Molecules in Motion

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Lecture-32
Molecular Motion in Liquids (Contd.)

Welcome to another lecture on Molecules in Motion. If you remember in the 13th lecture, we had talked about applying whatever equations which we have obtained so far for a ion moving in a under electric field. We will try to see whether those equations which we had derived can be applied to a ion, which is not charged a neutral ion or ion not applied in electric field. So, that validation we are going to take up, which we had started in lecture 13th lecture, 13th had was the beginning of it, but we are going to be revisiting that and coming to validate the Ficks law, Ficks diffusion law.

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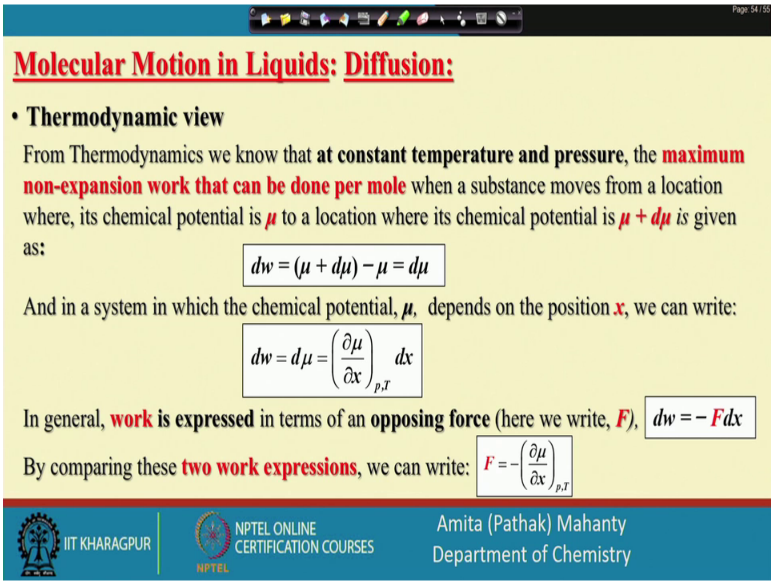

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Molecular Motion in Liquids: Diffusion:

- **Thermodynamic view**

From Thermodynamics we know that **at constant temperature and pressure**, the **maximum non-expansion work that can be done per mole** when a substance moves from a location where, its chemical potential is μ to a location where its chemical potential is $\mu + d\mu$ is given as:

$$\boxed{dw = (\mu + d\mu) - \mu = d\mu}$$

And in a system in which the chemical potential, μ, depends on the position x, we can write:

$$\boxed{dw = d\mu = \left(\frac{\partial \mu}{\partial x}\right)_{p,T} dx}$$

In general, **work is expressed** in terms of an **opposing force** (here we write, F), $\boxed{dw = -F dx}$

By comparing these **two work expressions**, we can write: $\boxed{F = -\left(\frac{\partial \mu}{\partial x}\right)_{p,T}}$

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Before that we need to know what is the thermodynamic principle involved. What is the thermodynamic principle involved when you have diffusion or we have a transport through the medium. So, for the most basic of thermodynamics if you remember at constant temperature and pressure, the maximum non expansive work that can be done by a mole of a substance comes from the location, where from the chemical potential from one location to another.

Suppose the thermodynamics the work done is actually going to be the difference in chemical potential of suppose the chemical potential of a substance; chemical potential is given to be for a pure substance it is Gibbs free energy per mole.

So, chemical potential when a substance moves from one location to another. If its chemical potential changes from mu in one location to being mu plus d mu in another then the maximum expansive non expansive work. Non expansive means we are talking about volume increase when we having a system where you have a volume increase then we say its expansive work. When we are talking about non expansive; that means, there is a no increase in volume of the system, this in non expansive work per mole is going to be given to be the chemical potential. As chemical potential I have told you is defined as the Gibbs free energy per mole of a pure substance.

So, if I have the chemical potential at one location as mu, and another location as mu plus delta mu, then the difference in the chemical potential is going to be mu plus delta mu minus delta mu and this difference is given to be the maximum non expansive work that we can get per mole of the substance at a given temperature and pressure.

So, this is what we have written, the w the work done is going to if the work done is supposed to be a non expansive work, then the non maximum non expansive work that we can obtain for a mole of a substance is going to be the difference. In the chemical upper potential at the two locations 1 is mu plus delta mu minus the chemical potential and another position which was mu. And this difference is going to be this is going to cancel off this is going to be the change in chemical potential.

So, the maximum non expansive work for a mole of a substance at a given temperature and pressure is the measure of the change in chemical potential of the substance. If the chemical potential of a substance is mu at one place and in another location it is mu plus delta mu then the change in the chemical potential of the two substance at the two locations is going to be the measure of the maximum non expensive work, that can be done by a mole of a substance.

Now, in a system the chemical potential mu depends on the position. So, by definition the if you have a system where the chemical potential at one position is not the same as the chemical potential in an another location. Ideally for an ideal solution you should have the chemical potential same throughout at equilibrium, but if you have the chemical potential which is going to be dependent on the distance from one point to the other; that means, the spatial distance from one location to the other, then we can say that the change in chemical potential with distance at a given temperature and pressure into the change in distance is the total change in mu, which we are associating this is a partial differential which we are saying.

The partial differential is the change this is the gradient in chemical potential with the distance at the two locations we are talking about. So, the gradient in chemical potential; the gradient in chemical potential into the total distance which is which we have transferred, transversed is going to be the total mu which we are going to have.

Now, when we talk about work what do we talk when we talk about work, we really general expression of work, work is usually expressed in terms of the opposing force ok. Force into distance which we is the standard expression of work. So, we can say this force is actually the opposing force against which the work is done, to move a distance dx. So, this is the expression which we have generally for work.

So, the force which we are talking about here let us represent that by F then the work done will be minus F into dx, the their work is going to be the force into the opposing force into the distance through which the system is moving. So, this opposing force minus F you have two expressions of work now. You see one in terms of the chemical potential and another in terms of the general expression of force, which is force in terms of force into distance the opposing force into distance.

If we compare these two expressions if you see, this is the gradient in chemical potential into dx and here what you have? You have work expression minus F into dx. If we compare the two expressions of work, one is this and another is this both have dx here. So, we can say that this expression what we have is the gradient in chemical potential at a given temperature and pressure, can be equated to minus F or we can say the force is the negative of the gradient in chemical potential at a given in temperature and pressure.

Suppose I have a plot of say chemical potential in the y axis and in the x axis I have a the distance x then what we have? We have the slope of that curve, the slope of that curve y axis is mu and x axis is x the distance. If we have something like that then the plot of that mu versus x plot gives you the slope and this slope is the gradient in chemical potential. So, chemical potential the negative gradient in chemical potential can be equated to the opposing force which we have identified for expressing the general expression of work. So, now we extrapolate this.

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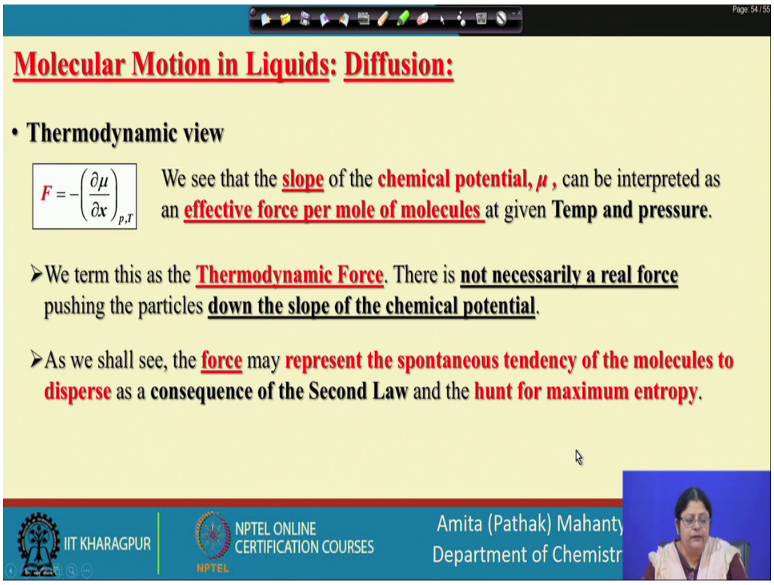

Molecular Motion in Liquids: Diffusion:

- **Thermodynamic view**

$F = -\left(\frac{\partial \mu}{\partial x}\right)_{p,T}$ We see that the **slope** of the **chemical potential, μ**, can be interpreted as an **effective force per mole of molecules** at given **Temp and pressure**.

➢We term this as the **Thermodynamic Force**. There is **not necessarily a real force** pushing the particles **down the slope of the chemical potential**.

➢As we shall see, the **force** may **represent the spontaneous tendency of the molecules to disperse** as a **consequence of the Second Law** and the **hunt for maximum entropy**.

So, what we have? The force which is which we have identified from a general work expression we see is the slope of the chemical potential mu and be interpreted as the effective force per mole of the molecule at a given temperature and pressure. So, it is this force can be taken as the slope of the chemical potential and as can be interpreted as the effective force per mole of the molecule.

So, in terms of the thermodynamic forces, we can say this as the this force as we can term this as the thermodynamic force ok. We call this as a thermodynamic force, it is not essentially real force which is pushing the particles down the chemical grey and the slope of the chemical potential. It is actually we can visualize as the force which may represent the spontaneous tendency for the molecules to disperse as a consequence of the second law, for the hunt of maximum entropy.

So, the this force may be expressed in terms of the spontaneous tendency of the molecules to spread or disperse in a medium to so, as to achieve the maximum entropy. So, in whatever we are doing, we are always trying to get the system under maximum entropy because all systems as a supposed to be approaching the maximum entropy to have stability.

So, the hunt is this force what we are calling and seeing and deriving is actually expression of thermodynamic force, which is can be visualized as force that represents the spontaneous tendency of the molecules to disperse or move into a medium on the grounds of maximizing the entropy of the system. So, because if you have maximum entropy, you will have maximum disorder you have all the spreading the maximum the spread is maximum you will get maximum disorderness and maximum entropy.

So, the driving force which is which we are seeing here, we are saying this force terming this force as a thermodynamics force which represents the spontaneous tendency of the molecules to disperse in a medium so, has to have the maximum spread or has to have a maximum randomness or maximum entropy.

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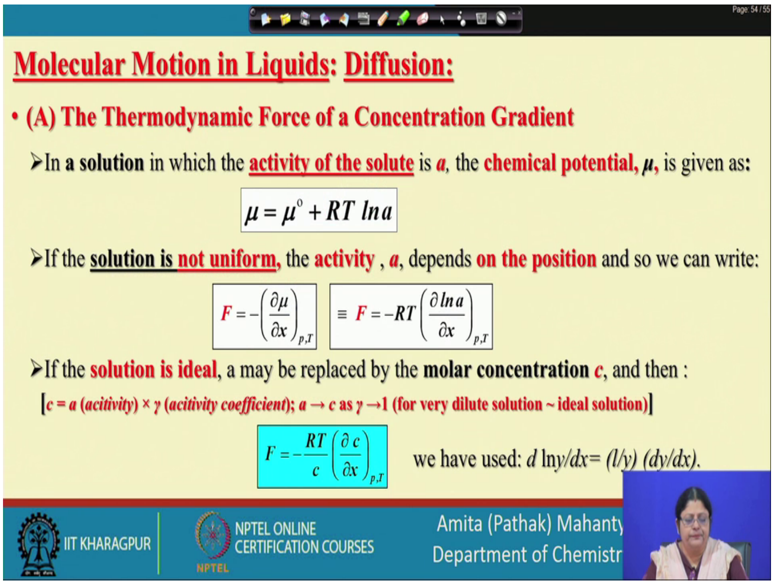

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Molecular Motion in Liquids: Diffusion:

- (A) The Thermodynamic Force of a Concentration Gradient

➢In **a solution** in which the activity of the solute is *a*, the chemical potential, *μ*, is given as:

$$\boxed{\mu = \mu^{0} + RT\, \ln a}$$

➢If the **solution is not uniform,** the activity , *a*, depends on the position and so we can write:

$$\boxed{F = -\left(\frac{\partial \mu}{\partial x}\right)_{p,T}} \quad \boxed{\equiv F = -RT\left(\frac{\partial \ln a}{\partial x}\right)_{p,T}}$$

➢If the solution is ideal, a may be replaced by the **molar concentration** *c*, and then :

[*c = a (acitivity) × γ (acitivity coefficient); a → c as γ →1* (for very dilute solution ~ ideal solution)]

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

we have used: *d* ln*y*/*dx*= *(l/y) (dy/dx)*.

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So, this force can how we can relate that force to what we have in a concentrated solution. The thermodynamic force of a concentration gradient see we have talked about the chemical potential in terms of the distance and the slope of chemical potential, we have the gradient in chemical potential we have taken it to be proportional to the force which we have called as thermodynamic force.

Now, in a solution, the if the activity of the solute is taken to be a then the chemical potential of the solution can be represented by something like this. I hope you are aware of this, because I have not talked about chemical potential in detail before and neither is the course going to be dealing with that, but I hope you understand what I am trying to say.

The chemical potential of a solvent a solution of a electrolyte of having some concentration of the electrolyte, we say the activity of the solute if it is represented by a, then the chemical potential of the solvent a solution can be given to be chemical potential of the solution equal to chemical potential not that of the pure solvent plus the [vocalised-noise] RT ln activity. So, this is the activity of the solute which we are having, this is the chemical potential of the solution.

So, chemical potential of a solution can be related to the activity of the solute in the medium by this expression. Suppose the solution is not uniform means it is not homogeneous. If the solution is not homogeneous, then the activity will be depend of the solute will be dependent on position in which they are located. So, if there if the solution is not uniform and the activity of one location is different from the activity of the other, then we can write from the thermodynamic forces which we know, the thermodynamic force is going to be nothing, but negative potential gradient of the chemical potential with distance at a given temperature and pressure.

Now, if I say that the chemical potential is dependent on the distance, then I can put the force in terms of the chemical potential and I differentiate the chemical potential term I have here. If I differentiate the chemical potential term I have here and substitute and get the value of force, what do I have? Chemical potential of this is going to be 0 because this is going to be a constant. So, you have RT is a constant, the gas constant into temperature. So, only thing which is going to be dependent on is the change in activity of the solute with distance. So, I can write ln a differentiated with respect to dx at constant temperature and pressure.

So, this expression of force can be now expressed in terms of the activity of the solute which we have. For a ideal solution what happens? For a ideal solution concentration is activity into activity coefficient of the solute. So, if I have the activity the activity coefficients approaching one, then the activities will be approaching concentration and that is for a ideal solution or a very dilute solution. So, if I have very dilute solution then what do I have? I have the activity term replaced by concentration term right. I can write

F equal to minus RT ln c differentiation with dx at constant temperature a given temperature and pressure.

Now, if I rewrite this expression of ln c versus ln c differentiated with may with dx in terms of something like this d ln y dx equal to 1 by x dy dx, ln d ln x dx can be this is the mathematical simplification, which we have done d ln y by dx is equal to 1 by x into dy by dx.

So, if I write the in terms of this you just see what will I get? I will get 1 by c outside, I we have to replace this with c now ln differentiation of ln c with respect to dx. If I have to write that then I can write 1 by c into dc by dx right the ln expression can be written like this. So, I can write down minus RT by c that is coming from 1 by c into ln c by into differentiation of c with respect to x at given temperature and pressure.

So, I have a different expression of force the driving thermodynamic force which we have talked about, when you have a concentration gradient concentration gradient meets if the solution is not uniform. So, the if the solution is not uniform, then the concentration gradient change in concentration with distance can be expressed in terms of the thermodynamic force, given something as RT by c coming from the definition of the chemical potential of a solution, which has a salt or solute with the activity a at a given temperature and pressure.

So, from rights from this, I we have gone to the thermodynamic force expression of thermodynamic force we have differentiated and we have got a term in terms of the gradient in concentration, the force is proportional to the gradient in concentration. So, gradient in concentration means we are talking about molar concentration here, you can see we are approaching to something which we already know that is the Fick’s law of diffusion.

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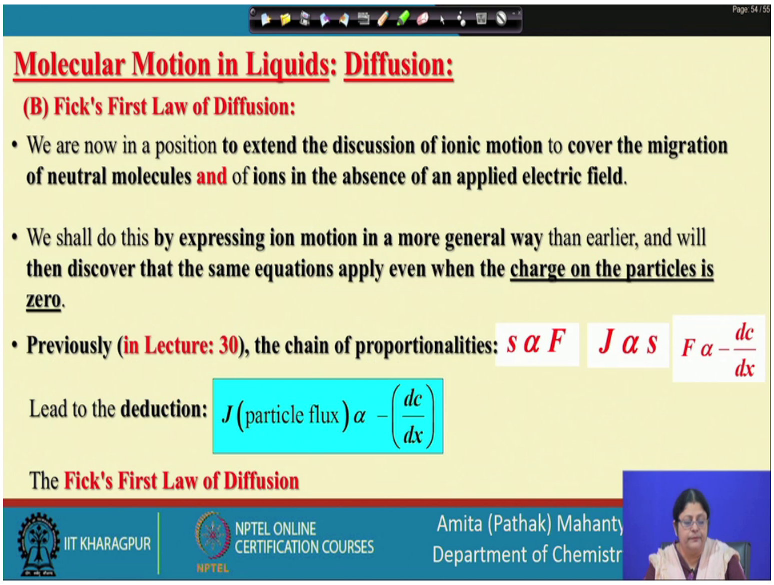

Molecular Motion in Liquids: Diffusion:

(B) Fick's First Law of Diffusion:

- We are now in a position **to extend the discussion of ionic motion** to **cover the migration of neutral molecules and of ions in the absence of an applied electric field.**
- We shall do this **by expressing ion motion in a more general way** than earlier, and will **then discover that the same equations apply even when the charge on the particles is zero.**
- **Previously (in Lecture: 30), the chain of proportionalities:** $s \; \alpha \; F$ $\quad J \; \alpha \; s$ $\quad F \; \alpha -\frac{dc}{dx}$

Lead to the **deduction:** $J\left(\text{particle flux}\right) \alpha \; -\left(\frac{dc}{dx}\right)$

The **Fick's First Law of Diffusion**

So, Fick’s law of diffusion this is I am not going to be look we are going to leave it at this we are going to use this wherever we want to apply. Now the Fick’s law of diffusion we are now in the position to discuss the extension of ionic solution motion to cover the migration of neutral ion this is what we had discussed in the last class. We have expressed the motion of the ions in more general way and we will then discover the same equations can be applied for a system, which is not charged or having no under no electric field.

This was discussed in lecture 30th, we had expressed we have we had seen how the chain of proportionalities were there was there we had the speed of the ions proportional to the and the force which was existing frictional force. And the flux of the particles were was proportional to the speed of the particles or ions and then we had seen how the force was proportional to the change in concentration gradient. So, this is the force which is we had talked about is frictional force here, and this frictional force being applied to the gradient in concentration. If you go back and visit lecture 30 we have derived this three proportionalities from s being a proportional to F again s is proportional to J.

So, we can say J and again F is proportional to the concentration gradient. From this proportionality we can say J is going to be proportional to F or F is in since is proportional to c by x. So, f will be the flux of the particle will be proportional to the concentration gradient and this proportionality we term as the Ficks law of diffusion.

Where the particles migrate not under electric field, but under the gradient of concentration if you have a gradient in concentration, the migration of particles will take place not even if it is not charged will be taken place in terms of the gradient in concentration.

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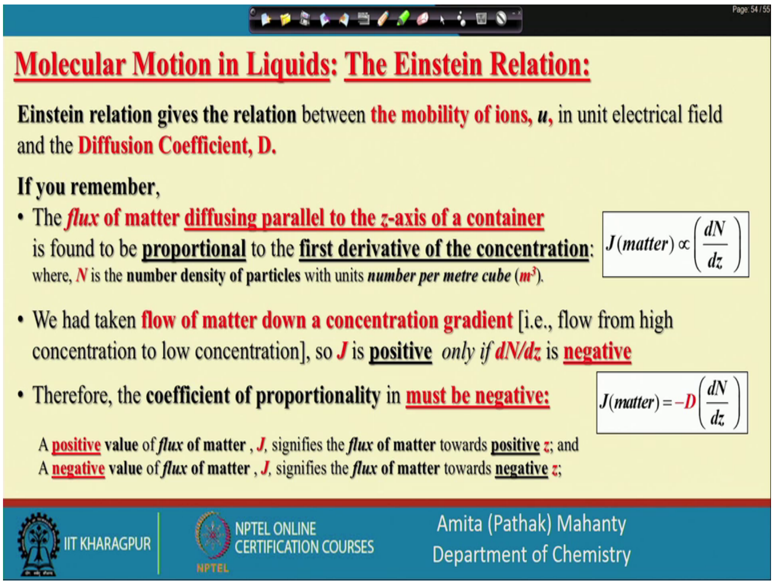

Molecular Motion in Liquids: The Einstein Relation:

Einstein relation gives the relation between **the mobility of ions, *u*,** in unit electrical field and the **Diffusion Coefficient, D.**

If you remember,

- The ***flux* of matter diffusing parallel to the *z*-axis of a container** is found to be **proportional** to the **first derivative of the concentration**: $J(matter) \propto \left(\frac{dN}{dz}\right)$
  where, *N* is the **number density of particles** with units ***number per metre cube*** (m^3).
- We had taken **flow of matter down a concentration gradient** [i.e., flow from high concentration to low concentration], so ***J*** is **positive** *only if* ***dN/dz*** is **negative**
- Therefore, the **coefficient of proportionality** in **must be negative:** $J(matter) = -D\left(\frac{dN}{dz}\right)$

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*;

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Now, there is a relationship which is called the Einstein relationship and then we have this solidification stoke Einstein relationship, we are going to derive this and see how the mobilities of the ions, how the mobilities of the ions in unit electric field can be related to the diffusion coefficient, which is diffusion is essentially occurring due to a concentration gradient.

So, if you remember flux of a matter diffusing parallel to the x axis of a container is found to be proportional to the first derivative of the concentration of the number concentration. This is the N is the total number of particles, the number density in a unit cube of substance with distance something like this.

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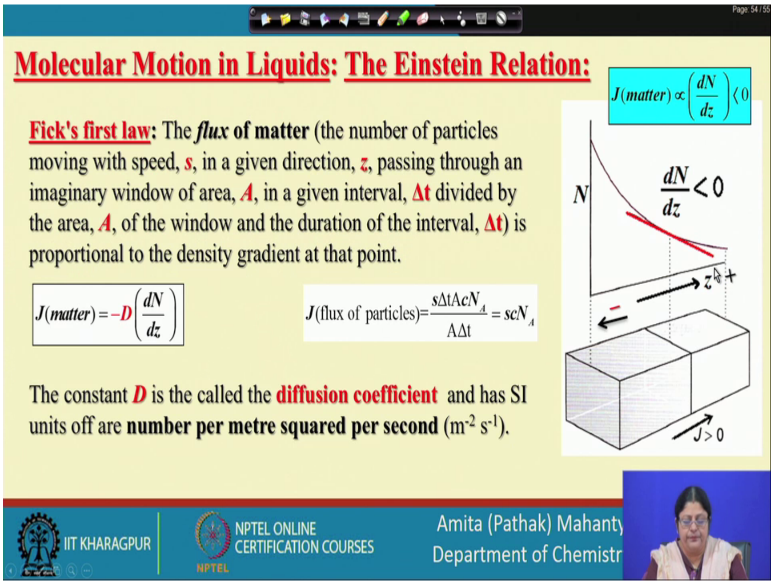

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Molecular Motion in Liquids: The Einstein Relation:

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

Fick's first law: The ***flux* of matter** (the number of particles moving with speed, *s*, in a given direction, *z*, 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.

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

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

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

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If you remember then if we have a concentration gradient then if I have; if I am moving from or along x axis z axis which is parallel to the container, then how is the flux defined is what we are going to be looking into.

So, what we have the flux of the matter diffusing parallel to the x axis of a container is found proportional to the first derivative of the concentration, that is the concentration is in terms of the number of particles and we are talking about the number density, with the gradient in the direction x which is supposed to be parallel to the unit volume on a unit container which we have taken.

Now, we know the flow of matter according to Fick's law we the flow of matter, is down the concentration gradient; that means, it is going to be from higher concentration to the lower concentration, moving if I am moving and I am seeing at each point say this point this point this point what is going to be the change in number of particles and the flux of particles are along this direction. Then what I see is if I have flow of matter down a concentration gradient from high concentration to a low concentration; that means, if I see that dN, it if I with a distance say I am moving towards x and I see dN what will be the final dN? Final dN since its going from a higher concentration to a lower concentration. So, dN in the final concentration will be always lower than the d in the original concentration from where it is moving.

So, what happens the change in number of particles which you are seeing from as the gradient as the particles are moving through the concentration gradient from high concentration to a low concentration, then what happens? Then this is going to be negative right and the coefficient of proportionality must be negative. Because the flux is to be positive when you have a we say a pause value of flux is positive then; that means, it signifies the Js flux of matter is moving towards the positive z direction, this is the positive z direction and if it is moving towards the negative z direction, then the flux is taken to be the flux is taken to be positive.

So, if I have a flux should be always positive and the gradient is negative. So, if I have to have the total flux to be positive, then I must have a proportionality constant which will have take the negative term. So, because this is always going to be negative. So, to and the flux has to be positive, the flux is defined if you remember flux is a matter is the number of particles moving with the speed say s at a given direction x, passing through a imaginary window suppose I take a window here corresponding to here of area A, at a given time interval delta t divided by the area divided by the duration of time.

If you remember if this was the volume which we are talking about the s into delta t was the distance, it travelled into area of the window. So, this is the volume element we had into the concentration molar concentration into the Avogadro number. This Avogadro number gives you the number density of the particles divided by A by t this gets cancelled. So, what you have the flux of particle is nothing, but the speed into molar concentration into the Avogadro number

So, we have another expression where we have just now derived that the this is from the Fick's law, that the flux of matter is going to be proportional to the number gradient or concentration gradient. I can write down this as x, I can write down this as z for this particular diagram I have taken this as z, but we can talk in terms of x as well it has to be any direction any special direction which we have. So, and this d we have said is the diffusion coefficient and it is having a s i unit of number per meter square per second for particular system.

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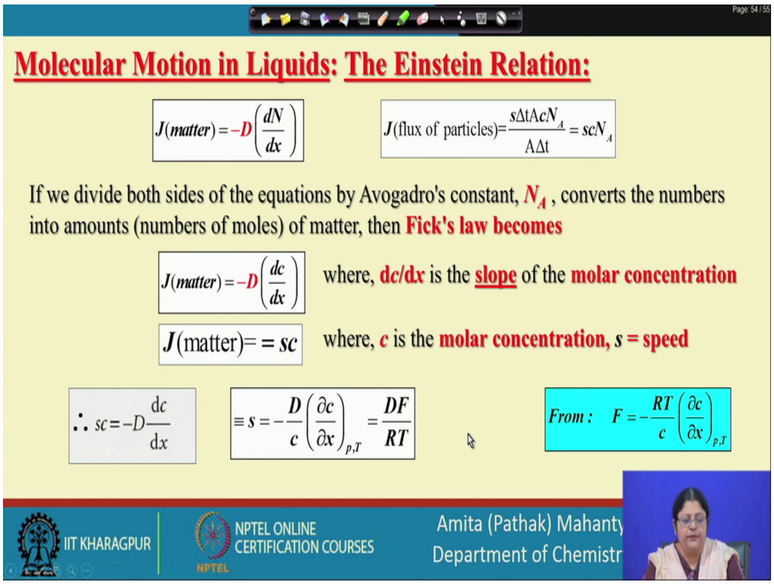

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Molecular Motion in Liquids: The Einstein Relation:

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

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

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 = speed**

$\therefore sc = -D\frac{dc}{dx}$

$\equiv s = -\frac{D}{c}\left(\frac{\partial c}{\partial x}\right)_{p,T} = \frac{DF}{RT}$

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

Now, we have two expressions of J the flux of particle, flux of particle is the total number passing with moving with particles moving with the speed s in delta time t grossing a window of area a will be total divided by the number area of the window into the time taken for it to cover.

So, from there we have these two expressions of number density, I have represented x here we can write z, but x is more convenient we are taking on we are going to be more simple to use it x now onwards. So, change in number of particles with distance is going to be proportional to the flux of matter. Now this is number this is also number, now I if I have if I divide the both the side both the equations with say Avogadro number, then converts the number into the amounts. So, it becomes more close to the Fick's law what this becomes? This becomes concentration gradient and from here you see it becomes sc.

So, I have two expressions now ones from the from the Fick's law and the other from the flux of particle which we have calculated for a charged molecule moving under a influence of electric field. But we say we are not talking about charged particles here we are talking about in general particles. So, it is only we are not having any charge associated with this. So, I have the speed of the particles into the molar concentration.

If I combine these two, then I have sc becomes equal to this minus diffusion coefficient into concentration gradient. Now if you go back what we had derived from the chemical potential we had derived that the force is going to be equal to RT by c. So, force is going to be RT by c into the gradient in concentration in any direction any special direction xyz. So, we have chosen x here at a given temperature and pressure.

So, if I have this expression known to me, then if I want to substitute what is going to be the concentration gradient the concentration gradient in terms of the concentration gradient if I want to substitute, then what I have from this expression? I have s D by c into concentration gradient and this concentration gradient if I have this that is nothing, but F c by RT ok.

So, the Fc by RT the Fc by RT is going to be here c here and c this will be cancelled. So, what I have is the new relationship which I call as the Einstein's relationship which is the relating the speed of the molecules, which are moving or ions which are moving or particles which are moving, with the diffusion coefficient. And defuse the if you remember the speed of the ion can be represented in terms of the mobility of the ions.

So, if I and mobility is going to be related to the say the particle diameter and the frictional force associated with that. If I apply that stokes law for the definition of the speed of the molecule then we get a further modification of this equation.

What we have right now derived a speed of the particle, which may be charged or may not be charged because we have not used any charged expression or electric field expression here, this is going to be equal to the ratio of the differential in the in this is the diffusion coefficient by RT into the thermodynamic force. And this thermodynamic force can be further modified in terms of the stokes law and we will take it up in the next class that time the equation will be modified as I the Einstein stokes relationship. So, the Einstein relationship gives the relation between the speed of the ions and the diffusion coefficient of the particular system, which we are use which we study. So, next class we take up the stokes Einstein's relationship.

Thank you so much.