Diffusion in Multicomponent Solids
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Lecture 13 - Fick's Law

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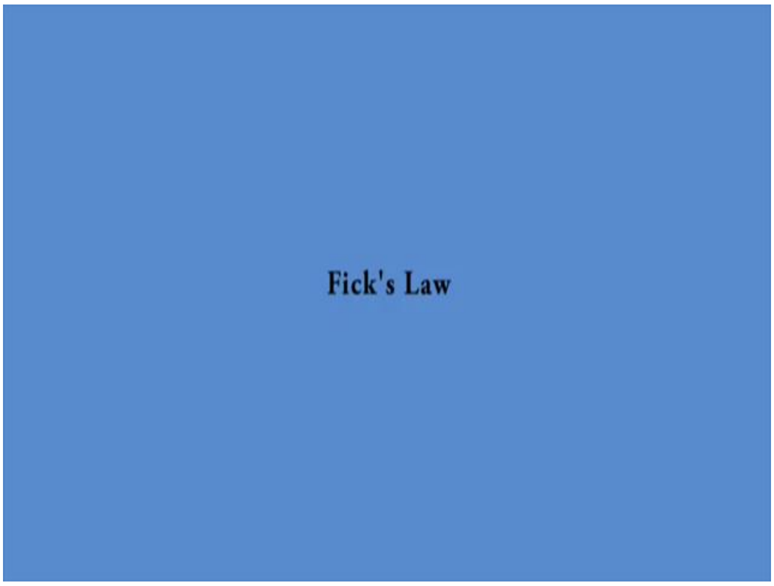

Fick's Law

Welcome to lecture 13 of the open course on Diffusion in Multicomponent Solids. In this lecture, I will introduce Fick's Law. We will also see with a simple atomic jump model, how the random atomic jumps give rise to a net flux down the concentration gradient. This helps in linking the phenomenological diffusivity term to atomic jump frequency and jump length.

Now, that we have become familiar with the concept of interdiffusion flux, we will now look into the phenomenology of diffusion. As I mentioned earlier, there are two approaches with which we can study diffusion. One is the atomistic approach, because in solids the diffusion occurs by discrete atomic jumps. So, by analyzing the atomic jump frequencies, we can analyze the diffusion. Or on the microscopic or macroscopic scale we can use the phenomenology. The second approach, as I said earlier is more important practically, because it helps us to predict the evolution of concentrations in a diffusion system with the help of some experimentally measurable parameters. And in studying this approach, Fick's Law is probably the most important that we need to study. So, we will talk about Fick's Law today.

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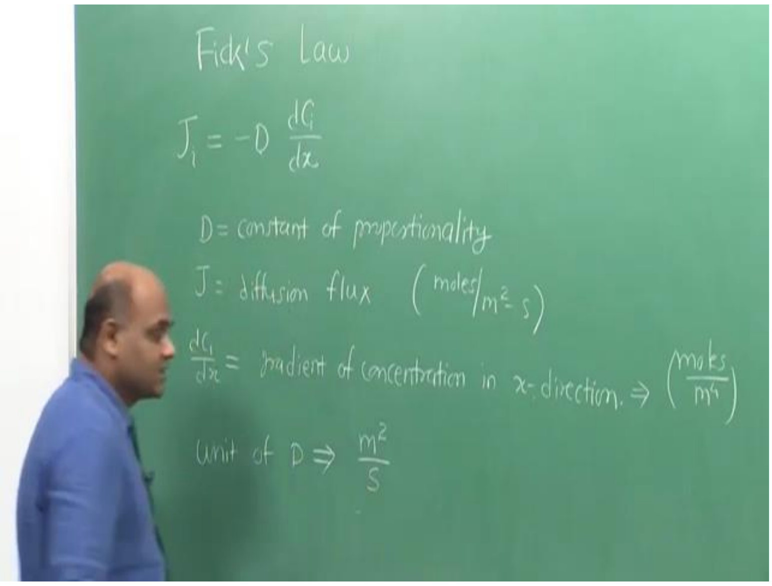

Fick's Law

$$J_i = -D \frac{dC_i}{dx}$$

D = constant of proportionality

J = diffusion flux $\left(\text{moles}/m^2 \cdot s \right)$

$\frac{dC_i}{dx}$ = gradient of concentration in x-direction. $\Rightarrow \left(\frac{\text{moles}}{m^4} \right)$

unit of D $\Rightarrow \frac{m^2}{s}$

What it says is that the diffusion flux of a component i is proportional to the concentration gradient. We can write it as:

$$J_i = -D \frac{\partial C_i}{\partial x}$$

In this case, D is the constant of proportionality, J is the diffusion flux and $\frac{\partial C_i}{\partial x}$ is the concentration gradient. This is the Fick's law equation as applied to unidirectional diffusion, which means the diffusion is taking place in one direction. Here it is in the x direction or x denotes the distance coordinate.

The unit of flux that we usually use is as:

$$\frac{no. of\ mole}{m^2 s}$$

and the concentration we express as moles per m^3. Concentration gradient will be $\frac{no.of\ mole}{m^4}$. On deriving the unit of D, it comes out to be $\frac{m^2}{s}$. Now, what does this mean? What is the physical significance of this D, we will see it later. But right now, it is sufficient to know that this is a phenomenological expression which was proposed by Fick.

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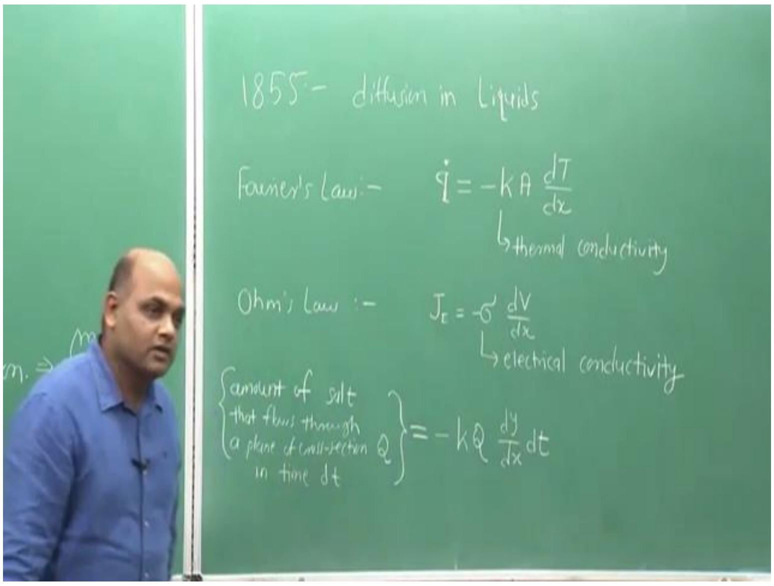

This was proposed back in 1855 by Fick and it was proposed basically for diffusion in liquids. In fact, the title of Fick's classical paper is “On the diffusion in liquids”. He studied basically the diffusion of salt in water. And he proposed this law by drawing an analogy with two other laws of transport, those are Fourier’s law of heat transport and Ohm’s law of electrical transport.

If we draw the analogy, it says that:

$$\dot{q} = -kA\frac{dT}{dx}$$

where k here denotes the thermal conductivity and A is the area of cross-section. $\dot{q}$ here is the rate of heat flow per unit time. If you take A to left side, left side becomes the heat flux and $\frac{dT}{dx}$ is the temperature gradient. So, heat flows down the temperature gradient and that is why you have a negative sign here.

Similarly, Ohm's law, you can write:

$$J_E = -\sigma\frac{dV}{dx}$$

In this case, σ is the electrical conductivity and $\frac{dV}{dx}$ is the electric potential gradient.

By drawing this analogy, Fick proposed in his original notation, the amount of salt that flows through a plane of cross-sectional area Q in time dt:

$$amount = -KQ\frac{dy}{dx}dt$$

Here, K is the constant of proportionality and he denoted y for the concentration and x is the distance unit.

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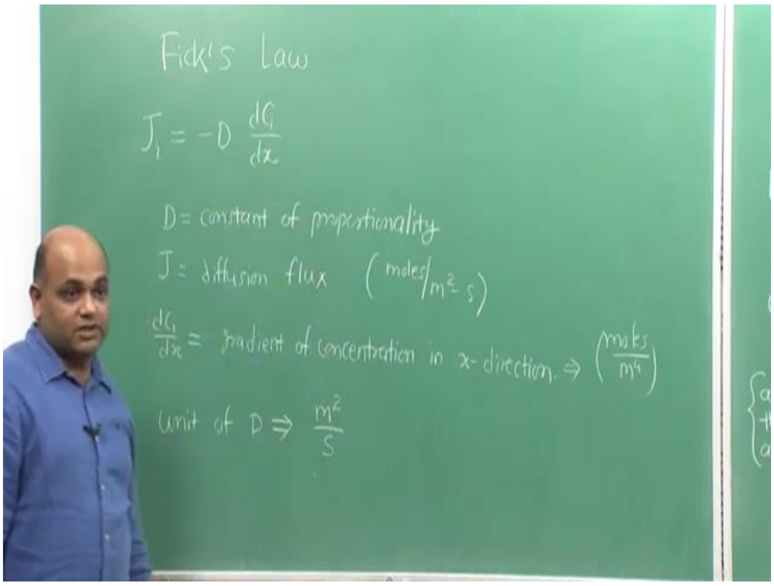

Fick's Law

$$J_1 = -D\frac{dC_1}{dx}$$

D = constant of proportionality

J = diffusion flux $\left(\text{moles}/m^2\text{-}s\right)$

$\frac{dC_1}{dx}$ = gradient of concentration in x-direction. $\Rightarrow \left(\frac{\text{moles}}{m^4}\right)$

Unit of D $\Rightarrow \frac{m^2}{s}$

If your take Q and dt to left side and if you denote K by D, this equation takes the form which is popularly written today as Fick's Law:

$$J = -D\frac{dC}{dx}$$

Obviously, now we denote concentration more generally with C. This is the law that he proposed and then Fick also carried out experiments to demonstrate the validity of this law. Again the experiments were with the salt and water solution.

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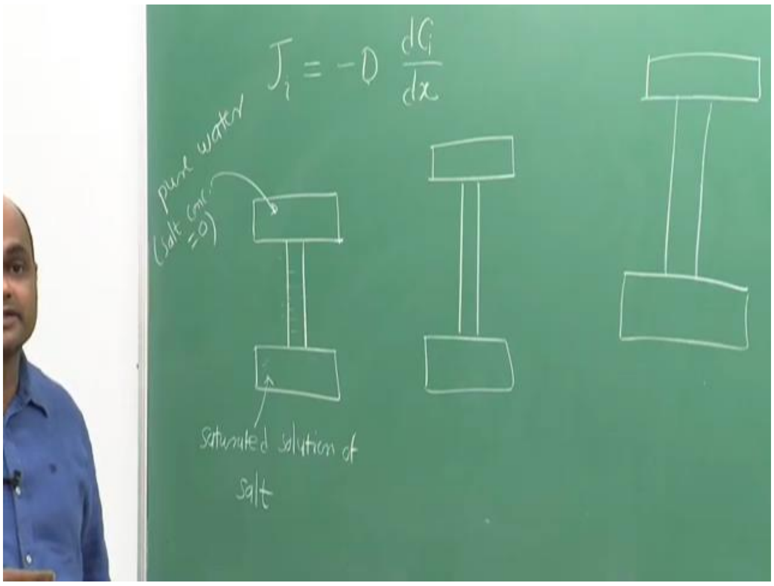

What he did is he connected two large reservoirs of solutions with a cylindrical tube. On one side there was saturated solution of salt, other side was pure water. Basically the salt concentration was approximately zero on top. And the salt diffused from bottom to the top. Bottom reservoir acted as a reservoir of salt and top reservoir acted as a sink of salt. And what was the purpose of these two, so that the concentrations at the two terminals of the tube were maintained constant.

This way, he could develop a steady-state condition for diffusion. Steady-state means as the diffusion occurs, concentration at any x position that is along the horizontal plane will remain constant, it will not change with time. In non-steady state the concentration at any x horizontal position will change with time.

By making sure that the concentrations at the two terminals remain constant we can develop a steady-state. Now, as we will see later in the steady-state, if D is constant we expect the concentration gradient to be linear. What he did, he made 3 such setups with change in the length of the tube, remaining else experimental conditions were same. Obviously, if D is a constant or if this equation is satisfied:

$$J = -D\frac{dC}{dx}$$

you should be able to measure flux in each of the case. Now, in steady-state, the flux in a given setup should be constant at any plane. Because at any plane, the matter that enters into the plane should be equal to the matter that leaves that plane such that there is no accumulation or depletion of the matter in that plane. The flux should be constant. And from that we can determine this constant D or in his notations K. He could determine the constant K. And he saw that this constant K was independent of the length of the tube.

His original experiments and the law proposed was for the diffusion in liquids. But it was also used in solids later on. The first scientist to use this law in solids was Robert Austin. You know, Robert Austin, what is he famous for? Yeah, he is famous for his work on iron carbon phase diagram. And as you rightly said, Austenite is the name given to the phase because of him. He studied diffusion of different elements in liquids. And he also conducted an experiment of diffusion of gold in solid lead. He measured the concentration at different x coordinates in his diffusion experiment and then applied this Fick's Law and measured the diffusivity of gold in lead. After that, this law has been used for many solids in single component system, binary or even in multicomponent systems and it has been now very popularly used across all 3 phases, solid, liquid or gases.

For this class more we will be interested in diffusion in solids. This flux based upon the concentration gradient of the component is also referred to as Fickian flux. What can be other reasons for getting a flux? If there is an external driving force, you might also get a net velocity of the components or the net velocity of a concentration plane because of the external driving force and it will be also be added to the flux term.

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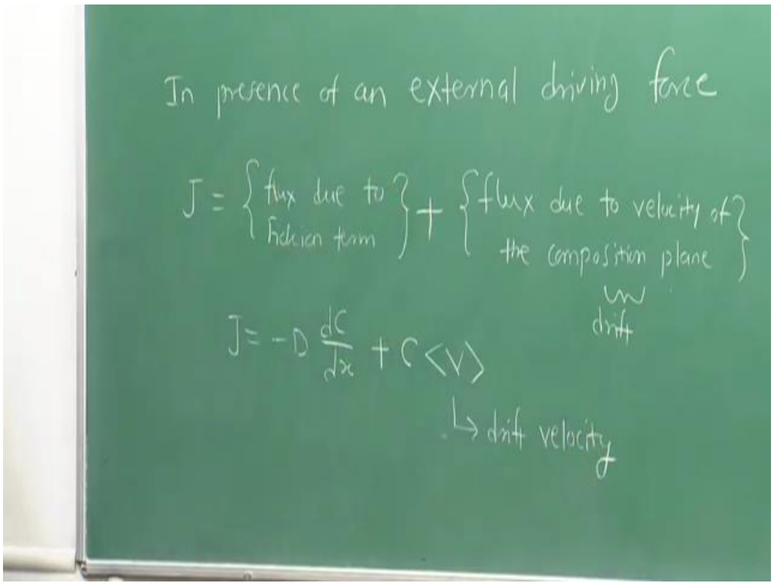

In presence of an external driving force

$$J = \left\{\begin{matrix}\text{flux due to} \\ \text{Fickian term}\end{matrix}\right\} + \left\{\begin{matrix}\text{flux due to velocity of} \\ \text{the composition plane}\end{matrix}\right\}$$

drift

$$J = -D\frac{dC}{dx} + C\langle V\rangle$$

↳ drift velocity

In presence of driving force or in presence of external driving force, the net flux will be flux due to Fickian term and also the flux due to velocity of the composition plane. This is more commonly referred to as drift. The flux term will have contribution from Fickian term as well as the drift term. We can express flux as:

$$J = -D\frac{dC}{dx} + CV$$

where V is referred to as the drift velocity.

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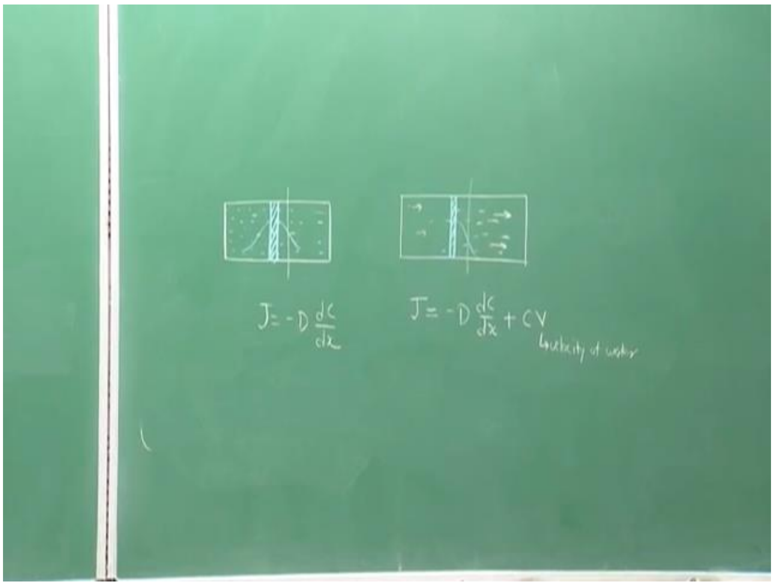

In order to understand this more clearly, let us consider a reservoir of water which is still. And suppose if I introduce a plane of ink at some position in the water, what should happen? The ink should start diffusing in the water. And as long as the water is steady or still, if I measure the flux at any point, it will be given by the Fick's law.

By the way what is the purpose of this negative sign in Fick's law? Because the diffusion occurs down the concentration gradient. In other words, the direction of flux and the direction of concentration gradients are opposite to each other. So, in order to get a positive value of constant, we apply a negative sign.

Now suppose instead of having a steady water, suppose the water was flowing with some velocity V. Now, I introduce this plane of ink here and if I measure the flux at any plane what should be the net flux here? The ink is diffusing rightwards, but any composition plane of ink is also moving with velocity V with the water. As long as the water flow is not too fast, we can have contribution from the diffusion or Fickian term plus the drift term because of the velocity of water. This will be:

$$J = -D\frac{dC}{dx} + CV$$

Second term is the drift term. And the drift term will come if there is an external driving force. The external driving force may be what? If you think of diffusion in solid, it may be an electric field or it may be a magnetic field or it may be temperature gradient. Even if there is no concentration gradient, you will still get some flux in presence of external driving force.

Now let us come to the diffusion in solid. Now we say in solids, diffusion occurs by discrete atomic jumps. There are interatomic planes, and the atom jumps from one plane onto the next plane or within the plane itself, right. It is a discrete atomic jump process. Whereas, here, the phenomenology we assume is continuous concentration gradient.

We will now let us see how these discrete atomic jumps give rise to the net flux down the concentration gradient. Let us try to link the two.

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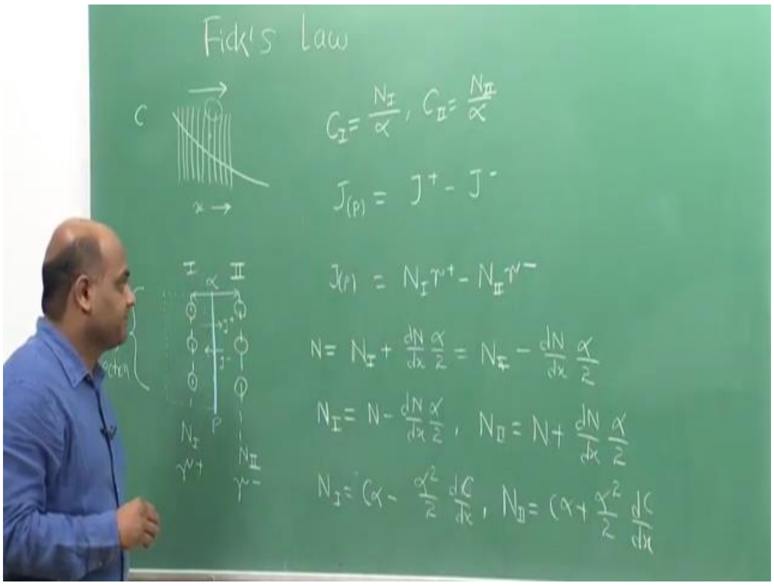

Consider a crystalline solid, in which there exists a concentration gradient. Now in solids, diffusion takes place by atomic hopping. If we consider adjacent atomic planes perpendicular to the direction of diffusion, the atoms are jumping from one plane to the other in +x as well as -x direction.

Let us call this plane 1, this plane 2 and suppose we are considering unit cross-sectional area of the plane. Let us say there are N_I number of atoms per unit area on plane 1 and N_{II} number of atoms per unit area on plane 2, and each atom is vibrating with certain frequency. So, per unit time, there will be certain number of successful jumps that each atom can make.

Let us call it a jump frequency. Let us suppose the jump frequency or the frequency of successful jump from plane 1 to plane 2 is γ^{+}. And the number of successful jumps from plane 2 to plane 1, let us denote it by γ^{-}. γ^{+} is basically the number of times an atom from plane 1 can jump into plane 2 per unit time. If there are N_I number of atoms, the total number of jumps that can occur from plane 1 to plane 2 are $N_I\gamma^{+}$.

Similarly, the total number of jumps that can occur from plane 2 to plane 1 per unit time are $N_{II}\gamma^{-}$. We can consider equal volume element around each atomic plane. And if α is the interplanar spacing, then what will be the volume around each element or around each plane? The volume of element around each atomic plane will be α times cross-sectional area, but we have a unit cross-sectional area, so the volume will be alpha.

If I determine the concentrations, C_I would be number of atoms per volume, it will be:

$$C_I = \frac{N_I}{\alpha} \quad and \quad C_{II} = \frac{N_{II}}{\alpha}$$

Now we need to measure let us say, the flux across the central plane, let us call this P. what will be the net flux across plane P? There are atoms jumping from left to right. That is from plane 1 to plane 2 and there are atoms jumping from plane 2 to plane 1. So, the net flux will be the difference between the two.

If I call the atoms jumping from plane 1 to plane 2 per unit time per unit area as J^{+} and 2 to 1 as J^{-}, then the net flux in P will be:

$$J_{(P)} = J^{+} - J^{-}$$

And what will be J^{+}, the number of atoms jumping from plane 1 to plane 2 per unit time, that will be $N_I\gamma^{+}$and J^{-} will be $N_{II}\gamma^{-}$:

$$J_{(P)} = N_I\gamma^{+} - N_{II}\gamma^{-}$$

Now, if I assume the gradient in number of atoms to be continuous then I can know the number of atoms per unit area on this plane P by knowing the gradient, because I know N_I and N_{II}. If I take N as the number of atoms per unit area on plane P in terms of the gradient and N_I or N_{II} we can express it as:

$$N = N_I + \frac{dN}{dx}\frac{\alpha}{2} = N_{II} - \frac{dN}{dx}\frac{\alpha}{2}$$

We are making a small assumption here that the gradient is linear which should be very close to reality because the interatomic spacing is very small. Now, in terms of N, we can express:

$$N_I = N - \frac{dN}{dx}\frac{\alpha}{2}$$

$$N_{II} = N + \frac{dN}{dx}\frac{\alpha}{2}$$

And we substitute for N as $C\alpha$, we get:

$$N_I = C\alpha - \frac{\alpha^2}{2}\frac{dC}{dx}$$

$$N_{II} = C\alpha + \frac{\alpha^2}{2}\frac{dC}{dx}$$

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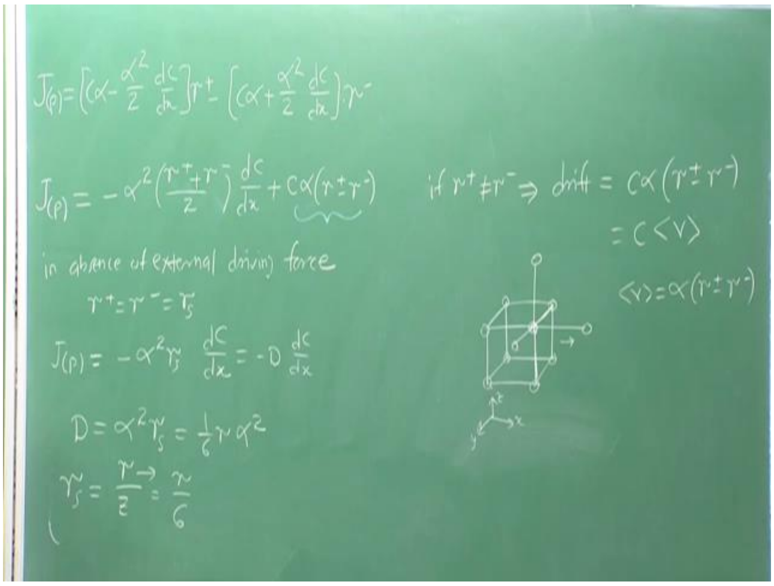


$$J_{(P)} = \left[C\alpha - \frac{\alpha^2}{2}\frac{dC}{dx}\right]\Gamma^+ - \left[C\alpha + \frac{\alpha^2}{2}\frac{dC}{dx}\right]\Gamma^-$$

$$J_{(P)} = -\alpha^2\left(\frac{\Gamma^+ + \Gamma^-}{2}\right)\frac{dC}{dx} + \underbrace{C\alpha(\Gamma^+ - \Gamma^-)}$$

if $\Gamma^+ \neq \Gamma^- \Rightarrow$ drift $= C\alpha(\Gamma^+ - \Gamma^-)$

$= C\langle v\rangle$

$\langle v\rangle = \alpha(\Gamma^+ - \Gamma^-)$

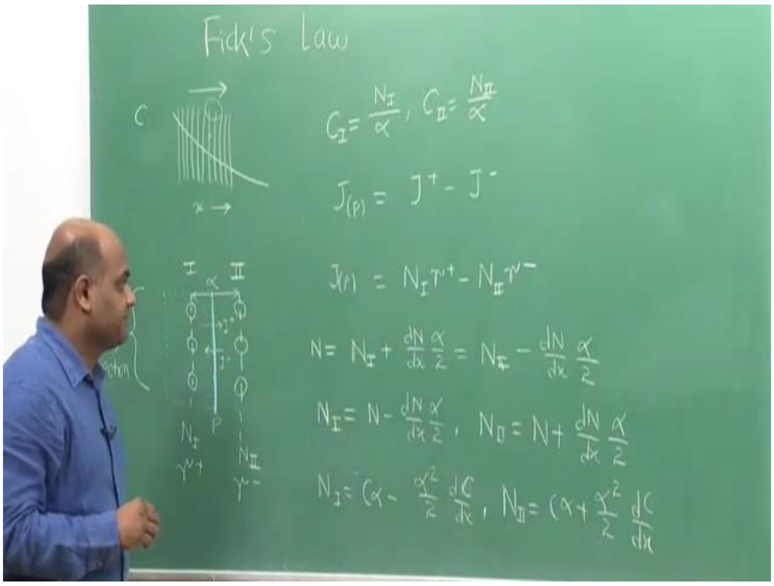
in absence of external driving force

$\Gamma^+ = \Gamma^- = \Gamma_s$

$$J_{(P)} = -\alpha^2\Gamma_s\frac{dC}{dx} = -D\frac{dC}{dx}$$

$$D = \alpha^2\Gamma_s = \frac{1}{6}\Gamma\alpha^2$$

$$\Gamma_s = \frac{\Gamma \rightarrow}{z} = \frac{\Gamma}{6}$$



If I substitute in J at plane P, I get:

$$J_{(P)} = \left(C\alpha - \frac{\alpha^2}{2}\frac{dC}{dx}\right)\gamma^+ - \left(C\alpha + \frac{\alpha^2}{2}\frac{dC}{dx}\right)\gamma^-$$

And if we rearrange, we get:

$$J_{(P)} = -\alpha^2\frac{(\gamma^+ + \gamma^-)}{2}\frac{dC}{dx} + C\alpha(\gamma^+ - \gamma^-)$$

In absence of any external driving force, the jump frequency in $+x$ direction or $-x$ direction should be same. So, we have:

$$\gamma^+ = \gamma^- = \gamma_s$$

We get $J_{(P)}$ as:

$$J_{(P)} = -\alpha^2\gamma_s\frac{dC}{dx}$$

γ_s will be the overall jump frequency, later on we will use it. We get a familiar expression, which is similar to the Fick's Law expression:

$$J = -D\frac{dC}{dx}$$

On comparing the two we get:

$$D = \alpha^2\gamma_s$$

Now γ_s is the frequency of jumps in x direction. If there is no external driving force, then all jumps should be equiprobable. And how many sites an atom can jump, if we consider only nearest neighbor jumps? In any crystal lattice, how many sites are available for an atom to jump?

Student: Coordination number.

Professor: Coordination number Z. We have:

$$\gamma_s = \frac{\gamma}{Z}$$

where γ is the successful jump frequency of an atom in any direction. If we consider a simple cubic case, what is the coordination number of simple cubic lattice? 6, right.

If I consider an atom in a simple cubic lattice, it can jump to $+x, -x, +y, -y, +z\ and - z$. So, there are six possible jumps. If we consider diffusion along $+x$ direction, then except $+x$ and $-x$, rest 4 jumps are basically not giving any contribution in the $+x$ direction, because they are within the plane itself, so they are not giving any contribution.

As, we are considering a unidirectional diffusion, the only jumps that matter are $+x$ and $-x$. For simple cubic this treatment that we applied will be valid and in that case it will be:

$$\gamma_s = \frac{\gamma}{Z} = \frac{\gamma}{6}$$

$$D = \alpha^2 \gamma_s = \frac{1}{6}\gamma\alpha^2$$

Now, let us look at this second term in the following expression:

$$J_{(P)} = -\alpha^2 \frac{(\gamma^+ + \gamma^-)}{2}\frac{dC}{dx} + C\alpha(\gamma^+ - \gamma^-)$$

Whenever there is an external driving force present, then the jump frequency in $+x$ direction will not be same as that in $-x$ direction, depending upon the gradient of the external field. That means, this term will not vanish, it will have some non-zero value. Obviously, if:

$$\gamma^+ \neq \gamma^-$$

second term on right side will have a nonzero value. And this is nothing but the drift term which is equal to:

$$Drift = C\alpha(\gamma^{+} - \gamma^{-})$$

We know that:

$$Drift = Cv$$

So the drift velocity comes out to be:

$$v = \alpha(\gamma^{+} - \gamma^{-})$$

This is how the discrete atomic jumps will give rise to the net diffusion flux down the concentration gradient. We have linked the atomistic random jump model to the phenomenological equation of Fick's law. Now, if the jump frequencies are not same, obviously, there will be a net average velocity of the atoms of i in one particular direction depending upon the sign of the term $(\gamma^{+} - \gamma^{-})$ and that will give rise to this drift.

So, flux has contribution from Fickian term as well as the drift term. We looked at the simple cubic structure. What about if I have BCC or FCC? Let us still consider cubic structure. Obviously, non cubic structure will be even more complicated. But let us consider either FCC or BCC. Now, if I have FCC or BCC, if you consider the contribution in $+x$ direction, there will be also jumps at different angles which will contribute to the diffusion in $+x$ direction.

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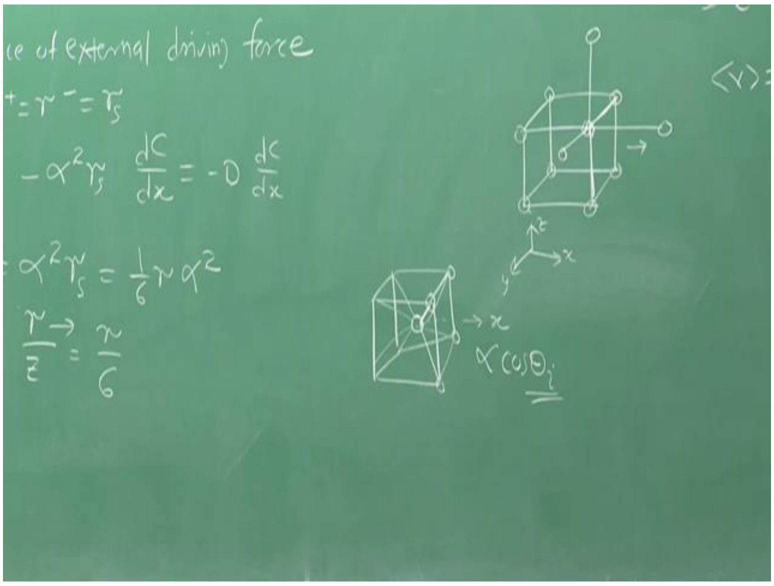

For example, let us consider a BCC lattice with a body center atom and let us day this atom jumps onto one of the eight corner atoms which are the nearest neighbors. Now, any of these jump is not exactly in $+x$ direction, but it will have some contribution in the x direction.

How much will be that? If the jump length is α, the contribution will be $\alpha cos\theta_i$. θ_i is the angle that the jump i makes with the x direction, the direction of diffusion. Okay. now, we need to modify this a little bit. Instead of α, the interatomic spacing for the jump i would be $\alpha cos\theta_i$.

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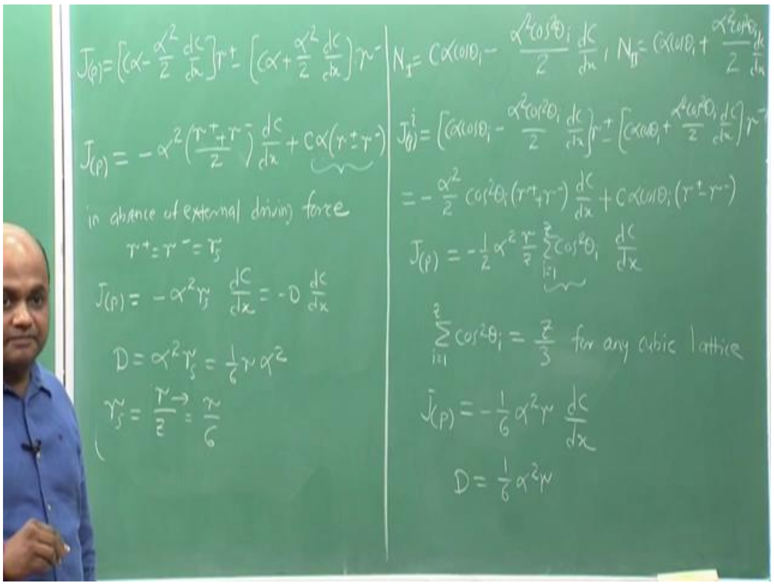

$$J_{(P)} = \left[C\alpha - \frac{\alpha^2}{2}\frac{dC}{dx}\right]\gamma^+ - \left[C\alpha + \frac{\alpha^2}{2}\frac{dC}{dx}\right]\gamma^-$$

$$J_{(P)} = -\alpha^2\left(\frac{\gamma^+ + \gamma^-}{2}\right)\frac{dC}{dx} + C\alpha\underbrace{(\gamma^+ - \gamma^-)}$$

in absence of external driving force

$$\gamma^+ = \gamma^- = \gamma_s$$

$$J_{(P)} = -\alpha^2\gamma_s\frac{dC}{dx} = -D\frac{dC}{dx}$$

$$D = \alpha^2\gamma_s = \frac{1}{6}\gamma\alpha^2$$

$$\gamma_s = \frac{\gamma_{\rightarrow}}{z} = \frac{\gamma}{6}$$

$$N_I = C\alpha cos\theta_i - \frac{\alpha^2 cos^2\theta_i}{2}\frac{dC}{dx}, \quad N_{II} = C\alpha cos\theta_i + \frac{\alpha^2 cos^2\theta_i}{2}\frac{dC}{dx}$$

$$J^i_{(P)} = \left[C\alpha cos\theta_i - \frac{\alpha^2 cos^2\theta_i}{2}\frac{dC}{dx}\right]\gamma^+ - \left[C\alpha cos\theta_i + \frac{\alpha^2 cos^2\theta_i}{2}\frac{dC}{dx}\right]\gamma^-$$

$$= -\frac{\alpha^2}{2}cos^2\theta_i(\gamma^+ + \gamma^-)\frac{dC}{dx} + C\alpha cos\theta_i(\gamma^+ - \gamma^-)$$

$$J_{(P)} = -\frac{1}{2}\alpha^2\frac{\gamma}{z}\underbrace{\sum_{i=1}^{z}cos^2\theta_i}\frac{dC}{dx}$$

$$\sum_{i=1}^{z}cos^2\theta_i = \frac{z}{3}$$ for any cubic lattice

$$J_{(P)} = -\frac{1}{6}\alpha^2\gamma\frac{dC}{dx}$$

$$D = \frac{1}{6}\alpha^2\gamma$$

So:

$$N_I = C\alpha cos\theta_i - \frac{\alpha^2 cos^2\theta_i}{2}\frac{dC}{dx}$$

$$N_{II} = C\alpha cos\theta_i + \frac{\alpha^2 cos^2\theta_i}{2}\frac{dC}{dx}$$

And $J^i_{(P)}$ becomes:

$$J^i_{(P)} = \left(C\alpha cos\theta_i - \frac{\alpha^2 cos^2\theta_i}{2}\frac{dC}{dx}\right)\gamma^+ - \left(C\alpha cos\theta_i + \frac{\alpha^2 cos^2\theta_i}{2}\frac{dC}{dx}\right)\gamma^-$$

If we rearrange the terms, we get:

$$J^i_{(P)} = -\alpha^2 cos^2\theta_i\frac{(\gamma^+ + \gamma^-)}{2}\frac{dC}{dx} + C\alpha cos\theta_i(\gamma^+ - \gamma^-)$$

Now let us assume that there is no external driving force. Second term on right side will vanish and:

$$(\gamma^+ + \gamma^-) = 2\gamma$$

Let us denote this $J_{(P)}$ more specifically with $J_{(P)}^{i}$, because we are considering only the jump vector i. There will be how many such jumps? Z number of jumps possible right, because the coordination number is Z. To get the total flux, we need to sum over the jumps i. Now, $(\gamma^{+} + \gamma^{-}) = 2\gamma$. But then only half of the jumps will be in $+x$ direction, the remaining half will be $-x$ direction, so we need to divide by half.

$$J_{(P)} = -\frac{\alpha^2}{2}\frac{\gamma}{Z}\sum_{i=1}^{Z} cos^2\theta_i \frac{dC}{dx}$$

We need to evaluate this summation $\sum_{i=1}^{Z} cos^2\theta_i$ over all possible jumps 1 to Z. And you will find out, if we do that for BCC or even FCC, this will be Z by 3 for any cubic lattice:

$$\sum_{i=1}^{Z} cos^2\theta_i = \frac{Z}{3}$$

This we will show as an exercise in the next lecture. If we substitute this relation in flux equation we get:

$$J_{(P)} = -\frac{1}{6}\alpha^2\gamma\frac{dC}{dx}$$

For any cubic lattice we can express D as:

$$D = \frac{1}{6}\alpha^2\gamma$$

where α is the jump length and γ is the frequency of successful jumps of an atom in any direction.

So we saw the phenomenology based upon Fick's Law and it is also consistent with the atomistic picture based upon the jump frequency model.