Diffusion in Multicomponent Solids
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Lecture 34
Physical Significance of Diffusivity: Einstein-Smoluchowski Equation

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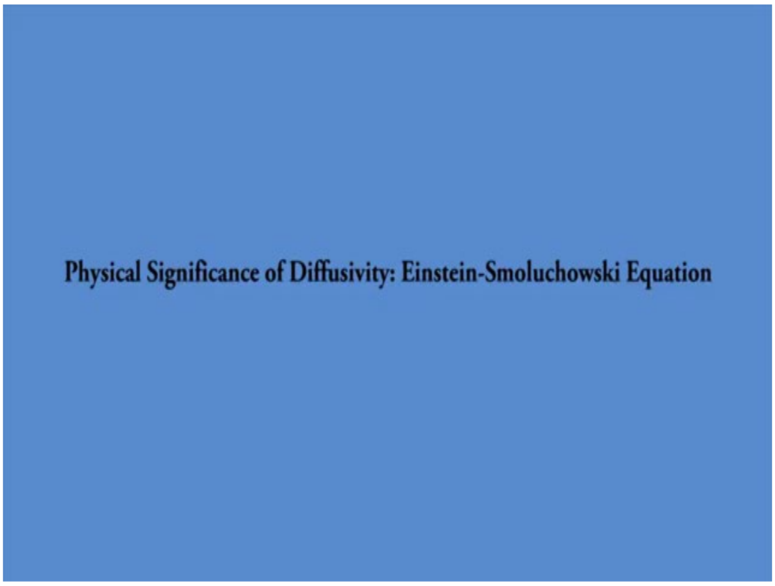

Welcome to the 34th lecture of the open course on Diffusion in Multicomponent Solids. In this lecture, I have presented the derivation of Einstein's equation, which is also known as Einstein-Smoluchowski Equation. This equation established the physical significance of the diffusivity term as a measure of Mean Square Displacement per unit time.

We are going over the theory of Random walk. In the last class, we derived the expression for mean square displacement of a large number of particles, when each particle makes n jumps. Why do we need this mean square displacement and how is it related to the term diffusivity? We will see it today.

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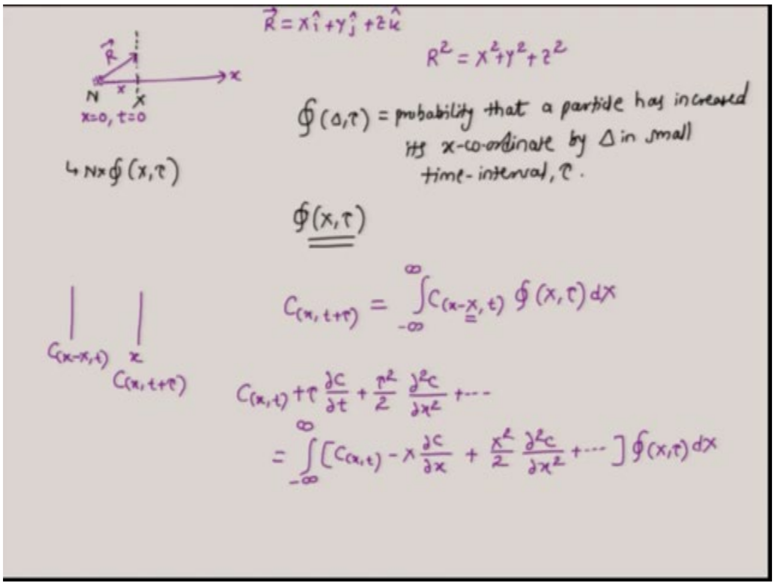

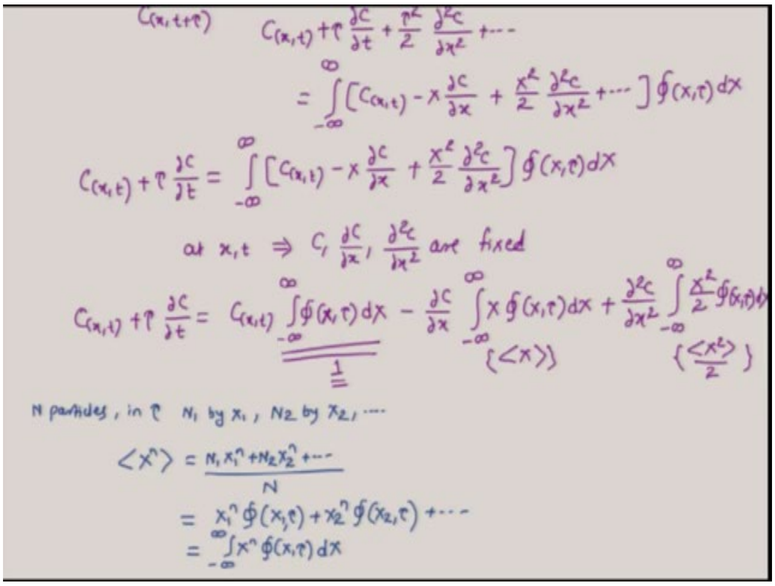

We consider an ensemble of large number of particles at $x = 0,\ t = 0$. Now these particles are undergoing random walk and this distribution will spread in space with time. If we track the individual particles, each particle would have made some net displacements in time t. if we define this net displacement as $\vec{R}$and if we write:

$$\vec{R} = X\hat{\imath} + Y\hat{\jmath} + Z\hat{k}$$

then X, Y, Z are the projections of $\vec{R}$ on x, y and z axis respectively. If we consider the x direction, the projection here would be X. And R^2 would be given as:

$$R^2 = X^2 + Y^2 + Z^2$$

Einstein defined a function ϕ of Δ, τ such that:

$$\phi(\Delta,\tau) = probability\ that\ a\ particle\ has\ increased\ its\ x - coordinate\ by\ \Delta\ in\ small\ time\ interval, \tau$$

In today's convention, we would like to write it as:

$$\phi(X,\tau)$$

where the X is the projection of the net displacement vector $\vec{R}$ on the x axis. $\phi(\mathrm{X},\tau)$ is the probability that a particle has increased its x coordinate by X in small time interval τ. Now, what is this $\phi(X,\tau)$?

To understand this, if we consider that at $t = 0$, there were n particles at $x = 0$ then the number of particles at plane $x = X$ after time τ would be given by n times the probability that a particle travels a distance whose projection is this X in time interval τ, $n\phi(X,\tau)$

Let us consider plane of concentration at x, let us denote it as $C(\mathrm{x})$ and if you want to find out the concentration at x at a time $t + \tau$, in terms of $C(x - X, t)$, that can be expressed as:

$$C(x,t+\tau) = \int_{-\infty}^{\infty} C(x - X, t)\,\phi(X,\tau)dX$$

This is simply the balance equation. Now we can expand this $C(x, t + \tau)$ as:

$$C(x,t+\tau) = C(x,t) + \frac{\partial C}{\partial t}\tau + \frac{\partial^2 C}{\partial t^2}\frac{\tau^2}{2} + \cdots$$

And inside the integral, we can similarly expand:

$$C(x - X, t) = C(x,t) - \frac{\partial C}{\partial x}X + \frac{\partial^2 C}{\partial x^2}\frac{X^2}{2} + \cdots$$

That would give:

$$C(x,t+\tau) = \int_{-\infty}^{\infty} \left[C(x,t) - \frac{\partial C}{\partial x}X + \frac{\partial^2 C}{\partial x^2}\frac{X^2}{2} + \cdots\right]\phi(X,\tau)dX$$

Now we are considering very small interval τ. on the left hand side of this equation, we can ignore the terms involving τ^2 and onwards. We can write approximately left hand side as:

$$C(x,t) + \frac{\partial C}{\partial t}\tau$$

And as $\tau \rightarrow 0$, most of the distribution would tend to be segregated towards $x = 0$. So, on the right hand side we can ignore the terms higher than X^2. We can write:

$$C(x,t) + \frac{\partial C}{\partial t}\tau = \int_{-\infty}^{\infty} \left[C(x,t) - \frac{\partial C}{\partial x} X + \frac{\partial^2 C}{\partial x^2} \frac{X^2}{2} \right] \phi(X,\tau) dX$$

At any given position of x and at any time t, we can take these terms $C(x,t)$, $\frac{\partial C}{\partial x}$, $\frac{\partial^2 C}{\partial x^2}$ outside the integral as they are fixed. Then we can write:

$$C(x,t) + \frac{\partial C}{\partial t}\tau = C(x,t) \int_{-\infty}^{\infty} \phi(X,\tau) dX - \frac{\partial C}{\partial x} \int_{-\infty}^{\infty} X\, \phi(X,\tau) dX + \frac{\partial^2 C}{\partial x^2} \int_{-\infty}^{\infty} \frac{X^2}{2} \phi(X,\tau) dX$$

Now what should be the value of this integral? Remember ϕ is the probability that a particle has increased its x coordinate by X in time interval τ. If we take the summation of these probabilities over all possible values of X, the first integral should be 1. What about second integral?

Let us consider N particles, In time interval τ let us say out of N, N_1 have increased their x coordinate by X_1, N_2 have increased their x coordinate by X_2 and on. If we write the average of X^n, that should be equal to:

$$\langle X^n \rangle = \frac{N_1 X_1^n + N_2 X_2^n + \cdots}{N}$$

Now this term $\frac{N_1}{N}$ is the fraction of particles which have increased their x coordinate by X_1. In other words, it is the probability that a particle has increased its x coordinate by X_1 in small time interval τ. So, we can write this as:

$$\langle X^n \rangle = \frac{N_1 X_1^n + N_2 X_2^n + \cdots}{N} = X_1^n \phi(X_1,\tau) + X_2^n \phi(X_2,\tau) + \cdots$$

And if X varies continuously, we can write this as an integral:

$$\langle X^n \rangle = \int_{-\infty}^{\infty} X^n\, \phi(X,\tau) dX$$

This gives me the values of other two integrals in the equation:

$$C(x,t) + \frac{\partial C}{\partial t}\tau = C(x,t)\int_{-\infty}^{\infty}\phi(X,\tau)dx - \frac{\partial C}{\partial x}\int_{-\infty}^{\infty} X\,\phi(X,\tau) + \frac{\partial^2 C}{\partial x^2}\int_{-\infty}^{\infty}\frac{X^2}{2}\phi(X,\tau)$$

So,

$$\int_{-\infty}^{\infty} X\,\phi(X,\tau) = \langle X\rangle$$

$\langle X\rangle$ is the average of x projections of net displacements of all the atoms. Similarly,

$$\int_{-\infty}^{\infty}\frac{X^2}{2}\phi(X,\tau) = \frac{\langle X^2\rangle}{2}$$

$\langle X^2\rangle$ is the mean square displacement of all the atoms. So we can write:

$$C(x,t) + \frac{\partial C}{\partial t}\tau = C(x,t) - \frac{\partial C}{\partial x}\langle X\rangle + \frac{\partial^2 C}{\partial x^2}\frac{\langle X^2\rangle}{2}$$

Or:

$$\frac{\partial C}{\partial t} = \frac{\langle X^2\rangle}{2\tau}\frac{\partial^2 C}{\partial x^2} - \frac{\langle X\rangle}{\tau}\frac{\partial C}{\partial x}$$

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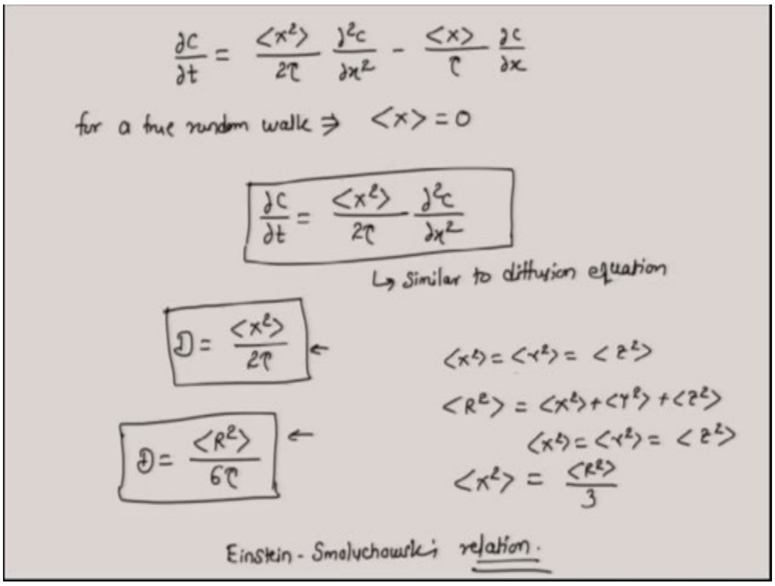

Again as we have seen before, for a true random walk problem the mean displacement of all atoms should be 0 because for every atom that has made a net displacement, let us say $\vec{R}_i$, there would be another atom which has made an exactly equal and opposite displacement; $\vec{R}_j$. And:

$$\vec{R}_i = \vec{R}_j$$

So the average of net displacements of all atoms should be 0:

$$\langle X \rangle = 0$$

We get:

$$\frac{\partial C}{\partial t} = \frac{\langle X^2 \rangle}{2\tau} \frac{\partial^2 C}{\partial x^2}$$

This looks familiar. This is similar to the diffusion equation with diffusivity D being written as:

$$D = \frac{\langle X^2 \rangle}{2\tau} \qquad (1)$$

Now, this we are considering in one particular direction. For a true random walk problem and for an isotropic cubic lattice where the distribution is spreading isotropically we can write:

$$\langle X^2 \rangle = \langle Y^2 \rangle = \langle Z^2 \rangle$$

So, we can write the mean square displacement as:

$$\langle R^2 \rangle = \langle X^2 \rangle + \langle Y^2 \rangle + \langle Z^2 \rangle$$

Further we can write:

$$\langle X^2 \rangle = \frac{\langle R^2 \rangle}{3}$$

And if we substitute here, we get D for an isotropic cubic lattice as:

$$D = \frac{\langle R^2 \rangle}{6\tau} \qquad (2)$$

And this is the equation that Einstein derived in 1905. It is called as Einstein relation, both Eq. (1) or (2), any of this. Simultaneously but independently, Smoluchowski also derived the similar equation. So, it is more commonly referred to as Einstein-Smoluchowski relation. And this clearly establishes the physical significance of the term diffusivity. Now what is it, if you want to describe the physical significance?

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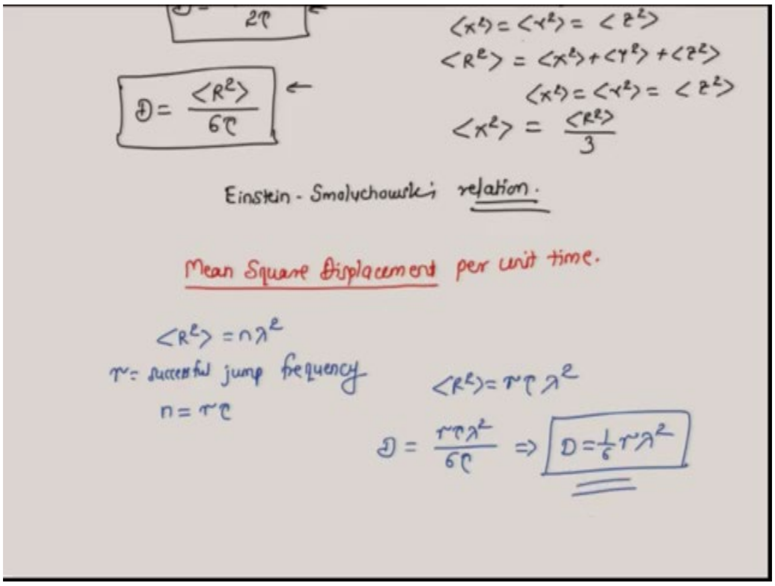

The diffusivity is the mean square displacement of an average atom per unit time and that is the physical significance of diffusivity which was established by this Einstein-Smoluchowski relation. Now remember when we defined this function $\phi(X,\tau)$, we made an assumption while deriving this equation. And the assumption was that the function ϕ is independent of x and t. In a way we assume that the diffusivity is constant and the mobility is constant. It does not change with x and t which means this expression for diffusivity is valid for absence of any concentration gradient or in presence of very small concentration gradient. So, this expression is valid for self-diffusivity or impurity diffusion.

But it is not valid for the case of diffusion under strong concentration gradient or in other words, not valid for inter diffusion. We have seen that for interdiffusion we need more than one diffusion coefficient because there are multiple concentration gradients.

So, this is the physical significance of the term diffusivity. Now we can make a substitution. In the last class, we derived the expression for mean square displacement. Mean square displacement was given as:

$$\langle R^2\rangle = n\lambda^2$$

where each particle has made n jumps. Now if:

$$\gamma = successful\ jump\ frequency$$

then γ is the number of jump an average atom makes per second. In time interval τ the total number of jumps made by an average atom would be:

$$n = \gamma\tau$$

We can write:

$$\langle R^2 \rangle = \gamma\tau\lambda^2$$

And if we substitute in the Einstein-Smoluchowski relation, we get:

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

for any cubic lattice. So, we get the same equation that we got a few classes back, based upon the simple jump frequency model. The point to take away is the Einstein-Smoluchowski relation established the physical significance or the theoretical meaning for the term diffusivity. The diffusivity is a measure of mean square displacement per unit time. And that is why the unit of diffusivity is m^2/sec.

The mean displacement is not a good measure, but mean square displacement is. And we say mean square displacement per unit time, that is the diffusivity in m^2/sec. Thank you.