Diffusion in Multicomponent Solids
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Lecture 14 - Proving summation i = 1 to z cos square θ i equal to z by 3 for any cubic lattice

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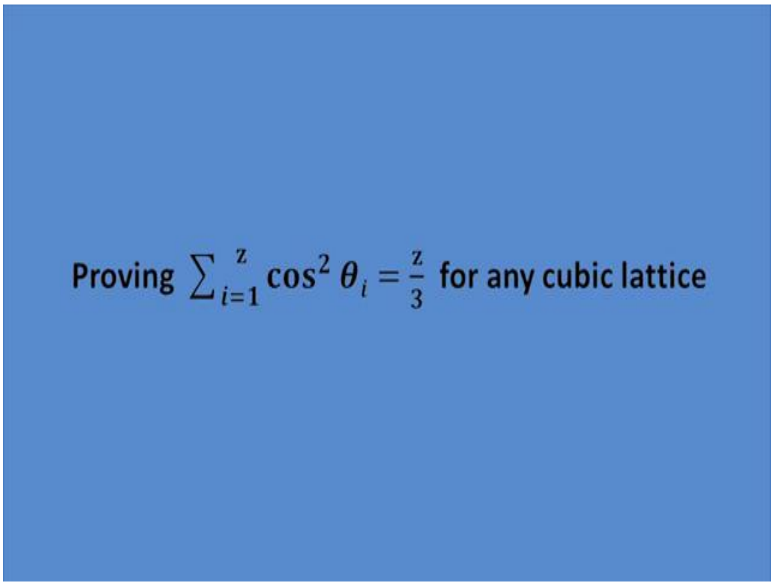

Welcome to the open course on Diffusion in Multicomponent Solids. This is the 14th lecture and in this lecture, we will try to prove:

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

This is true for any cubic lattice. This will help in visualizing how the nearest neighbour atomic jumps occur in various directions in a cubic lattice which may be simple cubic, BCC or FCC.

We have already gone through the Fick’s Law equation and we also derived the equation for diffusion coefficient based upon atomic jump frequencies.

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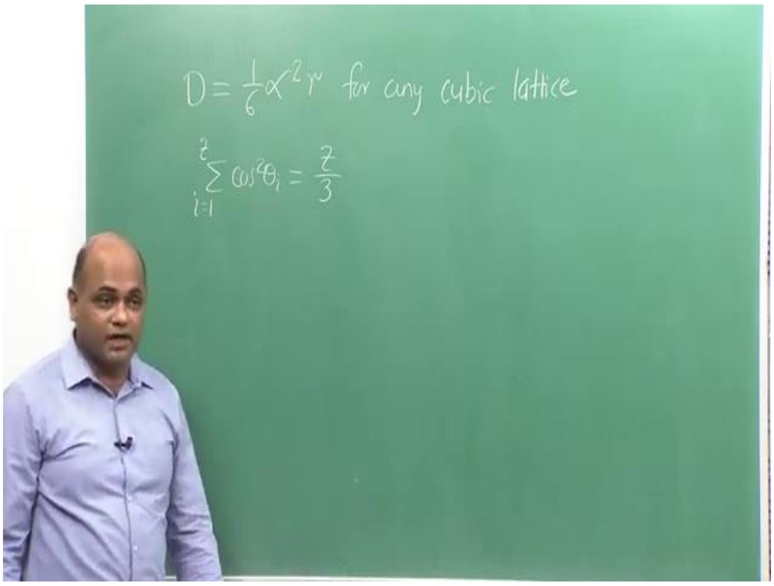

We obtained:

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

for any cubic lattice may be simple cubic, FCC or BCC. In this equation α denotes the jump length and γ is the successful jump frequency of an atom. While deriving this equation we use as the coordination number. Any atom has Z possible atomic sites onto which it can jump and θ_i is the angle that a specific jump vector i has with the diffusion direction. We will try to show this for all three cubic lattices. This was an exercise that I had given you. Let us try to derive this for all three lattices.

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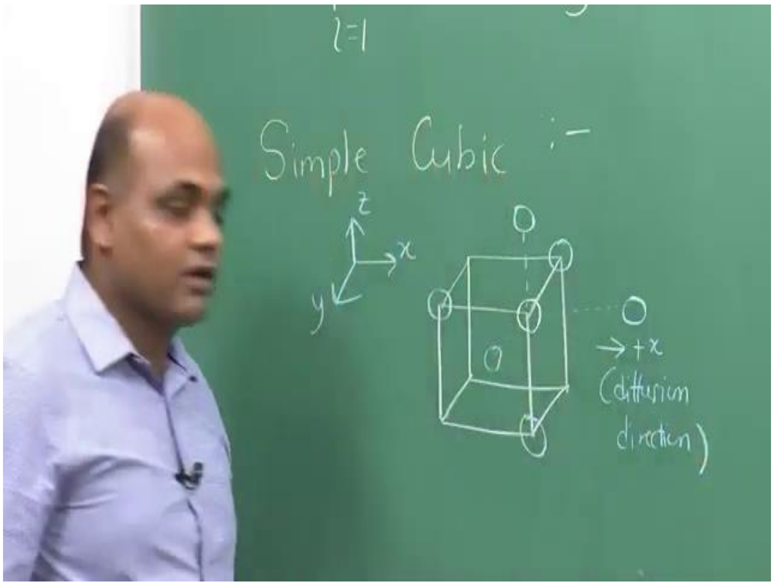

If we consider simple cubic, what is its coordination number? coordination number 6, which means any atom has 6 nearest neighbours, or any atom has 6 possible sites onto which it can jump. If we consider a particular atom at one of the corners, let us say at origin, we can show it has 6 nearest neighbours, 3 of them in this lattice itself and 3 more. Three are in the lattice itself and other three in +x, +y, +z, direction in other lattice, so there are 6 neighbours. If this particular atom has to jump, and if x direction is our diffusion direction….

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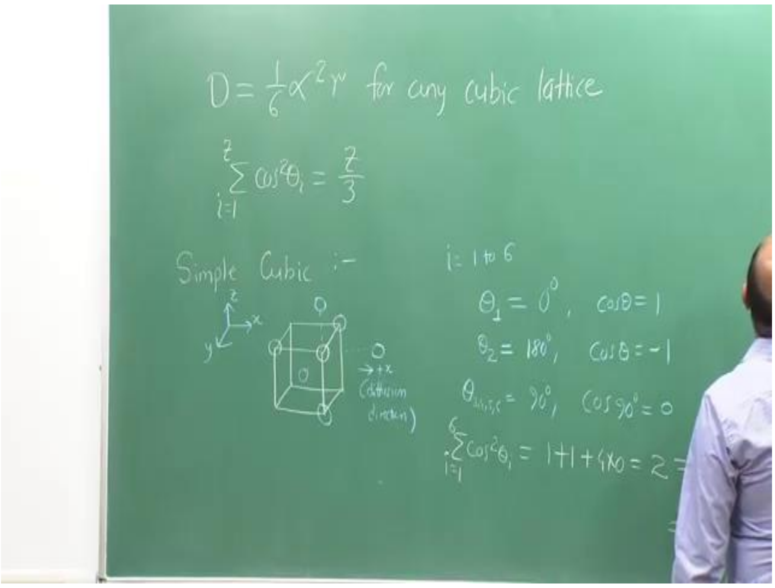

….i goes from 1 to 6. what are different angles, θ_i? This atom can jump either onto +x site, θ_i for this is let us call it θ_1, so cos θ_1 is 1 or it can jump exactly in the reverse direction that is -x direction. θ_2 for this is 180°, cos $\theta_2$here is -1. Then for these four atoms the jump vectors is 1, 2, 3 or 4, so they are all making angle of 90° with the diffusion direction. theta θ_3, θ_4, θ_5, θ_6, are all 90°, cos 90° is 0.

$$\theta_1 = 0°, \quad \cos\theta_1 = 1$$

$$\theta_2 = 180°, \quad \cos\theta_2 = -1$$

$$\theta_{3,4,5,6} = 90°, \quad \cos\theta_{3,4,5,6} = 0$$

If we take the summation for the cubic lattice, we will have:

$$\sum_{i=1}^{6} cos^2\theta_i = 2 = \frac{Z}{3}$$

So the coordination number for simple cubic is Z by 3.

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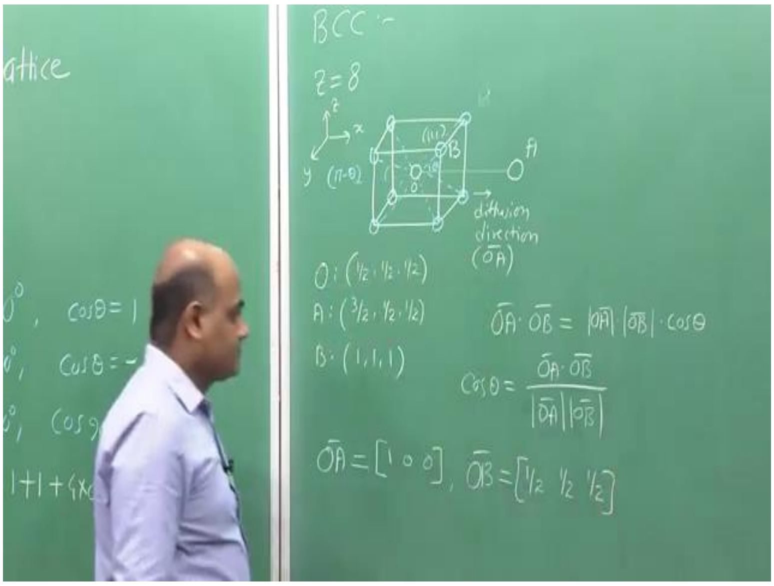

Consider next for unit cell of BCC and if we consider the body centred atom, the coordination number for BCC is 8 which means there are 8 nearest neighbour. For the body centre all nearest neighbours are located on the corner sites. If +x is our diffusion direction, then we have 4 jump vectors which are making the same angle. Let us call it θ and there are 4 other jump vectors and the angle they are making with the jump direction are by symmetry $\pi - \theta$.

Let us try to find out what is this angle θ. Suppose the jump vector is to 111 site. Let us join this body center atom with the body centre atom on the next cube. This site can be represented by O, this as A and this as B. The coordinates for atom O is $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. What are the coordinates for A? $\frac{3}{2}$ in x direction, ? $\frac{1}{2}$ in y and ? $\frac{1}{2}$ in z. This corner is the origin considered here. And for B, the coordinates are obviously ? $(1,1,1)$. Now what should be the cos θ?

The diffusion direction is $\overline{OA}$ and the jump vector we are considering is $\overline{OB}$, then how do we find out cos θ? By dot product. If we take the dot product of the two:

$$\overline{OA}.\overline{OB} = |\overline{OA}||\overline{OB}| \cos\theta$$

So:

$$\cos\theta = \frac{\overline{OA}.\overline{OB}}{|\overline{OA}||\overline{OB}|}$$

Let us see what is $\overline{OA}$ now, $\overline{OA}$ is (1,0,0) and OB bar is $\left[\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\right]$.

$$\overline{OA} = [1\ 0\ 0]$$

$$\overline{OB} = \left[\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\right]$$

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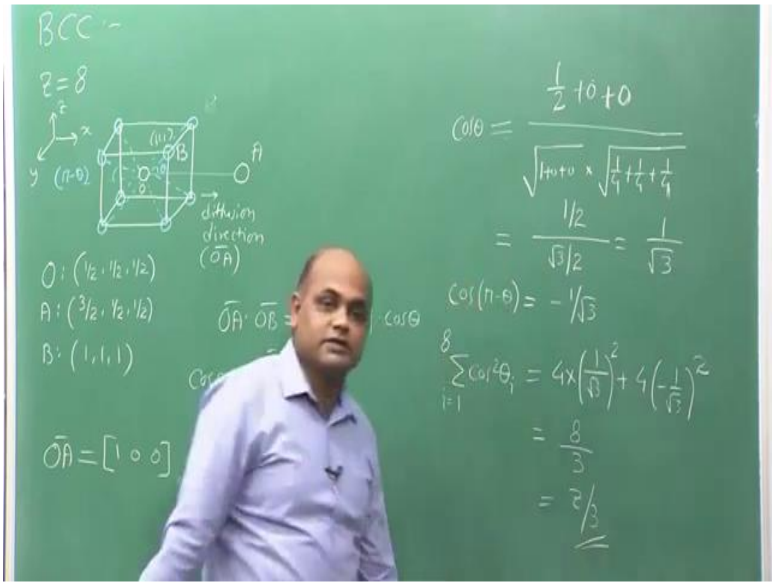

$\cos\theta$ will be the dot product of [1 0 0] and $\left[\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\right]$ which will be:

$$\overline{OA}.\overline{OB} = \frac{1}{2} + 0 \times \frac{1}{2} + 0 \times \frac{1}{2} = \frac{1}{2}$$

Magnitude of $|\overline{OA}|$ would be:

$$|\overline{OA}| = 1$$

And :

$$|\overline{OB}| = \frac{\sqrt{3}}{2}$$

So:

$$\cos\theta = \frac{\frac{1}{2}}{\frac{\sqrt{3}}{2}} = \frac{1}{\sqrt{3}}$$

$\cos \pi - \theta$ would be $-\frac{1}{\sqrt{3}}$, that is the angle that the reverse jump vectors make on this site. As As $Z = 8$ in this case summation $\sum_{i=1}^{8} cos^2\theta_i$ would be:

$$\sum_{i=1}^{8} cos^2\theta_i = 4 \times \left(\frac{1}{\sqrt{3}}\right)^2 + 4 \times \left(-\frac{1}{\sqrt{3}}\right)^2 = \frac{8}{3} = \frac{Z}{3}$$

Because 4 jump vectors make $\frac{1}{\sqrt{3}}$ and 4 jump vectors make $-\frac{1}{\sqrt{3}}$. This you can show for any diffusion direction. We are showing for one particular but you take any diffusion direction and you will get the same result.

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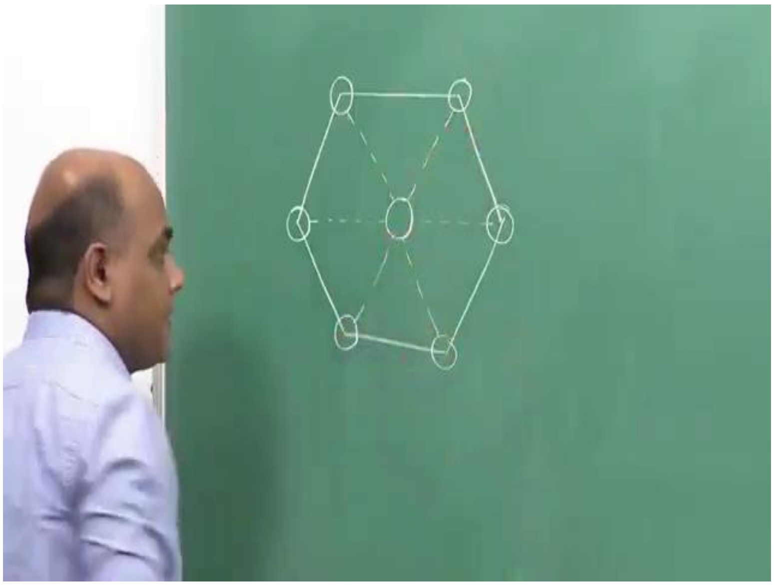

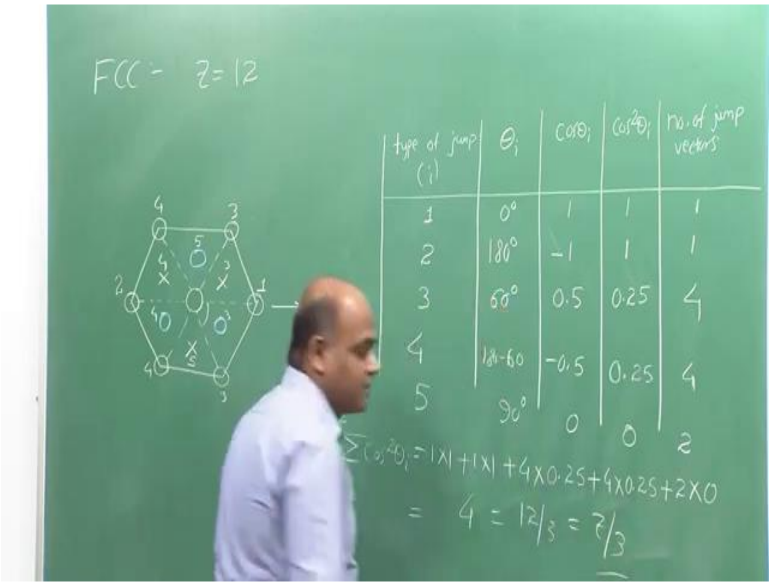

Now let us consider for FCC, for which the coordination number is 12. Easiest way to visualize this coordination in FCC is to consider stacking of 111 plane which is the closest pack plane. If we consider the 111 plane, within plane there are 6 neighbours, they are basically hexagonal arrangements. If we consider this atom at the centre, there are 6 neighbours in plane, so 6 are left. How are the remaining 6 arranged? Remaining 6 are out of the plane and they are arranged in a way such that 3 are on the top plane which is the plane lying above this 111 plane and 3 are in the plane below it. How many different types of jump vectors are there depending upon the angle that they make with the diffusion direction? Suppose our diffusion direction in this case is this one. Let us say the angle that the jump makes with diffusion direction is θ_i, we need $\cos\theta_i, cos^2\theta_i$ and then the number of jump vectors that make this particular angle θ_i. The first one is in the same direction as the diffusion direction, let us call this 1. So, there is only 1 atom which is straight in the diffusion direction and it makes an angle of 0 degree. The second one is in the reverse direction to the diffusion direction -x, so it makes an angle of 180 degree. Again there is only one such jump vector. Now, what is the next type? If you consider in plane atoms, these two, what is the angle that they make with this diffusion direction? This is a hexagon, this is $360°$ and $\frac{360}{6}$, this is 60^o degree. Type 3 is 60 degree, how many such atoms are there? Obviously, this one and this one and also these two which are out of the plane, one on top, one at the bottom. So, four such sites are there which make the angle of 60 degree. And for type 4, by symmetry you know these 4 are making angle of $\pi - 60°$, or $180° - 60°$. So there are four such atoms. Now two atoms are left, and those two are type 5. What is the angle they are making with diffusion direction? $90°$. So

$$\theta_1 = 0°, \quad \cos\theta_1 = 1$$

$$\theta_2 = 180°, \quad \cos\theta_2 = -1$$

$$\theta_3 = 60°, \quad \cos\theta_3 = \frac{1}{2}$$

$$\theta_4 = 180° - 60°, \quad \cos\theta_1 = -\frac{1}{2}$$

$$\theta_5 = 90°, \quad \cos\theta_1 = 0$$

Let's take the summation of $cos^2\theta_i$ and i varies here for FCC from 1 to 12. We have:

$$\sum_{i=1}^{12} cos^2\theta_i = 4 = \frac{12}{3} = \frac{Z}{3}$$

For any cubic lattice, we get the above result. Now we have:

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

Why we take cos θ? Because our diffusion direction is in one direction, but the jump vector is making some angle to the diffusion direction, it is not exactly in the diffusion direction. If you take this jump for example, its contribution to the + x direction to the diffusion direction is given by this projection. And that projection is nothing but cos θ times the jump vector because this length divided by this length is the cos θ.

So, in this case we see it is exactly half as angle is $60°$ and the cos $60°$ is $\frac{1}{2}$. In this other case the projection is 0. Any jump to this type 5 atom is not making any contribution to the diffusion direction, whereas this is exactly reverse jump, the contribution is -1, cos θ is -1. Okay, thank you.