Diffusion in Multicomponent Solids
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Lecture 12 - Diffusion Flux and Frames of Reference

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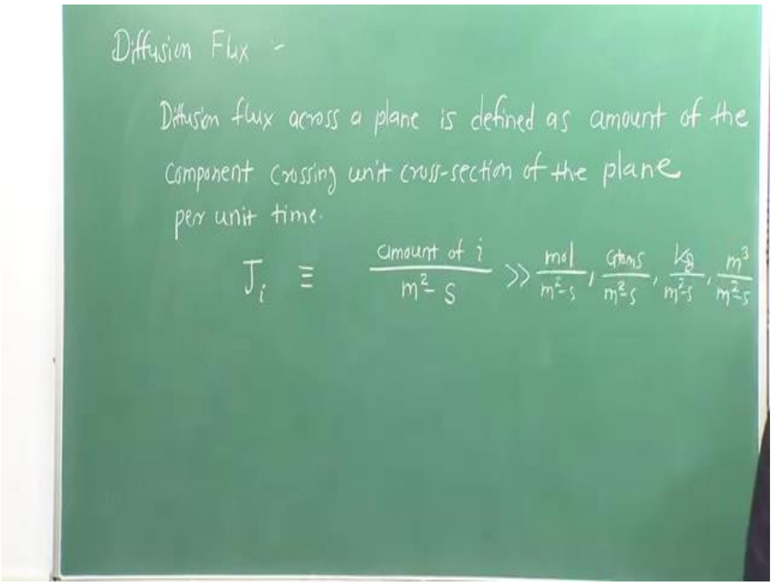

Hello friends and welcome to the open course on Diffusion in Multicomponent Solids, this is the 12th lecture in this series and in this lecture I will explain the concept of diffusion flux and various frames of reference used to measure the diffusion fluxes.

Diffusion flux is a very important quantity in the analysis of diffusion. Today we will talk about this concept of diffusion flux and various frames of reference that we need for the measurement of diffusion flux. Diffusion flux is defined as the amount of a component that crosses unit cross sectional area of a plane per unit time. Diffusion flux of a component is usually denoted by the symbol J_i and unit of diffusion flux will be amount of the component i per unit area per unit time.

$$J_i = \frac{amount\ of\ i}{m^2 s}$$

Amount of i can be expressed in various units like number of moles, number of atoms, weight or it can be even volume. So, the various units of flux can be:

$$J_i = \frac{mole\ of\ i}{m^2 s} = \frac{atoms\ of\ i}{m^2 s} = \frac{kg\ of\ i}{m^2 s} = \frac{m^3\ of\ i}{m^2 s}$$

Let us try to understand physically the quantity flux.

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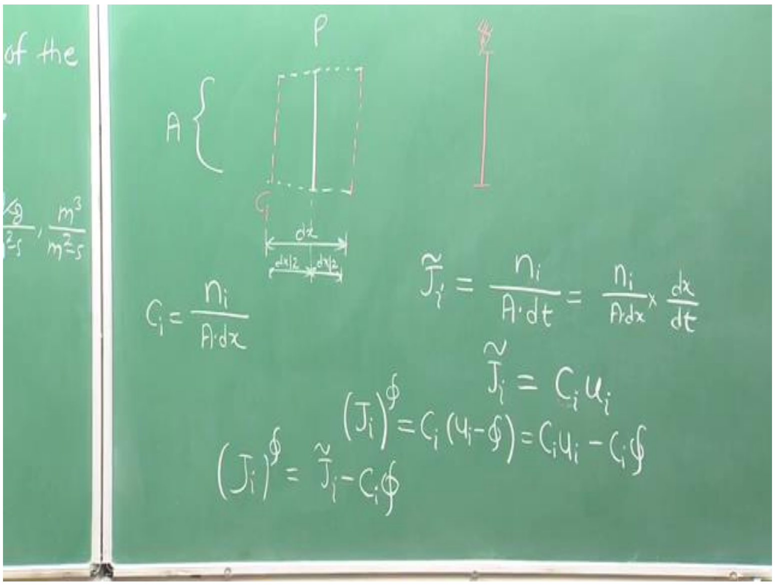

Let us consider a certain plane P at which you need to determine the flux and our frame of reference is fixed at some physical plane which is fixed in the laboratory fixed frame. And we are seeing how much of amount of component i is crossing this plane P per unit time. Let us say the cross sectional area of the plane is A, suppose we are considering a composition front with composition C_i as is fixed through a distance dx across the plane P this is distance dx. this is dx by 2, this is dx by 2 in small interval of time dt.

This forms a small volume element around P, and if there are n_i number of atoms of i in this compositional front, then we can write the concentration of i in the small volume element as:

$$C_i = \frac{n_i}{Adx}$$

By definition what will be the flux? n_i number of atoms have crossed plane P in time dt. So, the flux of i with respect to a laboratory fixed frame is n_i crossing per unit area A per unit time dt:

$$\tilde{J}_i = \frac{n_i}{Adt} = \frac{n_i}{Adx} \times \frac{dx}{dt}$$

Flux is usually denoted by a symbol $\sim$ on top of J, or $\tilde{J}_i$. It is also referred to as interdiffusion flux. Now if you see $\frac{n_i}{Adx}$ is nothing but the concentration C_i and as dt tends to zero $\frac{dx}{dt}$ is the velocity of this compositional front. Let us denote this by U_i. Interdiffusion flux with respect to a laboratory frame is simply:

$$\tilde{J}_i = C_i U_i$$

U_i is also referred to as the mean velocity of atoms of i.

Now, suppose if plane P was also moving, would the flux still be same? No.

Consider an analogy for example, you are standing on the median of a road and then your job is to count the number of vehicles crossing you on one side of the road. Suppose initially you are stationary and all the vehicles are moving with some constant average velocity. You will see in certain amount of time certain number of vehicles will cross you. Suppose, instead of being stationary, if you are also moving in the same direction of vehicles, now would the number be same or different? Because you are moving in the same direction as the vehicles number of vehicles crossing you now will be lower. If you were moving in the opposite direction, the number would be higher because more number of vehicles now will cross you per unit time. Similarly, if the plane P is moving in the same direction as this composition front, then the flux seen by plane P will be lower.

If we express J_i with respect to the frame of reference which is fixed to plane P, we will call the flux as $(J_i)^{\phi}$ where ϕ is the velocity of plane P. Then, in the new coordinate system the effective velocity will be $(U_i - \phi)$. So,

$$(J_i)^{\phi} = C_i(U_i - \phi) = C_iU_i - C_i\phi = \tilde{J}_i - C_i\phi$$

This shows us that the value of flux will depend upon the frame of reference that we are choosing and the fluxes from one frame of reference can be converted into fluxes in another frame of reference, if we know the velocity of the frame of references.

Now, what are the different frames of reference that we use for determining diffusion fluxes?

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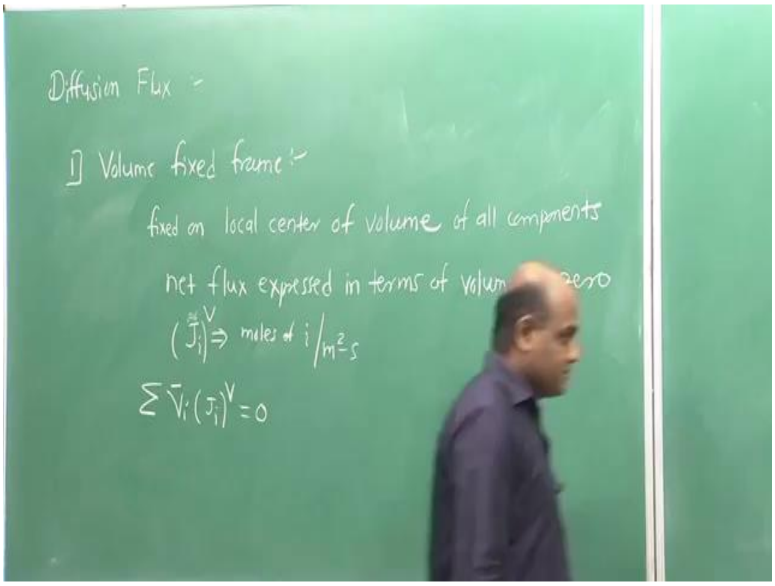

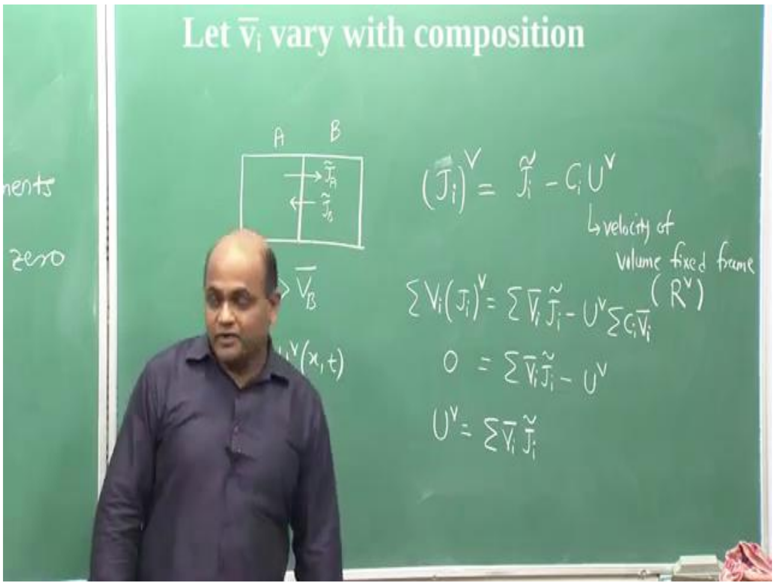

The first one is called volume fixed frame. Volume fixed frame is basically fixed on local center of volume of all components such that net flux expressed in terms of volume is 0. let us try to understand this a little more.

Suppose partial molar volume varies with composition and we consider the diffusion between two elements, A and B. Let say they are completely miscible into each other. Then what happens? As some A atoms move from left to right and some B atoms move from right to left, the net flux of A will be from left to write, B will be from right to left. Consider when initially only one atom of A jumps from left to right, and one atom of B jumps from right to left. Although in terms of atoms there is only only one atom exchange but, in terms of volume it will be different because A will have different partial molar volume than B and suppose $\bar{V}_A >$

$\bar{V}_B$. After some time there is an accumulation of A on right side, accumulation of B on left side and depletion of A on left and depletion of B on right.

In effect, there will be increase in volume on the right side, so the center of volume has moved towards the right because A is having higher partial molar volume than B. Now, if we fix the frame of reference along the local center of volume then the net flux in terms of volume (net volume movement) across that plane will be zero. So that is our volume fixed frame.

Typically we express flux in terms of:

$$(J_i)^v = \frac{moles\ of\ i}{m^2 s}$$

$(J_i)^v$ is the flux in volume fixed frame of reference. Now, the net flux expressed in terms of volume is zero. So we need to convert this moles of i into meter cube of i. So, we multiply by meter cube of i divided by mole of i (which is basically the multiplication by partial molar volume) followed by summation over all the components we get:

$$\sum \bar{V}_i (J_i)^v = 0$$

In terms of volume fixed frame, again there are only $n-1$ independent fluxes, so the nth one will be dependent because there is a constraint. Now from the equation that we derived we can write :

$$(J_i)^v = \tilde{J}_i - C_i U^v$$

Where $\tilde{J}_i$ is flux with respect to stationary frame of reference and U^v is the velocity of volume fixed frame. This volume fixed frame is generally denoted as R superscript V, R^V.

If you multiply both sides by molar volume and then take the summation over all components we get:

$$\sum \bar{V}_i (J_i)^v = \sum \bar{V}_i \tilde{J}_i - U^v \sum C_i \bar{V}_i$$

As we know the left hand side is zero because of the constraint put by the volume fixed frame we get:

$$\sum \bar{V}_i (J_i)^v = 0$$

So,

$$\sum \bar{V}_i \tilde{J}_i - U^v \sum C_i \bar{V}_i = 0$$

As $C_i \bar{V}_i$ is basically the volume fraction:

$$\sum C_i \bar{V}_i = 1$$

We get:

$$\sum \bar{V}_i \tilde{J}_i - U^v = 0$$

$$U^v = \sum \bar{V}_i \tilde{J}_i$$

Now, this U^v is an important quantity and varies with distance and with time. It will not be same as we go from left to right, it varies with x as well as t or U^v is a function of x and . Similarly, there are other frames of reference.

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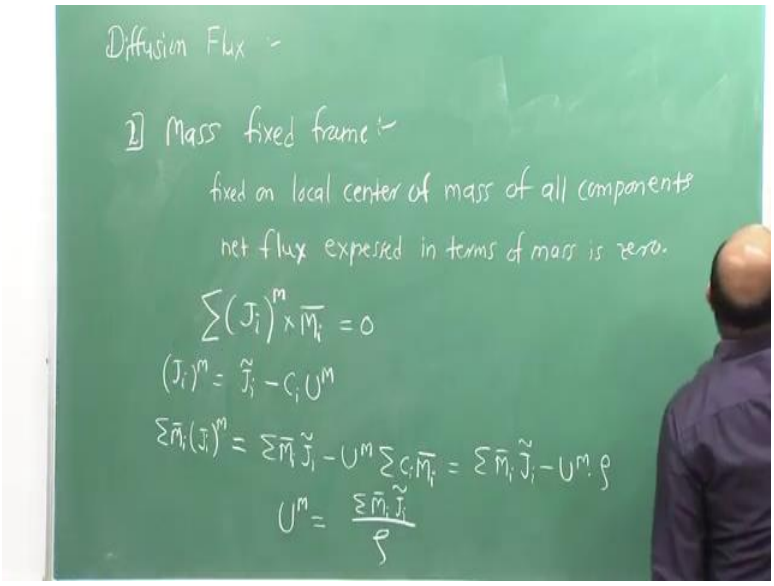

The second one is mass fixed frame. Mass fixed frame is fixed on local center of mass of all components such that net flux is zero with respect to this frame. Obviously we can give the similar analogy as volume fixed frame that the molar mass of each component is not same or atomic mass of each component is not same. Local center of mass will shift in the direction of diffusion of heavier element in case of the binary diffusion.

If we stick our frame of reference to that local center of mass then obviously, the net mass movement will be zero. If you consider $(J_i)^M$ as the flux expressed in terms of mass fixed frame, to convert it in terms of mass we multiply by kg divide by mole of i. kg of i per mole of i is basically the molar mass.

$$\sum (J_i)^M \bar{M}_i = 0$$

This is the constraint put by the mass fixed frame of reference. We can express:

$$(J_i)^M = \tilde{J}_i - C_i U^M$$

where U^M is the velocity of our mass fixed frame. If we multiply by molar mass and take the summation we get:

$$\sum \bar{M}_i (J_i)^M = \sum \bar{M}_i \tilde{J}_i - U^M \sum C_i \bar{M}_i = 0$$

What is $C_i \bar{M}_i$?

$$C_i \bar{M}_i = \frac{no. of\ mole\ of\ i}{m^3\ of\ alloy} \times \frac{kg\ of\ i}{no. of\ mole\ of\ i} = \frac{kg\ of\ i}{m^3\ of\ alloy}$$

and the summation will be density:

$$\sum C_i \bar{M}_i = \rho$$

So,

$$\sum \bar{M}_i \tilde{J}_i - U^M \rho = 0$$

And expression for U^M will be:

$$U^M = \frac{\sum \bar{M}_i \tilde{J}_i}{\rho}$$

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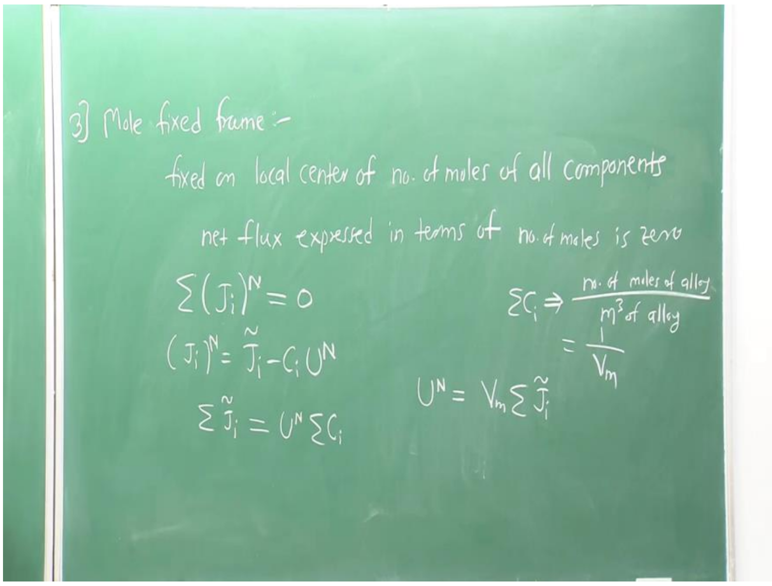

We can also fix the frame of reference with respect to local center of number of moles of all the components and that is called as mole fixed frame. Nnet flux expressed in terms of number of moles with respect to this frame is zero.

We typically express flux in terms of number of moles, so you can write:

$$\sum (J_i)^N = 0$$

Now, $(J_i)^N$ denotes the diffusion flux of i with respect to the mole fixed frame of reference. We know:

$$(J_i)^N = \tilde{J}_i - C_i U^N$$

where U^N is the velocity of number fixed frame and if we take the summation we will ge:

$$\sum (J_i)^N = \sum \tilde{J}_i - U^N \sum C_i = 0$$

Or

$$\sum \tilde{J}_i = U^N \sum C_i$$

What is $\sum C_i$?

$$\sum C_i = \frac{no. of\ mole\ of\ alloy}{m^3\ of\ alloy} = \frac{1}{V_m}$$

V_m is the molar volume of the alloy. So:

$$U^N = V_m \sum \tilde{J}_i$$

Remember these expressions that we are deriving are assuming that the flux is in terms of moles per meter square per second or moles per area per unit time. Our inherent assumption is typically we express fluxes in terms of moles per unit area per unit time. The advantage of using these different frames of reference is that we can make one flux dependent. We will see later on that it will help us to reduce the number of diffusion coefficients needed to describe the diffusion in a particular n component system.

There can be also be another frame of reference which is fixed to a particular lattice plane and that is referred to as lattice fixed frame of reference or it is also referred to as Kirkendall frame of reference. We will talk in depth about that sometime later.