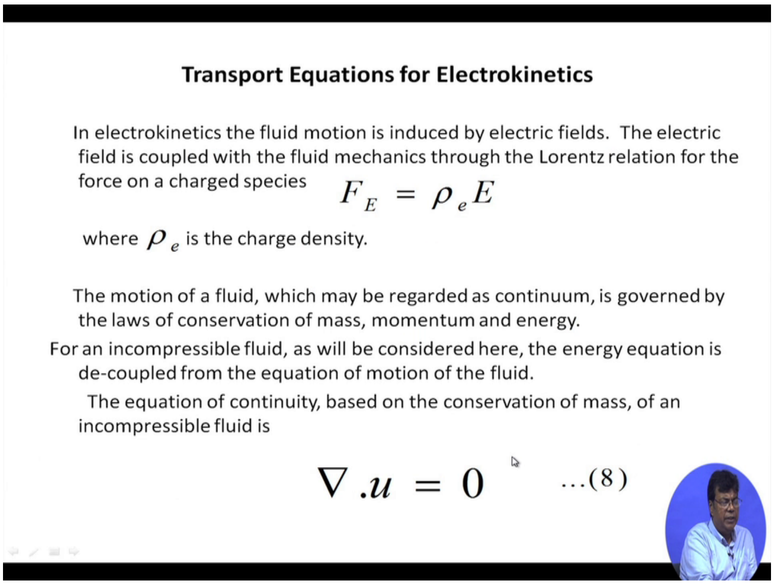

Transport Equations for Electrokinetics

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

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

So next will talk about the transport of transport equation for Electrokinetics. Now in the aqueous media or ionized fluid what you have is a ions are dissolved in the medium that maybe someone dissolved are there other multicomponent situations because this is for example H2O and NaCl solution so after dissociation you will have Na + and CL - ions and the uncharged H2O molecules and all.

Now if there is a electric field as we discussed before so there will be a flow will generated then ions will also experience electrostatic force, because of the Columbic attractions and all so that way there will be a transportation of ions so this transportation of ions we create an electric field so we need to know the how the distribution of the ions, as well as we need to know the fluid flow also.

First we talk about the equation for fluid flow down how it is connected now we are considering fluids which have a charge density Rho e. So because of the presence of this volume charge density Rho e, so the fluid, if I considered a volume element within the fluid, so fluid will experience a force electrostatic force which is also governed by the Lorentz relation is governed by this Rho e, e is the electric field at elementary volume.

So this is the electric body foods will be experienced by the following elements is governed by this Rho e, now so that means we cannot isolate this situation the transport of fluid from the transport of ions.