

Molecules in Motion
Prof. Amita Pathak Mahanty
Department Of Chemistry
Indian Institute Of Technology, Kharagpur

Lecture – 36
Molecular Motion in Liquids (Contd.)

Welcome to another lecture on Molecules in Motion.

(Refer Slide Time: 00:20)

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

11

What we were talking about in the last class was a new diffusion equation. The diffusion equation so far was discussed was Fick's 1st law of diffusion, where the particles move through the medium in one dimension, due to concentration gradient. what we are looking going to look into today is the time-dependent diffusion processes; that means, how the in homogeneities of the particles exist and how do they distribute in the medium with time. So, what we are trying to establish? We are trying to establish a rate of change of concentration of particle in a homogeneous region.

So, the concentration distribution can be taken a visualised as a example where you are, having a solvent medium into which you are adding a solute and we will see how the particles diffuse and how that is going to be change in the rate of change of concentration of the particles in the various regions. It applies to the same conditions as we have a change in the diffusion in that physical properties such as, temperature when you are heating up rod, which is going to be high temperature at, one source is there and you

heating the rod the temperature- rod temperature is going to increase, but the temperature at the point of the source heat source is going to be different from that of the other end of the rod.

Eventually when you remove the heat source the iron bar is going to be equilibrate and we will have a steady temperature uniform for that bar for throughout the bar. Now, if you have a, heat source continuously heating the rod and you do not remove the, heat source you keep heating the rod higher and higher what happens at a point the rods may start radiating and also it may give rise to in homogeneity in temperatures throughout the rod. So, these are the two conditions we are you can visualise as the processes where you have in homogeneities in particle in a medium and how it spreads with time.

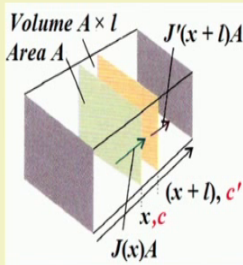
(Refer Slide Time: 02:43)

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:

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

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



Volume $A \times l$
Area A
 $J'(x+l)A$
 $(x+l), c'$
 x, c
 $J(x)A$

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES | Amita (Pathak) Mahanty, Department of Chemistry | 12

So, in the last class what we had talked about, we are going to be establishing a equation which we said the Fick's 2nd law of diffusion starting from the Fick's 1st law of diffusion on this basis we are going to do the derivation for getting this differential form where we see the, rate of change of concentration; that means, cha[nge]- rate of change of concentration means, the change of concentration with time, at a given point is equal to the spatial variation. Spatial means, it is x y z radiation in any of this, x y three z coordinates. How the concentration of that particle is going to change with x y z coordinate at that point of time and that this relationship is what we are going to derive.

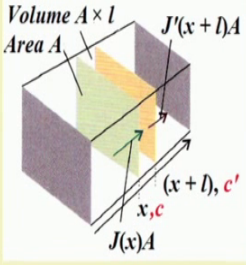
The rate of change of concentration of a particle in a homogeneous region, is given by this equation.

(Refer Slide Time: 03:48)

Molecular Motion in Liquids: The Diffusion Equation:

- Consider a thin slab of cross-sectional area A that extends from x to $(x + l)$
- Let the concentration of the solution at x be c at the time t .
- The amount (number of moles) of particles that enter the slab in the infinitesimal time interval, $dt = J \times A \times dt$,
- So, the **rate of increase in molar concentration inside the slab** (which has volume $A \times l$) on account of the **in flow of flux of particles from the left (high concentration)** =

$$\frac{\partial c}{\partial t} = \frac{J A dt}{A l dt} = \frac{J}{l}$$



IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES | Amita (Pathak) Mahanty, Department of Chemistry | 13

So, for this we had first taken up what is the interest, which we had we are looking into area window area, with area A , a thin slab is our volume, with cross section area A and thickness of the slab is suppose l . So, it extends from x into x plus l ok, so, initially my position is x and after in the end of the slab the are[a]-, the point x plus l is the zone which we have marked. So, within this area we are going to see the change in concentration.

Let the concentration of the solute at x at this point be c at time t ok, c is the molar concentration of the particles at this point where x the where the volume element starts. The amount of particles that enter this lab, at infinitesimal small time t can be given as J into A into Δt . What is J ? J is the flux of the particle.

If you remember what we had talked about what is the flux of the particle, flux of the particle is the total number of particle moving with a certain velocity, through a unit area volume area at given time t Δt will be equal that number of particles or number of moles, numbers of particle in that particular volume element divided by area into Δt .

So, if we want to find out the number of particles here then, what it will be number of particles since J equal to number of particles in unit volume divided by A into Δt . So,

the J will be the number of particles will be into J into A into Δt right, am I clear here? The total number of particles is given as, if you first you remember what is J ? J is the flux of particle. What is the flux of particle? J equal to number of particles per unit volume, whatever the unit volume is in Δt passing through a area of cross section A divided by A into Δt .

So, the number of particles in passing through a unit volume, A into, say whatever the volume length is in time t Δt divided by A by t Δt is the flux. So, if you want to find out the total number of particles then, flux should be multiplied by A into Δt right, I hope you are getting what I am saying. So, the number of particles or number of moles of particles that enter the slab is going to be flux at that point of entry that is $\times J$ flux at x into the area A into Δt ok. So, the rate of increase in molar concentration inside the slab of volume A into l , on account of flow of particle from the left side from this side to this side.

Because, when you are talking about Fick's law, it is going always going to flow from a higher concentration to lower concentration my particles are going to move from higher concentration to lower concentration. So, what we have finding out what is going to be the rate of increase in molar concentration inside the slab ok. So, molar concentration increase with the rate of molar concentration increase means how is the concentration changing with time. So, rate of increase is given by dc by dt ok, so, how is this dc by dt going to change with the inflow of flux of particle from left side to right side. So, you have number of particles coming into this slab.

What is the number of particles that is coming into the slab? Is the flux into A into Δt ok, this is what we are writing, right and divided by what the volume element that is dV into Δt ok. So, this is the dV into Δt is, A into this is the number of particles and this is the at unit time which we are measuring. So, what we get? We get this cancelled off, what we are left with J at x divided by l length of the slab right.

So, the rate of increase in molar concentration inside the slab of area A and l on account of inflow of part flux from left side from higher concentration side is going to be the change in concentration with time.

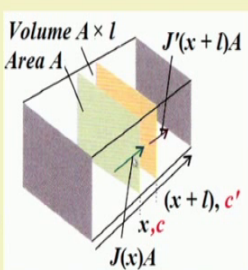
I mean; that means, dc is the initial con[centration]- c is the initial concentration. So, dc by dt , the change in concentration or rate of change of concentration is equal to flux into

A into Δt . This gives you the total number of molecules, which are passing in the time which we have taken here as $A l \Delta t$ ok. So, everything cancel of we have the flux of the particles divided by l right.

(Refer Slide Time: 10:19)

Molecular Motion in Liquids: The Diffusion Equation :

- There is **also** an **outflow through the right-hand window**
- Let the **outflow of flux of particles** through that window, A , be $= J'$
- The **NET flux of particles** in a region is the difference between the **flux of particles** entering from the region of **high concentration** (on the left) and the **flux of particles** leaving to the region of **low concentration** (on the right).



The diagram illustrates a rectangular slab of volume $A \times l$ and area A . It shows an inflow flux $J(x)A$ at position x with concentration c , and an outflow flux $J'(x+l)A$ at position $x+l$ with concentration c' . The net flux is the difference between these two.

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

Now, what happens? Since, we are seeing this diagram you can see, some amount of particles move into the slab, but there maybe the possibility of some amount moving out as well. So, there is also out flow through the right, hand window, so, the outflow flux from this A area let us designate by that by J prime. J prime is at which position x plus l .

So, at x plus l what will be the flux which is going to be moving from the left side to outside. So, if I look into this window, we have some particles which is moving into the slab, some because of the high concentration, particle moving from high concentration to low concentration and again we have some particles out flowing from this slab which is of interest. The so, the to find out the net flux in the region; what we have to take? We have to take the difference between the flux of particle entering from the high concentration area region that is the left side and the flux which is leaving the region of the towards the low concentration.

So, this is the low concentration side, so, some flux of particles are moving out and some are moving in. So, what is the net flux which we want to look into the net flux will be say the first let us say what is going to be going out.

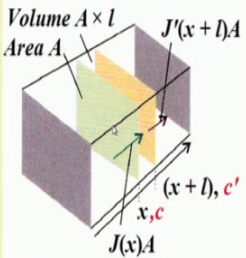
(Refer Slide Time: 11:55)

Molecular Motion in Liquids: The Diffusion Equation:

- So, the rate of decrease in molar concentration inside the slab (which has volume $A \times l$) on account of the out flow of flux of particles towards the right (low concentration) through that window, A will be =

$$\frac{\partial c}{\partial t} = - \frac{J' A \Delta t}{A \Delta t} = - \frac{J'}{l}$$

- Therefore, the NET rate of change of concentration of the particles will be =

$$\frac{\partial c}{\partial t} = \frac{J - J'}{l}$$


The diagram illustrates a rectangular slab of volume $A \times l$ and cross-sectional area A . It shows particle flux $J(x)A$ entering from the left face at position x and $J'(x+l)A$ exiting from the right face at position $x+l$. The concentration at the left face is c and at the right face is c' .

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

So, if it is going out J' is the flux which we are taking at $x + l$ that is the if point this point into A into Δt is the total number of particles which is supposed to be there in the, this area volume element and since, they are going out, so, I put a minus sign divided by $l A$ into Δt . So, $l A$ into Δt is the denominator what we have for change- finding out the change in concentration with time. So, I can rewrite this as minus J' divided by l .

So, the next change in flux concentration of the particles in the volume element which is going to be given as $c \Delta c$ by t is nothing, but the flux which was there initially and the flux which is going out, through from what from this, length l ok. So, if we put the equation write in the form like this let us, first we are supposed to be putting what J is at x and what J is at $x + l$?

(Refer Slide Time: 13:09)

Molecular Motion in Liquids: The Diffusion Equation:

- Each **flux** is **proportional to the concentration gradient at the window**. So, by using **Fick's First Law**, we can write

$$J - J' = -D \left(\frac{\partial c}{\partial x} \right) + D \left(\frac{\partial c'}{\partial x} \right) = -D \left(\frac{\partial c}{\partial x} \right) + D \left\{ c + \left(\frac{\partial c}{\partial x} \right) l \right\} = D l \left(\frac{\partial^2 c}{\partial x^2} \right)$$

where, $c' = \left\{ c + \left(\frac{\partial c}{\partial x} \right) l \right\}$

- Substituting this expression of $(J - J')$ in $\frac{\partial c}{\partial t} = \frac{J - J'}{l}$
- We get the **rate of change of concentration in the slab**: $\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$

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

So, for that let us find out what is J minus J' ? According to Fick's law Fick's 1st law what you have J is nothing, but minus D , $d c$ by $d x$ right and J minus will be what the concentration I at x plus l . If, you remember x plus l this is the [pos/position] position I am talking about.

So, at this position what will be the concentration it will be the concentration which was initially there plus the change in concentration with distance into the distance which is travelled. So, this is the new c which you have ok, at x plus l distance the c concentration will be the concentration which was initially there plus the change in concentration with distance that is the slope into the l that is the distance through which it is moved ok. So, that is the that distance moved is l , so, if this is the change per unit length then whatever change per unit length into the length will give you the concentration at that particular point.

So, this plus this should be the new concentration at x plus l ok. So, now I before that let us see, what happens? If, I applied Fick's 1st law J equal to minus $D d c$ by $d x$ and again this should be also minus $d c$ by $d x$ and the c here is prime, but here we have a minus sign and this minus sign and the minus sign of the Fick's equation give you a flux ok.

So, we can rewrite this in terms of the concentration which we have. So, we write D minus, this is the diffusion coefficient the change in concentration with x plus this $d I$

kept outside into the new concentration term which is c' I am replacing c' by this. So, c' is something like $c + \frac{dc}{dx} \cdot l$.

So, if I have this term then if you see this equation you can if you have this into $\frac{dc}{dx}$ by dx that will cancel off you multiply this into this ok, that will give you this into this once and this into this. If you are multiplying this into this, then you will have a plus sign of $\frac{dc}{dx}$ by dx and that will cancel off, but again this l term here. So, if you are looking into this you take the common what you get is $D \cdot l$ please do it yourself otherwise you will get confused because, doing this on the blackboard would have been better, but no worries.

We I have given you the expression one is this term and one is this term if you take the D common then you have the $\frac{d^2c}{dx^2}$ by $\frac{dc}{dx}$ square. So, $D \cdot l$ into $\frac{d^2c}{dx^2}$ by $\frac{dc}{dx}$ square, if you substitute this in this then what you get? You get the l eliminated then, you get the expression which we had started off with the rate of change of concentration in the slab of interest of length l thickness l is nothing, but the change in concentration with t equal to the diffusion [coefficient] coefficient into the 2nd power of concentration with position ok. This is the 2nd law of Fick's 2nd law and this is a differential equation which we have.

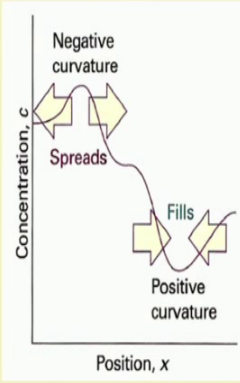
(Refer Slide Time: 17:49)

Molecular Motion in Liquids: The Diffusion Equation:

- The **Diffusion Equation** shows that the **rate of change of concentration is proportional to the curvature** (more precisely, to the **second derivative**) of the concentration with respect to distance.

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

- If the **concentration changes sharply from point to point** then the **concentration changes rapidly with time**. We say the **distribution is highly wrinkled**



IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES | Amita (Pathak) Mahanty, Department of Chemistry | 17

So, the [diff/diffusion] diffusion coefficient the diffusion equation which we have from this we can see, that the rate of change of concentration what can we see from this equation, the rate of change of concentration is proportional to the curvature or we can

say that second derivative of concentration with respect to distance you just see this, this is I have plotted concentration and this side is x is the position.

Now, since it is second differential equation; that means, I am seeing the c versus x change and the rate of change in concentration as you see; that means, rate of change of concentration with time which is c is with respect to t is actually the curvature of the plot of concentration versus t and actually it is the second derivative which we are looking into.

So, if we are having a second derivative what we are looking we are looking at the dip this is the hip and this is the dip, this is the curvature we are looking into. The concentrations of the concentrations from this graph you can see the concentration changes sharply from point to point then, the concentration changes rapidly with time.

If, we have in homogeneity in the system, when the concentration at one point changes drastically from another point then, the concentration changes with time we say then we can then say that the distribution is highly wrinkled ok. Now, what happens, when you have to have a condition sorry what happens if you have a condition like this we can discuss that in the next class.

Thank you so much.