Molecules in Motion

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Lecture - 33
Molecular Motion in Liquids (Contd.)

Welcome to another lecture on Molecules in Motion. So, what we are going to discuss today is summarising what we have done previously.

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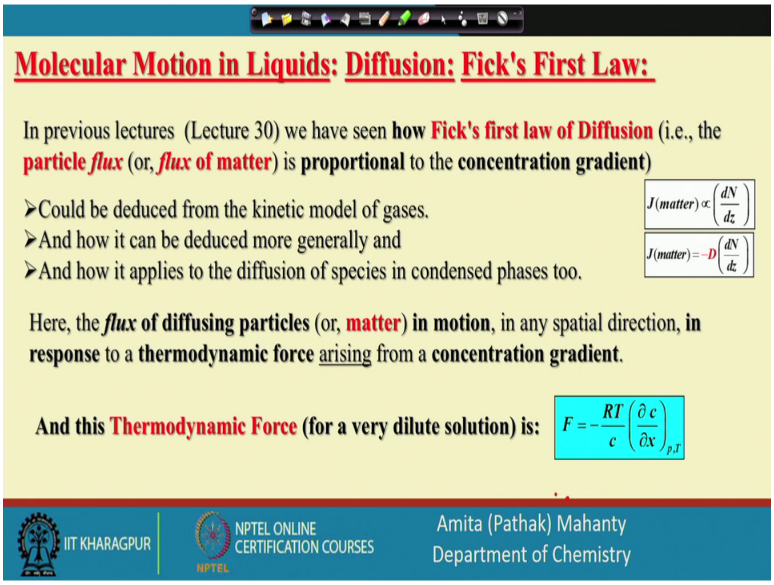

Molecular Motion in Liquids: Diffusion: Fick's First Law:

In previous lectures (Lecture 30) we have seen **how Fick's first law of Diffusion** (i.e., the **particle *flux*** (or, ***flux* of matter**) is **proportional** to the **concentration gradient**)

- Could be deduced from the kinetic model of gases.
- And how it can be deduced more generally and
- And how it applies to the diffusion of species in condensed phases too.

$$J(matter) \propto \left(\frac{dN}{dz}\right)$$

$$J(matter) = -D\left(\frac{dN}{dz}\right)$$

Here, the ***flux* of diffusing particles** (or, **matter**) **in motion**, in any spatial direction, **in response** to a **thermodynamic force** arising from a **concentration gradient**.

And this Thermodynamic Force (for a very dilute solution) is: $F = -\frac{RT}{c}\left(\frac{\partial c}{\partial x}\right)_{p,T}$

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In the 30th lecture we had talked about Fick's first law and since this is the basis of whatever we are going to discuss now or in the forthcoming lectures. So, I would like to recapitulate what we had talked about in the lectures previously. So, in previous lecture particularly one which is the 30th one, we had seen how Fick's law of diffusion, we are talking about diffusion of particles, here essentially we are talking about particles which were previously taken as charged. And, now we are going to look into how they are going to behave and under certain conditions if they were not charged or not under electric field.

So, what we had seen in 30th lecture was Ficks law of diffusion. That means, migration of ion through a medium where the particle flux, flux can whenever we talk about flux as particles, we are talking about movement of matter. So, it can be either represented as a flux of matter or it can be represent as a flux of particles. So, both of them is actually going to mean the same. Sometimes the matter or particles will be represented in terms of the number of molecules, sometimes in terms of the number of the amount of the material that can be expressed in concentration.

So, the flux of particle or matter from according to first law of diffusion of Fick's first law of diffusion is proportional to the concentration gradient and how this Fick's first law of diffusion is proportional to the concentration gradient could be deduced from the kinetic model of gases which was taken much earlier. And, how it can be deduced more generally was what we had done in the 30th lecture and how it can be applied to diffusion of species which are in the condensed phase.

So, condensed phase means it is going to be the solid states, solid particles in liquid medium. So, here what we are looking into is, we are looking to that flux of the diffusing particles that is in motion in any spatial direction x y z; in response of a particular thermodynamic force and this thermodynamic force which we had derived in the last class was due to the concentration gradient. And, for a very dilute solution, the thermodynamic force which was supposed to be existing for the particles to move from one region to the other. When we talk about Fick's law of diffusion, we are essentially talking from of moving of the particles or the molecules or the ions from a high concentration to a low concentration region.

Here we are not going to talk about any charge particle. We are going to talk about any particle in general. So, the thermodynamics force which was derived in the last class for a very dilute solution where the conditions are limiting conditions, where you have the activity coefficients to be 1 and the activity approaches the concentration unit. So, when the activity coefficient is 1 and the activity is approaching concentration that we are calling as almost a dilute solution, a very dilute solution or ideal solution. For that the thermodynamic force which we derived in the last class was given by this is the thermodynamic force which is equal to RT by c and the gradient in concentration at a given temperature and pressure.

What we had talked about in the last class was this force is not essentially a force per se, but it is a driving force towards having back towards the possibility or towards the conditions of towards the hunt of the maximum entropy for the system. So, when we are approaching system is according to second law. The system is supposed to be going for the highest order of disorder and only then we have a system which is at equilibrium or at stable. So, this is the thermodynamic force which we had derived which was a negative gradient of the concentration at a given temperature and pressure condition.

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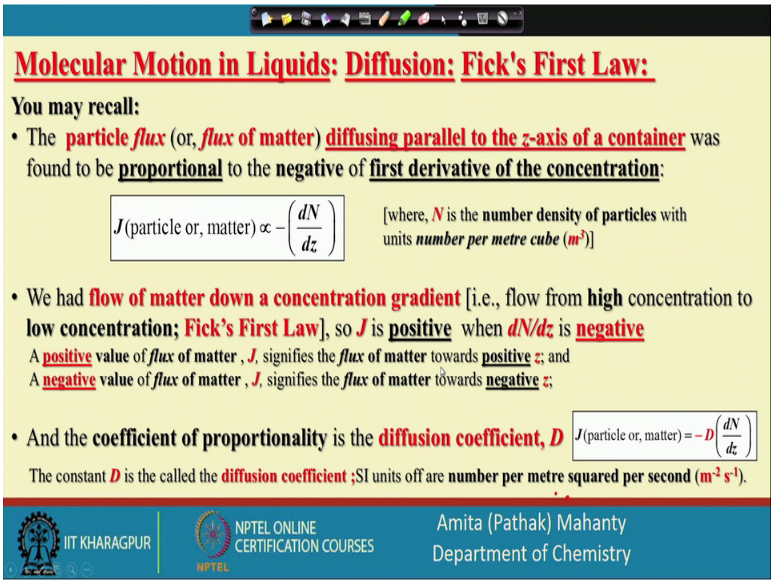

Molecular Motion in Liquids: Diffusion: Fick's First Law:

You may recall:

- The **particle *flux*** (or, ***flux* of matter**) **diffusing parallel to the *z*-axis of a container** was found to be **proportional** to the **negative** of **first derivative of the concentration**:

$$J\text{(particle or, matter)} \propto -\left(\frac{dN}{dz}\right)$$

[where, *N* is the **number density of particles** with units ***number per metre cube*** (*m^3*)]

- We had **flow of matter down a concentration gradient** [i.e., flow from **high** concentration to **low concentration; Fick's First Law**], so ***J*** is **positive** when ***dN/dz*** is **negative**

A **positive** value of ***flux* of matter** , ***J***, signifies the ***flux* of matter** towards **positive** *z*; and
A **negative** value of ***flux* of matter** , ***J***, signifies the ***flux* of matter** towards **negative** *z*;

- And the **coefficient of proportionality** is the **diffusion coefficient, *D***

$$J\text{(particle or, matter)} = -D\left(\frac{dN}{dz}\right)$$

The constant ***D*** is the called the **diffusion coefficient** ;SI units off are **number per metre squared per second** (**m^{-2} s^{-1}**).

So, if you recall what was how we define as the flux of particle diffusing through say any axis said of a container which was found to be the negative gradient of the number of particles or the number of the concentration. Here if we talk about the number of particles, then we say the flux of particle which is flowing through the medium is proportional to the gradient in the number density, ok. We are talking about z direction.

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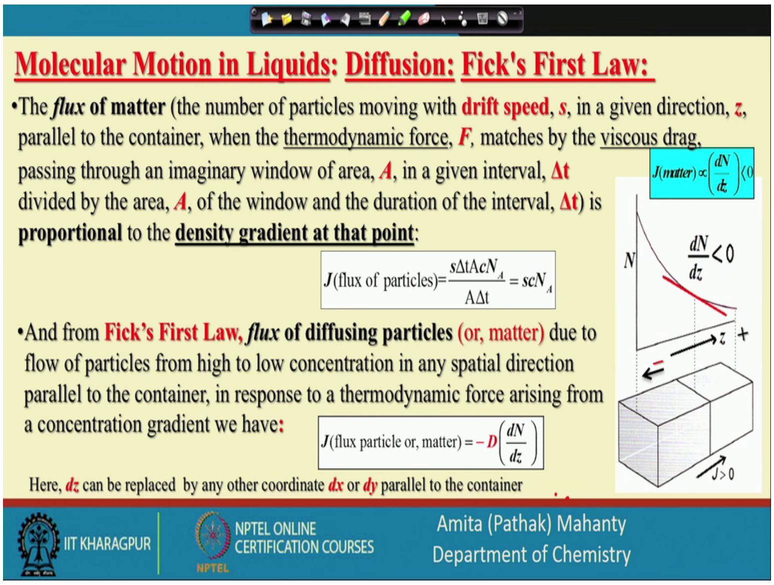

Molecular Motion in Liquids: Diffusion: Fick's First Law:

- The ***flux* of matter** (the number of particles moving with **drift speed**, *s*, in a given direction, *z*, parallel to the container, when the thermodynamic force, *F*, matches by the viscous drag, passing through an imaginary window of area, *A*, in a given interval, **Δt** divided by the area, *A*, of the window and the duration of the interval, **Δt**) is **proportional** to the **density gradient at that point**:

$$J(\text{flux of particles}) = \frac{s\Delta t A c N_A}{A\Delta t} = scN_A$$

- And from **Fick's First Law, *flux* of diffusing particles** (or, matter) due to flow of particles from high to low concentration in any spatial direction parallel to the container, in response to a thermodynamic force arising from a concentration gradient we have**:**

$$J(\text{flux particle or, matter}) = -D\left(\frac{dN}{dz}\right)$$

Here, *dz* can be replaced by any other coordinate *dx* or *dy* parallel to the container

$$J(matter) \propto \left(\frac{dN}{dz}\right) \langle 0$$

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This direction z is actually if you can see this, if you can see this diagram, you can see this diagram I have a region where this N is high here, this is the axis when you have the number density and this is the axis where you have the spatial coordinate. If we are taking this as z, we are taking this as z assuming this is the container and we are talking about a condition where I have a window through which the particles are passing and I am having observation or we are looking at that particular window.

When we are talking about a window, we are essentially talking about a point where you have the origin across that window you will have minus and plus z. Minus z is this direction and plus z is this direction. If you can see this, if I imagine this as the window, then if I am moving towards this side I am moving towards the positive z and if I am moving towards this side, I am moving towards the negative side, clear.

So, what we are having here if you just have a look, closer look at this. I can easily represent this z by x and say this is my x coordinate, ok. So, if any direction if I say this is the z, I define this as z, but I can take this as x as well, ok. I can say represent this as y as well. What I want to say is along the direction which we are moving is parallel to the container, we are looking into, so the parallel conditions apply and the window is the place where you have the centre of the axis. From that window, you can either go towards plus of that axis or minus of that axis and what does it essentially mean, let us go into what we are meaning.

So, we have this flux of particle, we have a flow of matter down a concentration gradient. According to Fick's law, the particles are going to move from high concentration to a low concentration region and J, if J has to be positive, then what we have? We have the slope has to be negative. The slope of number of particles with distance, this distance is any axis in spatial coordinate xyz parallel to the container we are watching, ok.

So, what do we mean by saying this, the flux is positive when the gradient in the number density or the number of particles or the concentration of particles along a particular axis is negative. See the flux is the number of particles. So, the number of particles moving through a window at a given per through a given area at a given unit time cannot be negative. That term cannot be negative because you are counting the number of particles. So, particles cannot be negative.

So, what does a negative or a positive sign mean? The negative and positive sign mean that if I have a positive value of flux, that means I am moving towards the positive direction z, ok. If I have a negative flux, value of flux what does it signify? It does not signify the particles are negative; it signifies that the flux of matter is moving from this window which we have seen taken as the origin of the coordinate spatial axis from towards the negative side of that.

So, if you look at that if you look at that, what I mean is when is going to be, when we are saying that the flux is going to be positive? Flux is going to be positive when we are moving this is the origin, when we are moving towards the positive z direction, when we are moving towards the positive z direction. If you see if you are moving from the positive z direction, then the slope of this curve, the slope of this curve is always negative.

How is the slope negative or how do we calculate the slope? The y coordinate y final minus y initial divided by x final x initial. So, the distance which we are saying taking is increasing x direction, that means the z denominator is always increasing final will be higher than the initial value because we are moving towards this side, we are gaining the distance. So, the final distance will be always more than the initial one. So, the denominator will be positive, but what happens when you are having the number of particles, you see the number was higher here and you are having a lower value here.

So, when we are moving towards x, we are gaining in the distance. So, the denominator of the delta y by delta x denominator of thus of this slope is going to be positive, but the number you see, the final number is going to be always less than the initial number.

So, since the final number is going to be less than the initial number, the dN value will be always negative. So, if dN value is negative, then the slope which is given by dN by dz will be negative. So, when we are moving towards the positive z direction and we are getting we are saying that the flux is positive, then the slope of this is supposed to be negative, and since it is a negative gradient of the concentration, so the flux becomes positive, ok. So, what we have here? So, from the coefficient from the proportionality equation which we have, we have say we have taken that the flux of particle is a negative gradient of the concentration or number density. This negative gradient is always going to be a positive term because this the ratio will become a positive term only when this becomes negative.

So, what we have seen when you are moving towards the positive z direction, then we are getting a flux as positive because the slope is negative and then, the whole thing comes positive. So, the flux becomes positive, then we are going from a higher region of concentration of particles to a region where the concentration particles are lower, right. So, if I keep this relationship, the flux of particle or matter is proportional to the number, gradient in number density, negative gradient in number density, then I can put a proportionality constant and this proportionality constant makes the equation something like this; the flux of particle equal to D into the concentration gradient or number gradient or particle number density gradient.

So, this is what we call as the diffusion coefficient and the diffusion coefficient can be the number of particles or number of moles whatever the in concentration per square per meter square per second, that is the unit we have. So, what we have now? You can see that if from this diagram you can see that this is the window we have and we are moving towards the positive direction of x or we can say this is nomenclature as z. So, we can say take it, z it does not matter whether we say whether we say xyz. It is actually a direction which is parallel to the container. If we designate the container to be parallel in the x axis, we can write it in x, it is any along any one of the spatial coordinates, ok. So, it is not necessarily that it has to be z, it can be x, it can be y, any one direction which is parallel to the container.

So, if you remember how do we define the flux and this is what we had done. When we are doing the kinetic theory, when we are talking about the flux of matter, we are talking about a particle moving with the speed, certain speed which we call that drift speed which is the steady speed terminal velocity or terminal speed in any particular direction xyz that is parallel to the container. When the thermodynamic force mass, this drift speed is obtained when this thermodynamic force matches the viscous force and only then, we attain the speed, the drift speed. So, they are moving in the drift speed s. When the thermodynamic force is balanced by the viscous force of the medium passing through a imaginary window, this is the imaginary window of area a at in time delta t.

So, the total number of particles which is the number, total number of particles passing through the window if I want to find out the flux, I have 2 divided by the area into the delta time. So, what is the total number of particles which is passing? It is whatever is contained in a volume element. Suppose it is moving with this speed s and in time delta t, so s into delta t is the distance, from Newton's law speed equal to distance by time. So, distance into time should be giving you the distance; the speed into time should be giving you the distance.

So, this distance into the area gives you the total volume element. So, the total volume element if it is moving towards distance of s delta t here, then the total volume element along this will be s delta t into A. So, in all the particles contained in the whatever concentration unit you are taking if you are taking in molar concentration, total number of particles which are there in the container will be given is given as c into the Avogadro number that gives you the number density, ok. So, c c into Avogadro number is the total number of particles contained in the volume element. This delta s delta t into s into a into the number concentration number, number density which is the molar concentration into Avogadro number. Molar concentration is the total moles contained in the total volume of the container into the Avogadro number, gives you the number density. This divided by the area into the time delta t gives you the flux, ok.

So, the flux is nothing, but the drift speed into the number density. This is moles per unit volume of the container into the Avogadro number and from Fick's first law what we have the flux of diffusing particle or matter due to flow of particles from high concentration to low concentration region in a special direction parallel to the container in response of the thermodynamic force arising out of the concentration gradient will be having a flux of say equal to J equal to d into the number gradient or number density gradient, ok. So, we have you see two values of J 1 from the diffusion and this is from the Newton's Kinetic theory explanation. So, these two J values, we need to compare.

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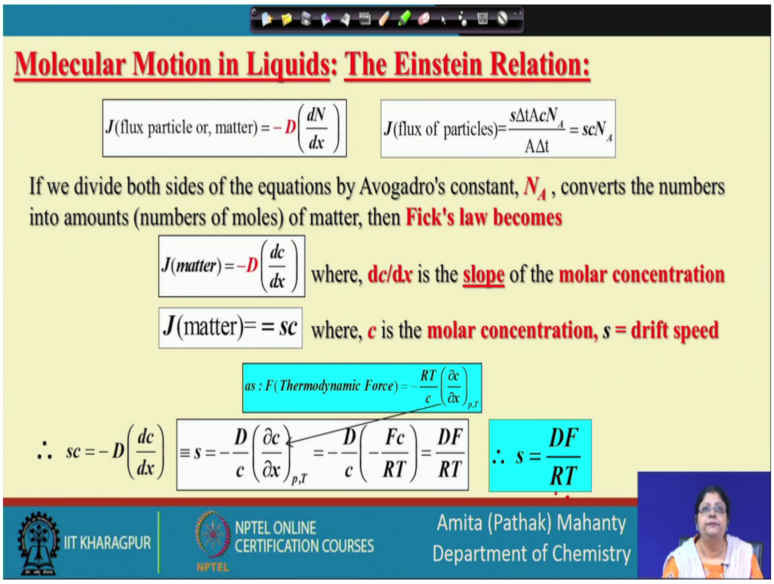

Molecular Motion in Liquids: The Einstein Relation:

$$J(\text{flux particle or, matter}) = -D\left(\frac{dN}{dx}\right)$$

$$J(\text{flux of particles}) = \frac{s\Delta t A c N_A}{A\Delta t} = scN_A$$

If we divide both sides of the equations by Avogadro's constant, N_A, converts the numbers into amounts (numbers of moles) of matter, then **Fick's law becomes**

$$J(matter) = -D\left(\frac{dc}{dx}\right)$$ where, **dc/dx** is the **slope** of the **molar concentration**

$$J(\text{matter}) = = sc$$ where, *c* is the **molar concentration, *s* = drift speed**

$$as: F(Thermodynamic\ Force) = -\frac{RT}{c}\left(\frac{\partial c}{\partial x}\right)_{p,T}$$

$$\therefore\ sc = -D\left(\frac{dc}{dx}\right) \quad \equiv s = -\frac{D}{c}\left(\frac{\partial c}{\partial x}\right)_{p,T} = -\frac{D}{c}\left(-\frac{Fc}{RT}\right) = \frac{DF}{RT} \quad \therefore\ s = \frac{DF}{RT}$$

Compare the two values. Here we have in terms of the number density, here also we have in terms of number density. Suppose I divide both the equations by Avogadro number, then it converts the number density into the molar concentration of moles or at the in terms of the amount of the substance that is passing or that is flowing, ok. So, when I can divide the this part and this part, both J conditions divided by Avogadro number, obviously this becomes sc and this becomes dc by dx. See I have taken x now ok, I can take z, I can take y, but we are going to maintain x for the sake of simplicity x being taken in place of z which should be again parallel to the container which we are taking.

So, what we have? We have one condition where you have the matter flux of matter or particle which is in terms of the amount which is equal to the diffusion coefficient into the concentration gradient. It is the molar concentration we are talking about. Similarly from this expression which we have got from the kinetic theory of particles moving under electric field, we had a expression where the flux of matter will be equal to drift speed into the concentration, where c is the molecular speed and s is the drift speed.

So, these two expressions we have the both are J. So, I can equate these two. Now, if I equate these two, I have a term in terms of the concentration gradient. Now, this concentration gradient I can replace that y whatever thermodynamic force, we which we had derived previously in the previous class, what we had derived for a limiting condition where the solution is very dilute approaching ideality that time, then thermodynamic force could be given by RT by c into the gradient in concentration at a given temperature and pressure. So, this value of D ca and the gradient in concentration dc by dx can be substituted in this expression of sc equal to minus D gradient of concentration. This we are whatever we derived as the thermodynamic force which we are replacing.

So, from here what is going to be Dc by Dx, it is going to be Fc by RT. So, from this expression we have the s equal to D by c into this and this we are replacing by what, Fc by Rt with a negative sign because this is a negative sign which we have and this outside also there is a negative sign. So, what we have come down to? We have come down to an expression of the diffusion coefficient into F divided by Rt, and what is this F, that is the thermodynamic force. So, it does not matter what the origin of the thermodynamic force is, the drift speed will be always the term in relation to the diffusion coefficient by Rt and the system according to the system we are studying we have the defining thermodynamic force.

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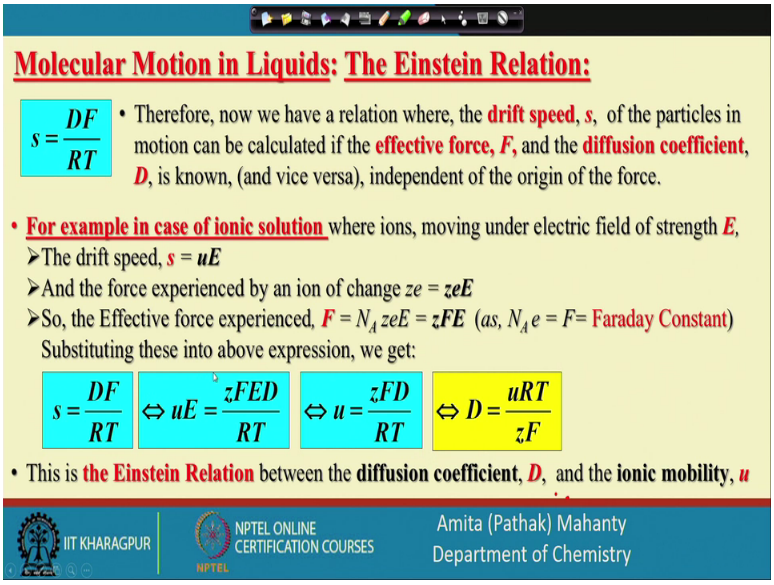

Molecular Motion in Liquids: The Einstein Relation:

$s = \frac{DF}{RT}$

- Therefore, now we have a relation where, the **drift speed**, *s*, of the particles in motion can be calculated if the **effective force, *F***, and the **diffusion coefficient**, ***D***, is known, (and vice versa), independent of the origin of the force.

- **For example in case of ionic solution** where ions, moving under electric field of strength E,
  - The drift speed, $s = uE$
  - And the force experienced by an ion of change $ze = zeE$
  - So, the Effective force experienced, $F = N_A zeE = zFE$ (as, $N_A e = F$= Faraday Constant)

  Substituting these into above expression, we get:

$$s = \frac{DF}{RT} \Leftrightarrow uE = \frac{zFED}{RT} \Leftrightarrow u = \frac{zFD}{RT} \Leftrightarrow D = \frac{uRT}{zF}$$

- This is **the Einstein Relation** between the **diffusion coefficient**, ***D***, and the **ionic mobility**, ***u***

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So, from this we have this expression. We have now a relationship between the drift speed of a particle in motion that can be calculated. If we know if we if we have relationship between s and d, then what we can see if the particles in a motion can be calculated. The drift speed of the particles in motion can be calculated if F, the effective force is known and the diffusion coefficient is known, ok.

If these two parameters are known, then I can find out the drift speed of the particle in the in that particular system. So, it does not matter what the origin of the force is. All we need to know is what is the effective force that is existing for example which we have already seen, we have in the case of a ionic solution where the ions are moving under the electric field.

If you remember the expressions which we which we had derived, the drift speed was equal to the ionic mobility, the mobility of the ions into the applied electric field strength of the applied electric field, and the force experienced by the each of the ion of say charge ze was taken to be what the total charge ze into the electric field, the force experienced by ion was ze into the electric field.

So, the effective force experience will be because of all the Avogadro number of particles which are there. So, Avogadro number of particles, total number of particles into the ze and you know F is the faraday constant which is Avogadro number into the electric charge. So, this can be replaced. So, we get a simplified form of the total effective force that is experienced by the ions is equal to z FE. Here F is see here to do not get confused. This is also F and this is also F. The red one is the effective force that is experienced by the particles in the system and this F is the faraday constant.

So, now what you do substitute these in the above expression. If we are substituting this in the above expression, what you get? You have this as the drift speed which we have derived in terms of the effective force. This is the effective force and from the expression which we have for the s in terms of the this mobility is going to be u into E, the total mobility of the ions into the strength of the electric field. So, I can equate these two uE equal to DF RT, where remember this F is the thermodynamic force or the effective force on the particles.

So, what we have, we can we can rewrite this in terms this e gets cancelled. If we are substituting the value of in this expression, in this expression, what we are doing you equating the two s's; this one and this one, ok. So, if you are equating these two, then what you get here? You have u E and then, you have DF RT and the thermodynamic force which we have taken is the effective force. That is nothing, but zFE, ok.

So, I have replaced the force here. This is the force and this force I have replaced by zFE. So, this F what I am having is the faraday constant. This is not the force which it was initially there. So, if you further look into the values, you will see that you have a relationship between the diffusion coefficient and the mobility of the particles in the system, right.

So, what we have derived is, we have derived the drift speed in terms of the thermodynamic effective force and in terms of the diffusion coefficient. This relationship we further exploited when we are talking about this example where you have ions moving in a solution under a electric field. If that is the condition, then what is the total effective force? This force was replaced by zFE, where here F is the faraday constant coming from the Avogadro number multiplied by the electric charge, right.

So, please remember this because we are going to be using this relationship in the constitutive relations, we are going to derive. So, what does Einstein relationship gives us? This is Einstein relationship. What is in yellow? It gives us an information about the diffusion coefficient of a particular particle when the mobility of the particle is known. So, you have the relationship where you have diffusion coefficient d link to the ionic mobility. So, we can find out, we can solve expressions to find out the value of diffusion coefficient for a particular ion which is for which the mobility is known to us.

Thank you so much.