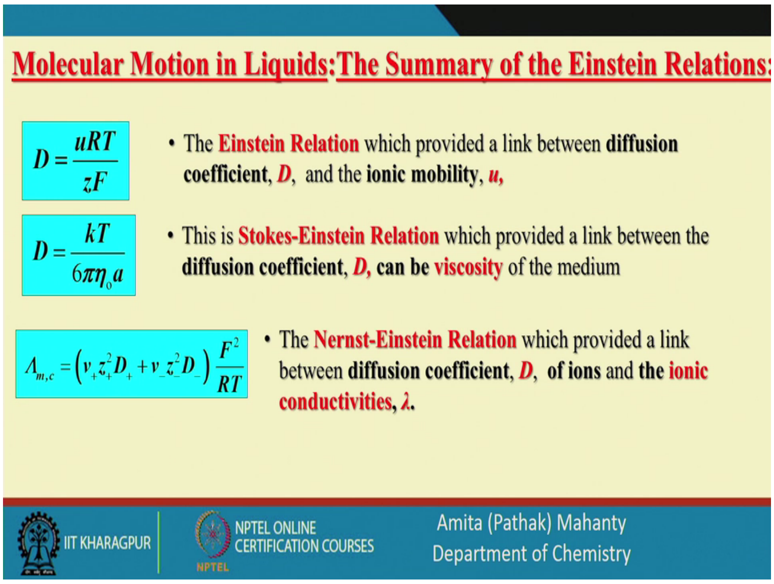
Molecules in Motion

Prof. Amita Pathak Mahanty
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture – 35
Molecular Motion in Liquids (Contd.)

Welcome to another lecture on Molecules in Motion.

(Refer Slide Time: 00:20)



Molecular Motion in Liquids:The Summary of the Einstein Relations:

$$D = \frac{uRT}{zF}$$

- The **Einstein Relation** which provided a link between **diffusion coefficient**, ***D***, and the **ionic mobility**, ***u***,

$$D = \frac{kT}{6\pi\eta_0 a}$$

- This is **Stokes-Einstein Relation** which provided a link between the **diffusion coefficient**, ***D***, **can be viscosity** of the medium

$$\Lambda_{m,c} = \left(v_+ z_+^2 D_+ + v_- z_-^2 D_-\right)\frac{F^2}{RT}$$

- The **Nernst-Einstein Relation** which provided a link between **diffusion coefficient**, ***D***, **of ions** and **the ionic conductivities**, ***λ***.

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES | Amita (Pathak) Mahanty, Department of Chemistry

What we were talking about in the last class was discussing the various equation which we had derived for a particle moving in a medium. We said that these particles which we have derived the expressions for can be moving in a electric field or it can be non charged particles without a electric field.

So, what we were essentially trying to establish is we had talked about motions of particle through the kinetic theory of gases. What we had derived through the kinetic theory? We were trying to extrapolate for the system which were charged and eventually we established relationships which were applicable for charged molecules and ions or whatever; 2 neutral ones when there was no application of electric field.

So, the equations which we had derived considering the particles to be charged and we were trying to establish a relationship with that of non charged particles were essentially 3 the Einstein's relationship, where we were trying to establish a link between the diffusion coefficient D and the ionic mobility. If it is not a ionic particle or a charged particle then we talked about the mobility as such.

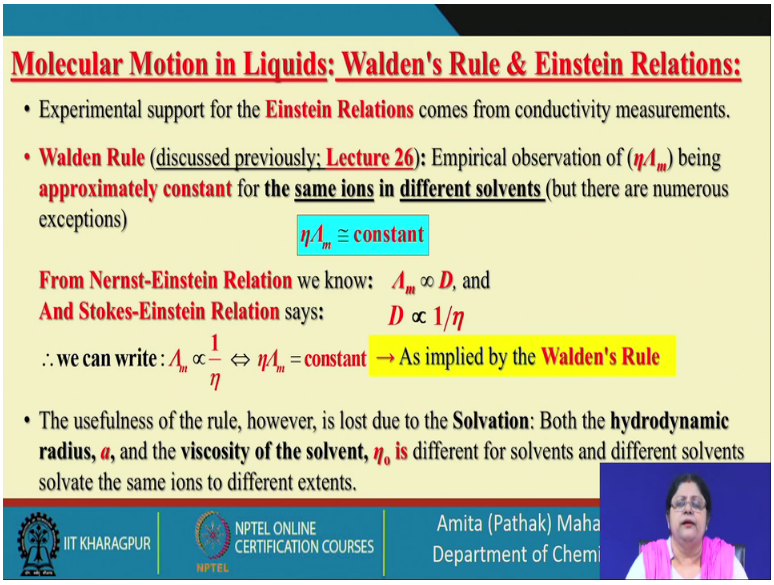
Similarly, we further modified the Einstein relationship and we got the Stokes-Einstein relationship to have a link between the diffusion coefficient D and the viscosity of the medium. And finally, we had talked about the Nernst-Einstein equation; a relationship is between the diffusion coefficient and the ionic conductivities lambda where these are the particles which were supposed to be charged and if they are not charged; we do not need to separate them out into the positive and negative ions, we overlooked the charge associated with it.

So, let us recapitulate what each of the term is representing in each of the equation. In the Einstein relationship the D, capital D is the diffusion coefficient of the ions or particles if they are not charged, u is the mobility of the ions if they are charged and if they are not charged they are just the velocity of the particles. If they are not charged then we do not have this z the charge of the ion which is associated and F is obviously the faraday constant.

Then k here is the Boltzmann constant, kappa naught is the viscosity of the medium, a is the radius of the ion or particle in that particular medium. And here this was the Stokes-Einstein relationship and then we had the conductivity of the electrolyte which was summation of the various charge numbers; that is the stoichiometric coefficient or the numbers of formula units of a particular charged cation or anion of a particularly electrolyte into the charge square of that ion into the diffusion coefficient of each of the ions.

Similarly, for the anion part this is the number of formula units of the anion which is generated from the electrolyte. This is the charge of the anion, and this is the diffusion coefficient of the anion F here is the Faraday constant, R is the gas constant, T is the temperature in Kelvin.

(Refer Slide Time: 04:34)



Molecular Motion in Liquids: Walden's Rule & Einstein Relations:

- Experimental support for the **Einstein Relations** comes from conductivity measurements.
- **Walden Rule** (discussed previously; **Lecture 26**): Empirical observation of ($\eta\Lambda_m$) being **approximately constant** for **the same ions in different solvents** (but there are numerous exceptions)

$$\boxed{\eta\Lambda_m \cong \text{constant}}$$

From Nernst-Einstein Relation we know: $\Lambda_m \infty D$, and

And Stokes-Einstein Relation says: $D \propto 1/\eta$

$$\therefore \text{we can write}: \Lambda_m \propto \frac{1}{\eta} \Leftrightarrow \eta\Lambda_m = \text{constant} \rightarrow \text{As implied by the Walden's Rule}$$

- The usefulness of the rule, however, is lost due to the **Solvation**: Both the **hydrodynamic radius, a,** and the **viscosity of the solvent, η_0 is** different for solvents and different solvents solvate the same ions to different extents.

So, these relationships we have established which can be more or less established through a experimentation through measurement of conductivity.

We will talk about the conductivity measurement towards the last of the lectures; what we have to recapitulate is the violins rule which we had discussed in lecture 26 in quite detail. The empirical observation was that the coefficient of viscosity eta into the molar conductivity of the electrolyte if they are the product of this is approximately a constant for the same ion indifferent solvent.

We have seen that discussed also various exceptions to this, but more or less we can assume the same ion and at different solvent, the product of the viscosity coefficient and the molar conductivity should be approximately a constant. So, this is what we had taken in the previous lectures; now let us justify as to how do we get this. From the Nernst-Einstein equation if you remember the Nernst-Einstein equation what we had? We had a relationship between the conductivity of the electrolyte and the diffusion coefficient right?

So, here we see the conductivity of the electrolyte is directly proportional to the diffusion coefficient. So, according to that this relationship gives us the fact that the molar conductivity is directly proportional to the diffusion coefficient of the particles in the medium. Then again from the Stokes-Einstein relationship what we had? This is the Stokes-Einstein relationship, we be from here we had the diffusion coefficients of the particle in the medium was inversely proportional to the viscosity coefficient of the solvent ok.

So, here we have the diffusion coefficient is inversely proportional to the eta naught the viscosity coefficient of the medium. From here we have the conductivity is directly molar conductivity of the electrolyte is directly proportional to the diffusion coefficient. So, what we have? We have D in both the terms we have D in both the terms; if this is proportional to D and D is proportional to 1 by eta; then what can we say? We can say that lambda that is that molar conductivity of the electrolyte should be inversely proportional to the eta the coefficient of viscosity or in other words we can say this is the relationship we have written. Or we other words we can say if we multiply eta with the molar conductivity, then it should be a constant this is what is implied in the Walden's rule

So, Walden's rule we had taken previously what we have established now; is from the relations of relationship which we have established previously the Nernst-Einstein relationship from where we had the molar conductivity was directly proportional to the diffusion coefficient of that particle in that medium. Again from Stokes-Einstein relationship; we had the diffusion coefficient of the particle inversely proportional to the viscosity of the solvent medium.

So, from these 2 relationship we conclude through further from this proportionality chain; we further confirm that lambda that is the molar conductivity of the particle of the electrolyte will be inversely proportional to the viscosity of the solvent medium. We can write we eta naught to make it more clear because we are meaning the viscosity of the solvent medium. So, eta naught you can put eta naught here it you can put eta naught here. So, the eta naught into the molar conductivity of the electrolyte should be a constant; if there is no exceptions associated.

And this implies that what we have talked about previously we are verifying that by the Walden's by the equations; we have derived and that is what we know as the Walden's rule. The usefulness of the Walden's rule; however, gets complicated or it is lost due to the solvation effect. Because you see in both the relationships which you are having you have a hydrodynamic radius associated and the viscosity coefficient which is associated.

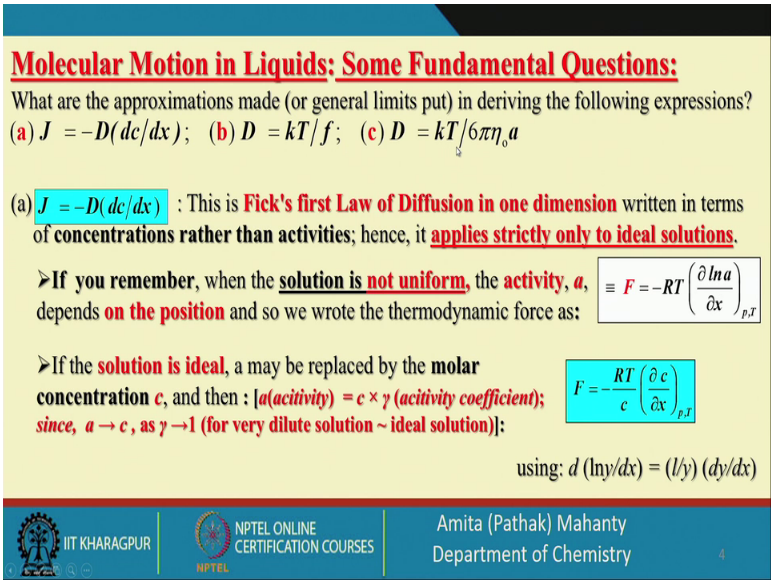
So, if you have the hydrodynamic radius; that means, the radius of the ion when they are in a particular solvent medium will change when you are changing the solvent. Because a degree 2 or that extent to which the ions get solvated in different mediums are different. This also we had taken up in the previous lecture 26, 27; how if we are having a water system or if we are having a non aqueous system how the eta the hydrodynamic radiuses are changed because of the extent of salvation.

We had talked about HCL being a very good very strong acid when taken in water medium aqueous medium and how it was does not behave as a very strong acid when taken in ethyl alcohol. So, this is the reason why we have exceptions to this Walden's rule because of the extent of solvation of the ions in the various solvent systems. And that is the animal you see and hence the Walden's rule at times; it does not give you a constant because the viscosity of the solvents will change with different medium.

So, one factor contributing to the discrepancy of this being a constant is because of the viscosity of solvent changes with different solvent system. And the radius of the ions which we are taking a as the hydrodynamic radius which we had taken a is here you see the diffusion coefficient to the Stokes law we have a here.

So, if we have a different we will have different we have a different because of the different extent of the solvated radius in different mediums ok. So, this confirms or this validates the or discrepancies of Walden's rule and how do we can relate an validate through a Einstein's relationship. So, this is what we have revisited in terms of the Einstein Nernst-Einstein relation and Stokes-Einstein relationship.

(Refer Slide Time: 12:19)



Molecular Motion in Liquids: Some Fundamental Questions:

What are the approximations made (or general limits put) in deriving the following expressions?

(a) $J = -D(dc/dx)$; (b) $D = kT/f$; (c) $D = kT/6\pi\eta_0 a$

(a) $\boxed{J = -D(dc/dx)}$: This is **Fick's first Law of Diffusion in one dimension** written in terms of **concentrations rather than activities**; hence, it **applies strictly only to ideal solutions**.

- **If you remember**, when the **solution is not uniform**, the **activity**, *a*, depends **on the position** and so we wrote the thermodynamic force as: $\boxed{\equiv F = -RT\left(\frac{\partial \ln a}{\partial x}\right)_{p,T}}$
- If the **solution is ideal**, a may be replaced by the **molar concentration** *c*, and then : [*a*(*acitivity*) $= c \times \gamma$ (*acitivity coefficient*); *since*, $a \rightarrow c$, as $\gamma \rightarrow 1$ (for very dilute solution ~ ideal solution)]: $\boxed{F = -\frac{RT}{c}\left(\frac{\partial c}{\partial x}\right)_{p,T}}$

using: $d(\ln y/dx) = (l/y)(dy/dx)$

IIT KHARAGPUR NPTEL ONLINE CERTIFICATION COURSES Amita (Pathak) Mahanty Department of Chemistry 4

Now, I would like to talk about few fundamental questions which may be asked when we are talking about these 3 fundamental equations of diffusion coefficient; this is the Fick's first law; this is the diffusion coefficient which we calculated through the Stokes-Einstein relationship and this is also the Stokes-Einstein relationship where F has been replaced ok.

If I have these 3 expressions what the question is what is the approximation made or what is the limits under which we derive these following expressions. So, let us look at the various approximations we have taken while deriving these expressions.

First one is the Fick's first law of diffusion, Fick's first law of diffusion in any one direction or in one dimension written in terms of the concentration. If this equation we had if you remember this concentration term was initially a activity term which we took as concentration applying to the conditions that the solution behaved ideally; that means, it was a very very dilute solution under which condition the solution could be taken as behaving an as ideal solution.

So, the concentration terms were replaced the activity terms by replaced by the concentration terms in this equation. If you remember in a solution which is not uniform; the activity was supposed to be depending on the position this is what we had derived and the thermodynamic force which we had taken if I will not revisit that, but I will just mention here please look up the lectures if you are having any doubt.

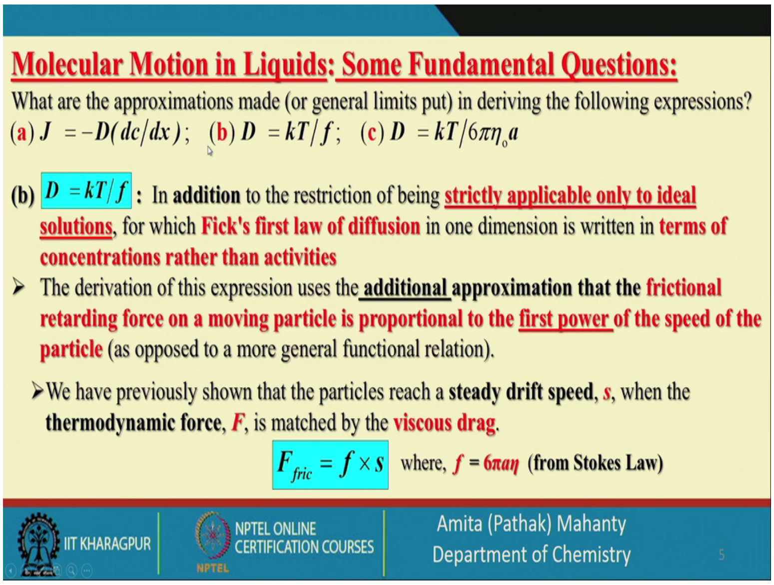
So, the thermodynamic force when we say the solution is non uniform is justified when the activity of the particular species is depending on the position where it is. So, if that is the position dependent that for then for a given temperature and pressure condition. Then the thermodynamic force which is driving the movement of the motion of the particles in the medium will be nothing but minus RT d ln a by dx ok; at constant temperature and pressure.

And we had taken this approximation that we replace this activity in terms of the molar concentration, for the conditions when the solution is very dilute. And if the solution is very dilute we say that it is behaving ideally and we replace the activity in terms of the concentration and activity coefficients to be 1.

So, the activity could be replaced by concentration only when the activity coefficients 10 to 1 and under very dilute condition or ideal condition. So, this is the concentration terms which we had written; if you remember we had written this how we had written this equation, this was written in terms of the d 1 by d y into dy dx this is what we had written by simplification.

So minus RT by c into the gradient in concentration; so, this was the driving force thermodynamic force involved. And the assumption which we had in the Fick's first law when we are replacing activities in terms of the concentration was the solution was very dilute. So, the first assumption for this equation to be valid was the approximation then the solutions behaved ideally; that means, the solutions were very very dilute.

(Refer Slide Time: 16:31)



Molecular Motion in Liquids: Some Fundamental Questions:

What are the approximations made (or general limits put) in deriving the following expressions?

(a) $J = -D(dc/dx)$; (b) $D = kT/f$; (c) $D = kT/6\pi\eta_0 a$

(b) $\boxed{D = kT/f}$ **:** In **addition** to the restriction of being **strictly applicable only to ideal solutions**, for which **Fick's first law of diffusion** in one dimension is written in **terms of concentrations rather than activities**

- The derivation of this expression uses the **additional approximation that the frictional retarding force on a moving particle is proportional to the first power of the speed of the particle** (as opposed to a more general functional relation).
  - We have previously shown that the particles reach a **steady drift speed**, *s*, when the **thermodynamic force**, *F*, is matched by the **viscous drag**.

$\boxed{F_{fric} = f \times s}$ where, $f = 6\pi a\eta$ **(from Stokes Law)**

What happens to the next one this is the next one. So, in addition to the restrictions being applicable to only dilute solution as for as the Fick’s law of diffusion in one dimension in the concentration terms were taken in rather than the activities. In addition to that here what we have; here we have a additional approximation than the frictional retarding force. If you remember the frictional retarding force was proportional to the first power of the speed of the particle; this was the speed drift speed and this was the constant which was obtained from the Stokes law.

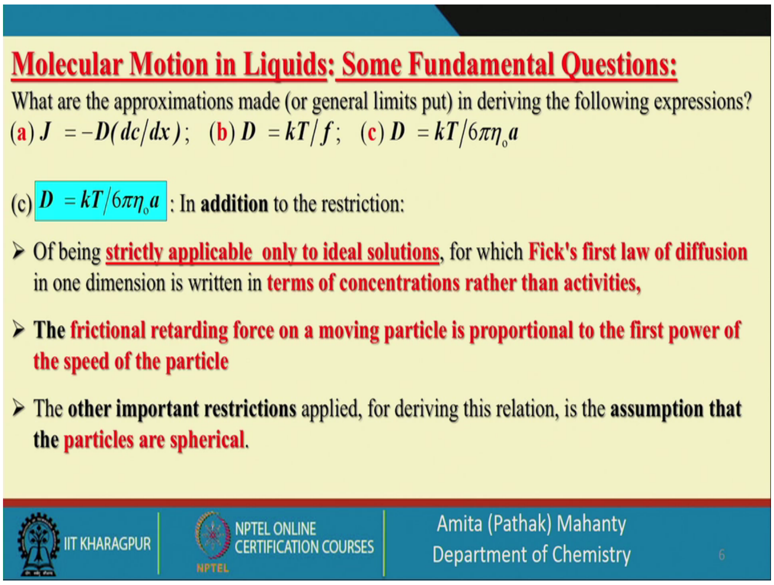
So, you see force is proportional to the first power of speed; what is usually force taken to be? Force is equal to mass into acceleration it is not the first power of speed, but here we have assumed the frictional force to be proportional to the first power of speed, ok. This is the assumption which we have taken in for this expression.

So, what we have? We have the expression in this the limitations or approximations we have taken first is that it is the fields where the Fick’s first law is applicable only for very dilute solution. So, we have taken that the solution is ideal first assumption so that we can replace the activity terms in terms of the concentration.

Second one is the frictional retarding force moving on the particle on the acting on a moving particle is proportional to the first power of speed of the particle instead of what is the general relationship of force. So, this 2 are the conditions or approximations we have taken in this relationship. What happens in the third expression?

Third expression is something similar this is the here we have written down what f is; the f is as you can see here if you replace this. So, these 2 expressions are the same, but the question which is asked is slightly different. So, here the frictional force is taken acting on the particle retarding frictional force acting on the particle is taken to be the first power of speed instead of as conventionally force as defined as mass into acceleration.

(Refer Slide Time: 19:02)



Molecular Motion in Liquids: Some Fundamental Questions:

What are the approximations made (or general limits put) in deriving the following expressions?

(a) $J = -D(dc/dx)$; (b) $D = kT/f$; (c) $D = kT/6\pi\eta_0 a$

(c) $\boxed{D = kT/6\pi\eta_0 a}$: In **addition** to the restriction:

- Of being **strictly applicable only to ideal solutions**, for which **Fick's first law of diffusion** in one dimension is written in **terms of concentrations rather than activities,**
- **The frictional retarding force on a moving particle is proportional to the first power of the speed of the particle**
- The **other important restrictions** applied, for deriving this relation, is the **assumption that the particles are spherical**.

IIT KHARAGPUR

NPTEL ONLINE CERTIFICATION COURSES

Amita (Pathak) Mahanty
Department of Chemistry

Next one is the Stokes-Einstein relationship; what is the approximation which we have? Apart from that the conditions of first law of diffusion a fixed first law of diffusion written, we have written in one dimension written in terms of the concentration in instead of the activities assuming that the solution is i behaves ideally.

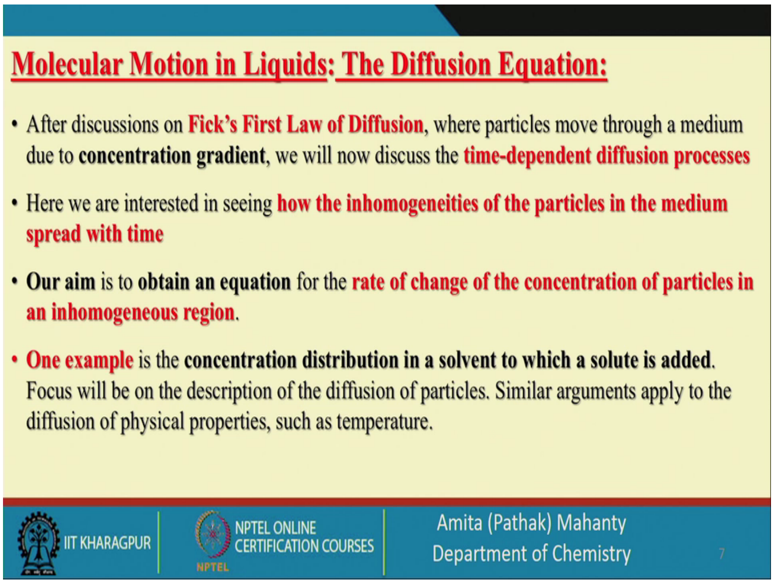
Second one the retarding force acting on the particle is proportional to the first power of the speed of the particle. These are this is the assumption we have taken in spite of the fact that force may not be; generally not proportional to the first power of speed. And the last restriction which is associated with this one in addition to the above 2 is the assumption that the particles are spherical.

See we are talking about the particle diameter; we are assuming the particles are hard spheres and they have a definite diameter or the definite size. So, in this expression what we have? We have put up the 3 assumption for each of them you can now identify this is only for movement of gradient of movement of particle against concentration gradient; where we have replaced the concentration term in terms of the instead of the activities assuming the solution is behaving ideally. Here we have taken apart from taking the solution to be behaving ideally where we are replacing the activity terms with the concentration terms. We have also introduced that the retarding force acting on the particles is proportional to the first power of speed.

In the third one what we have taken in addition to the solution being applicable to only dilute solution; where the Fick's law of diffusion in one dimension where the terms of activities have been replaced by concentration. In addition to the fact that the frictional force or retarding force acting on the particle is proportional to the first power of speed what we have additionally put in is the assumption that the particles are spherical.

If the particles are spherical only then we apply a; the radius of the particle is the ah of the particle which is having of a different definite spherical shape right. So, these are the 3 equations and the assumptions associated with them I hope you understand and recollect when you write them.

(Refer Slide Time: 21:44)



Molecular Motion in Liquids: The Diffusion Equation:

- After discussions on **Fick's First Law of Diffusion**, where particles move through a medium due to **concentration gradient**, we will now discuss the **time-dependent diffusion processes**
- Here we are interested in seeing **how the inhomogeneities of the particles in the medium spread with time**
- **Our aim** is to **obtain an equation** for the **rate of change of the concentration of particles in an inhomogeneous region**.
- **One example** is the **concentration distribution in a solvent to which a solute is added**. Focus will be on the description of the diffusion of particles. Similar arguments apply to the diffusion of physical properties, such as temperature.

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES | Amita (Pathak) Mahanty
Department of Chemistry

Now, we move on to the discussion further; after the first law of diffusion where particles move through a medium due to concentration gradient. We now discuss the time dependent diffusion processes; that means, you understand what do you mean by time dependent processes diffusion processes; we are talking about movement of particles in a fluid medium, in a liquid medium.

So, what happens is what we what is of interest is to see how the inhomogeneities of the particles in the medium spread with time? So, you have a you if you see certain processes like when you are adding a colored liquid into a solution how fast and how quickly they mix and how they diffuse through the medium you can do that experiment or you have done that experiment in from your childhood you can you understand; how this liquid spreads the particle spreads through the medium.

So, how we are what we are interested in this part of the discussion is we are trying to put in another diffusion equation which is slightly different from the Fick's first law of diffusion. Fick's first law of diffusion is only movement of the particles considering the concentration gradient. Now, what we are going to discuss is a time dependent processes; how the diffusion process depends on time the how in inhomogeneities of particle in the medium spreads or what do you say it propagates when we have change in time.

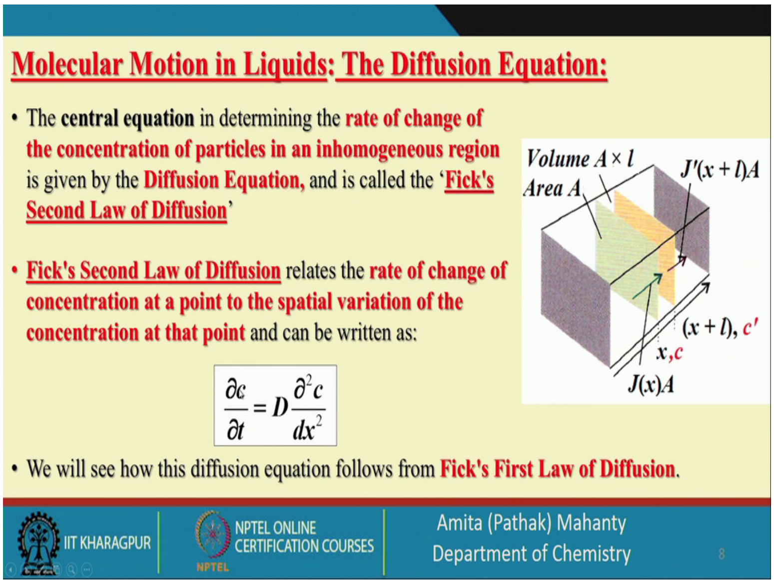
So, our aim here will be to obtain a equation, to write down an equation for the rate of change of concentration of particle in a inhomogeneous region ok. So, what we are writing? We our aim is to obtain another equation where differential equation where we are going to relate the rate of change of concentration of a particle in a inhomogeneous medium. So, what happens for example, in the concentration distribution in a solvent to which solute is added ok. When you have a solvent the concentration distribution when you are adding a solute to the medium what happens? The particles diffuse ok.

The focus is on the description of the diffusion of the particles; what sometimes we can take physical examples. Suppose you have a rod or a bar of iron now you have a heat source at one point. What you have you are heating the bar from one point if you keep heating the bar what happens? And after some time then the bar gets heated up after some time you withdraw this heat what happens? The bar is going to now reach a steady temperature and the temperature will be uniform all throughout.

When you are heating the bar initially the initially the temperature of the point where you are heating the bar is maximum and the particles the particles which are of high energy is not yet reach to the other end. So, you will have a inhomogeneity in the temperature of the bar. But as soon as you remove the heat source what happens? The temperature the bar gradually tries to equilibrate and you would have a thermal equilibrium and the temperature reaches a steady condition and it will be same throughout.

So, similar to those arguments which applies to the diffusion of physical properties like temperature. We are going to look into how the concentration distribution can occur in a solvent medium when you are adding a solute.

(Refer Slide Time: 25:58)



Molecular Motion in Liquids: The Diffusion Equation:

- The **central equation** in determining the **rate of change of the concentration of particles in an inhomogeneous region** is given by the **Diffusion Equation,** and is called the '**Fick's Second Law of Diffusion**'
- **Fick's Second Law of Diffusion** relates the **rate of change of concentration at a point to the spatial variation of the concentration at that point** and can be written as:

$$\boxed{\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{dx^2}}$$

- We will see how this diffusion equation follows from **Fick's First Law of Diffusion.**

So, this is what we are going to be looking into today. And for the next class what we have sent looking into is a central equation to determine the rate of change of concentration of a particle in a inhomogeneous region given by diffusion equation this is called as the Fick's second law of diffusion. And the same Fick's second law of diffusion relates the change of concentration at a point to the spatial variation of the concentration at that point. And we can write the equation as the change of concentration with time equal to the means the rate of change of concentration rate means with time; the rate of change of concentration at any point is equal to the spatial variation of concentration at that point ok.

So, this is the spatial variation and this spatial variation in the double derivative; that means, D square cc by dx square is what we are going to be looking into; this is known as the Fick's second law of diffusion, where the rate of change of concentration of a particle in a inhomogeneous region is given by this differential equation. And this differential equation is the diffusion equation and this diffusion equation is known as the Fick's second law of diffusion.

We will now see how the diffusion equation follows from the Fick's law of the first Fick's law of diffusion. So, here we have a say section in which we have we are looking into how the particles are moving. The particles are supposed to be moving under the Fick's first; law from high concentration to low concentration. So, if this is my area of interest, this is the window in which we are looking into having a area.

And the length of this unit if it is say x l and this distance which we are traveling is initially was x and now this distance if it is l then this new point is going to be x plus l. So, concentration at this point let us be c and what is the concentration at this point let that be c prime. So, what we are going to be seeing, what is going to be the flux which is going to pass through this and exit through this?

So, what we are looking actually is the window which is having a volume of A into l. So, this is the area of interest we are looking into this area or this volume element how the flux of particles are changing in this volume element A into l ok. So, this is going to be guided by the diffusion coefficient; a diffusion equation and this is going to be following the how we derived this using the first law of diffusion is what we are going to see in the next class.

Thank you so much.