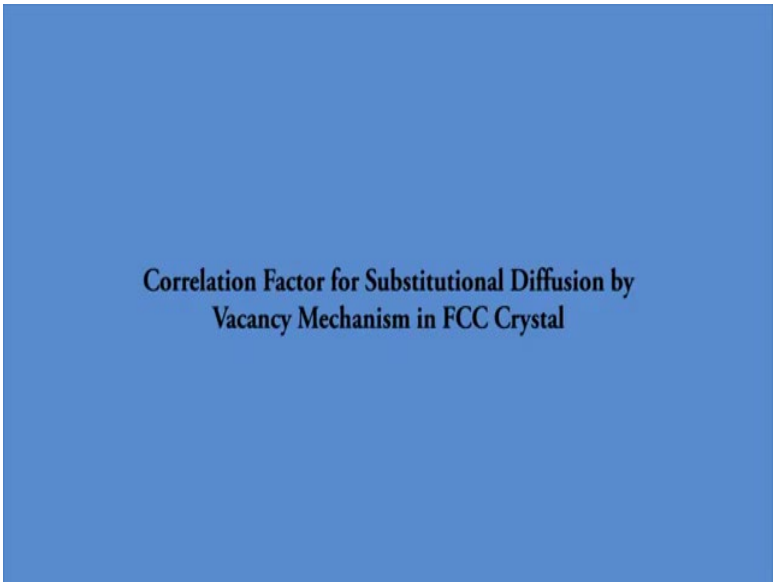
Diffusion in Multicomponent Solids
Professor Kaustubh Kulkarni
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur
Lecture 36
Correlation Factor for Substitutional Diffusion by Vacancy Mechanism in FCC Crystal

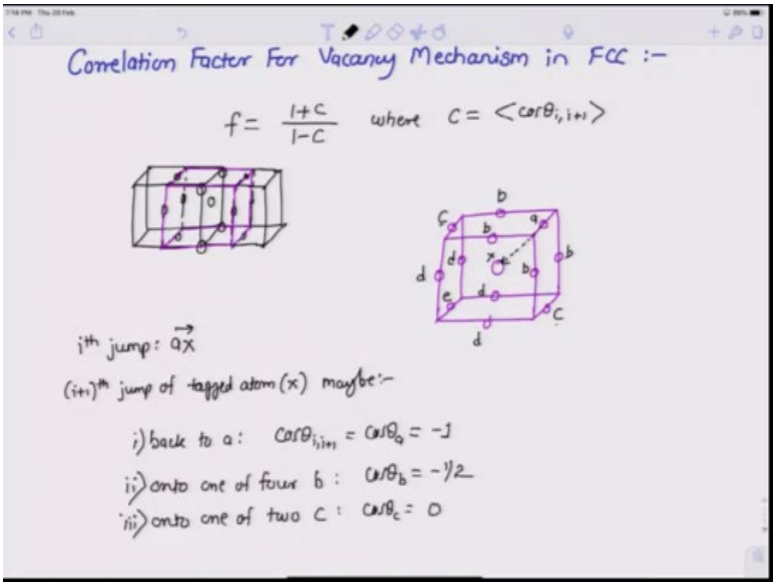
(Refer Slide Time: 00:14)

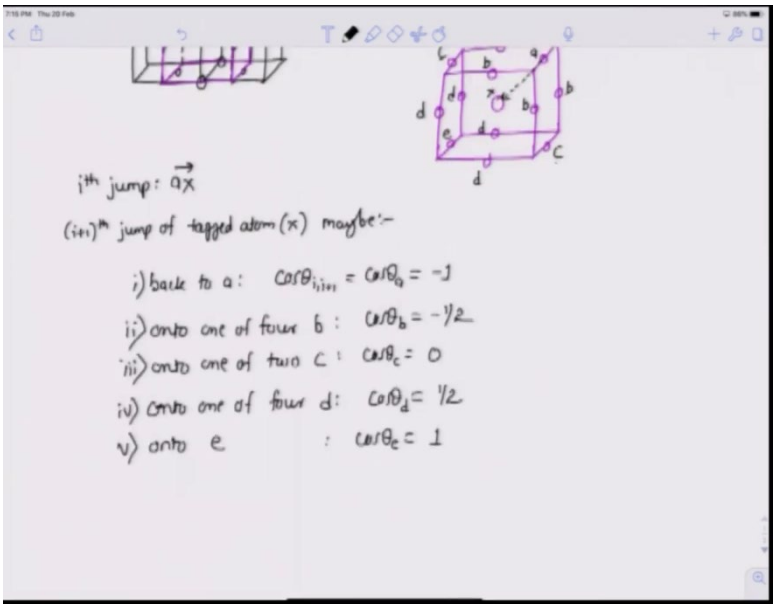


Welcome to the 36th lecture of the open course on Diffusion in Multicomponent Solids. In this lecture I have illustrated the determination of correlation factor in FCC crystal for diffusion of an atom by vacancy mechanism. I have followed the three frequency model of Lidiard and Leclaire for this.

Last class we derived the expression for Correlation Factor for a cubic material. Today, we will try to apply the expression to evaluate correlation factor in an FCC lattice particularly for the diffusion of a substitutional atom by vacancy mechanism.

(Refer Slide Time 01:02)





We got the expression for Correlation Factor as:

$$f = \frac{1 + C}{1 - C}$$

Where:

$$C = \langle \cos \theta_{i,i+1} \rangle$$

C is nothing but the average of cosines of successive jumps for all the atoms. Let us try to evaluate this for FCC. In order to look into the jumps of a tagged atom in FCC let us try to draw the FCC lattice in a little bit different way just because it is more convenient through

our perspective. Let us consider the stacking of (100) plane of FCC by drawing two FCC unit cells side by side as shown in black in the figure. We can also represent the FCC lattice by considering violet coloured unit cell, but now we are putting atoms on the centres of all the edges and one atom at the body centre of this cube. Now, why this is more convenient for us?

Because, if we consider the jump vector $\overrightarrow{ax}$, then we can divide the atoms in different classes. The atoms in each class making the same angle with the jump vector $\overrightarrow{ax}$. For example, one class contains only one atom a and it makes an angle of 180° with $\overrightarrow{ax}$, the other class contains 4 atoms of type b and they make an angle of 120° with $\overrightarrow{ax}$ then, we have type c which make an angle 90°, type d making an angle of 60° and type e making an angle of 0°.

Now, let us consider the first jump of our tagged atom. A tagged atom is the atom that we are tracking. Remember that we derive the expression for mean square displacement for a large number of atoms. When we are tracking an atom and it's jump then we are calling it a tagged atom. The first jump of the tagged atom is let us say from a to x now, our tagged atom is at position x and the vacancy has gone to position a. Let us say i^{th} jump is from a to x. So:

$$(i+1)^{th}\ jump\ of\ tagged\ atom\ (X)\ may\ be$$

$$1)\ back\ to\ a\text{:}\quad cos\ \theta_{i,i+1} = cos\theta_a = -1$$

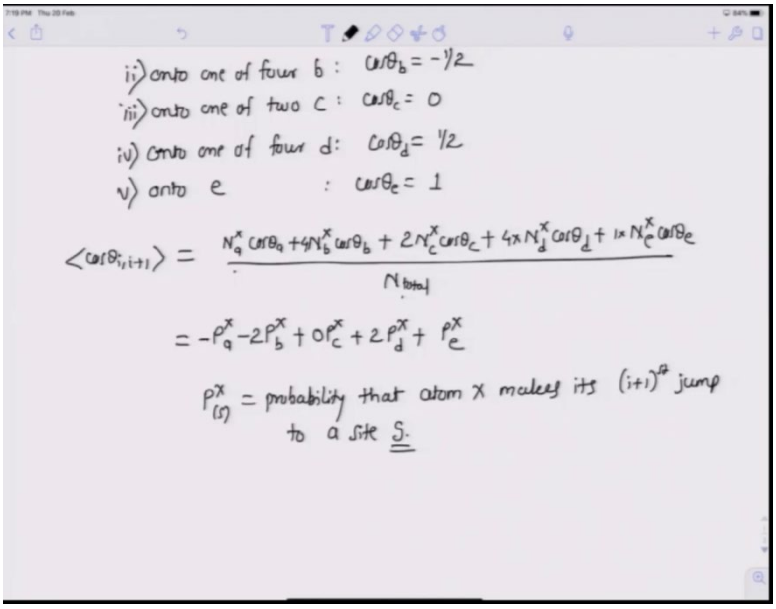
$$2)\ onto\ one\ of\ four\ b\text{:}\ cos\theta_b = -\frac{1}{2}$$

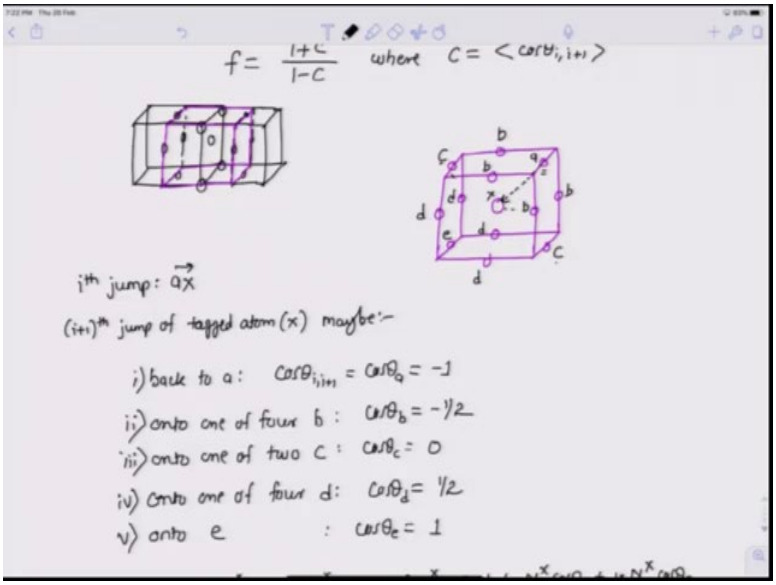
$$3)\ onto\ one\ of\ two\ c\text{:}\ cos\theta_c = 0$$

$$4)\ onto\ one\ of\ four\ d\text{:}\ cos\theta_d = \frac{1}{2}$$

$$5)\ onto\ e\text{:}\ cos\theta_e = 1$$

(Refer Slide Time: 07:30)





If you want to evaluate the average of $\cos\theta_{i,i+1}$ we can write it as:

$$\langle \cos\theta_{i,i+1} \rangle = \frac{N_a^x \cos\theta_a + 4N_b^x \cos\theta_b + 2N_c^x \cos\theta_c + 4N_d^x \cos\theta_d + N_e^x \cos\theta_e}{N_{total}}$$

Where N_i^x represent number of x atoms that make a jump onto site i. Factor in the second term of right hand side means there are four such sites. Remember, when we evaluate the average of $\cos\theta_{i,i+1}$ and we have a large number of atoms we are tracking each of the x atom for its i and $(i+1)^{th}$ jump, evaluate the $\cos\theta$ and take the average of it. So, we need the number of each type of jumps that the x atom makes.

$\frac{N_a^x}{N_{total}}$ is nothing but the fraction of total number of atoms which make the jump onto a site of type a and this is nothing but the probability that the atom x will make its second jump back to a. Let us denote it as P_a^x. Similarly, P_b^x is the probability that atom x makes its $(i+1)^{th}$ jump to a site of the type b and so on. So:

$$\langle \cos\theta_{i,i+1} \rangle = -P_a^x - 2P_b^x + 0P_c^x + 2P_d^x + P_e^x$$

Now, we need to find the probability $P_{(s)}^x$:

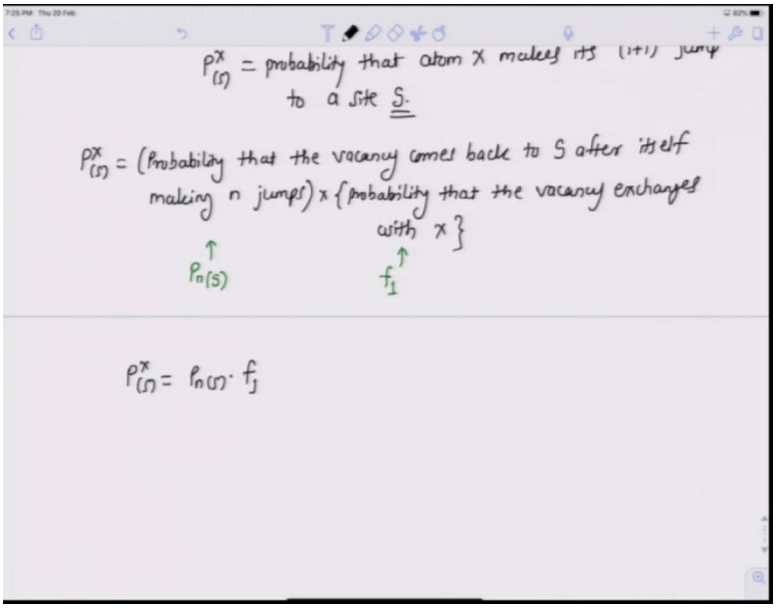
$$P_{(s)}^x = probability\ that\ atom\ X\ makes\ its\ (i+1)^{st}\ jump\ to\ a\ site\ S$$

Now, what is this probability $P_{(s)}^x$? If the atom x here has to make a jump onto any of the sites let us say on to site b for example, then the vacancy has to be on site b and we are considering the correlation effect. When we were considering random walk, the summation of $\cos\theta$ was 0, so the only contribution to the summation of $\cos\theta$ is from the correlated jumps. So, we are considering only correlated jumps. That means we are considering the exchanges of atom x with the same vacancy. In our case the vacancy is now at position a. This vacancy itself can make n number of jumps and come back to any of the nearest neighbour of x before x has already exchanged second time and then if the same vacancy exchange with this x it is a correlated jump. It is because now x is exchanging successively with the same vacancy.

If x exchanges with a different vacancy before this vacancy at a comes back to one of the nearest neighbour sites then, the correlation effect is lost or we say that vacancy is lost and the second jump of x was again a random jump because the fresh vacancy has arrived randomly and it has already exchanged with the fresh vacancy. So, we need to only consider the exchanges of x with the same vacancy. Since the activation energy for the diffusion of a vacancy is much lower, the vacancy itself would make a large number of jumps before the x again exchanges with it. So we need to find the probability that after making n jumps the vacancy at a comes back to anyone of this $a, b, c, d\ and\ e$ type of sites.

Now, P_b^x for example, is the probability that the atom x on its $(i+1)^{st}$ jump exchanges with the same vacancy, which had arrived at b. P_b^x is nothing but the probability that the vacancy after $n-1$ jumps of its own has arrived at site b times the probability that on its n^{th} jump the vacancy exchanges with x.

(Refer Slide Time: 14:14)



We can write $P^x_{(s)}$ as:

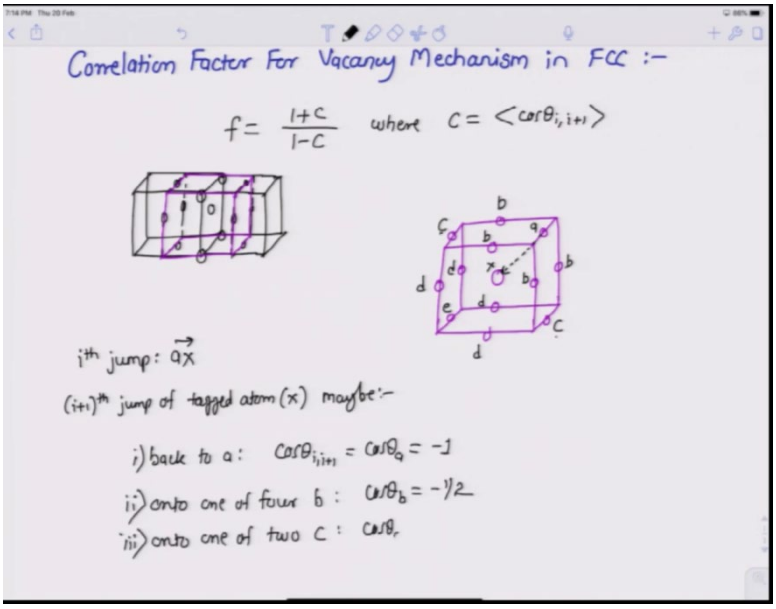
$$P^x_{(s)} = (probability\ that\ the\ vacancy\ comes\ back\ to\ S\ after\ itself\ making\ n\ jumps) \times (probability\ that\ the\ vacancy\ exchanges\ with\ x)$$

Let us denote this as:

$$P^x_{(s)} = P_{n(s)} f_1$$

Now, we need to define the exchange frequency of the vacancy in order to get the probability that the vacancy exchanges with x.

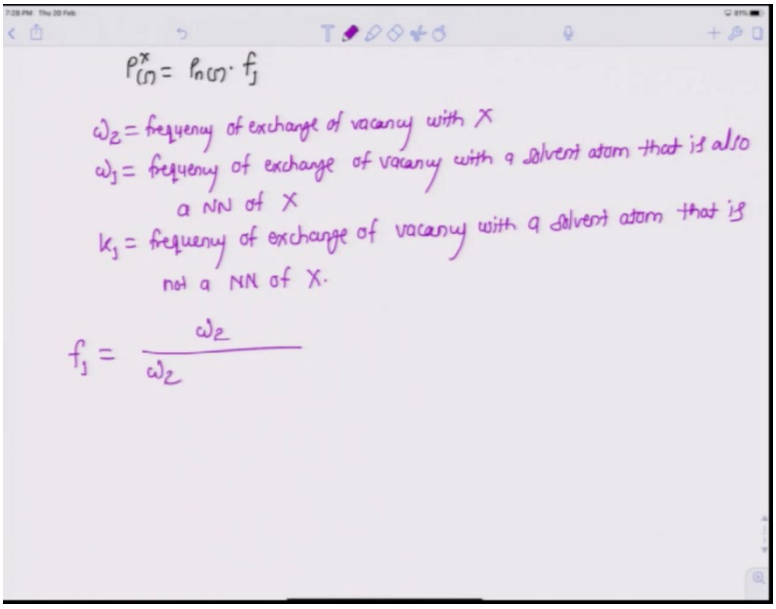
(Refer Slide Time 15:42)

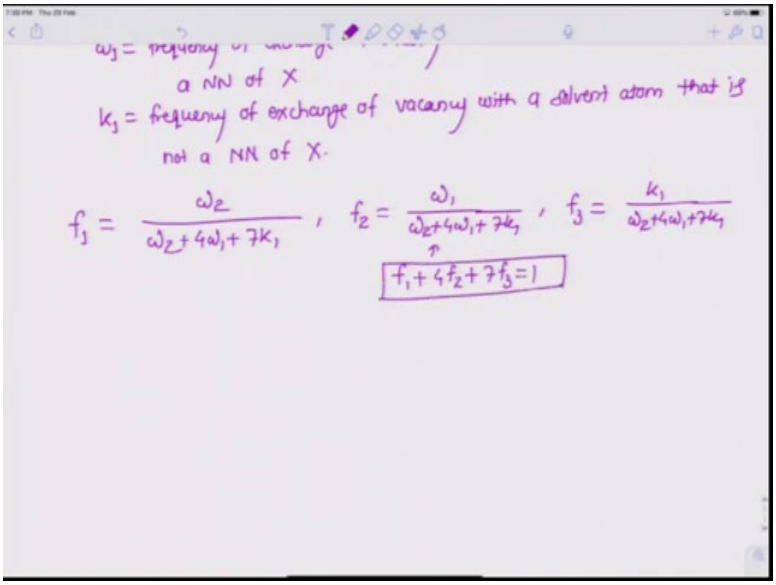


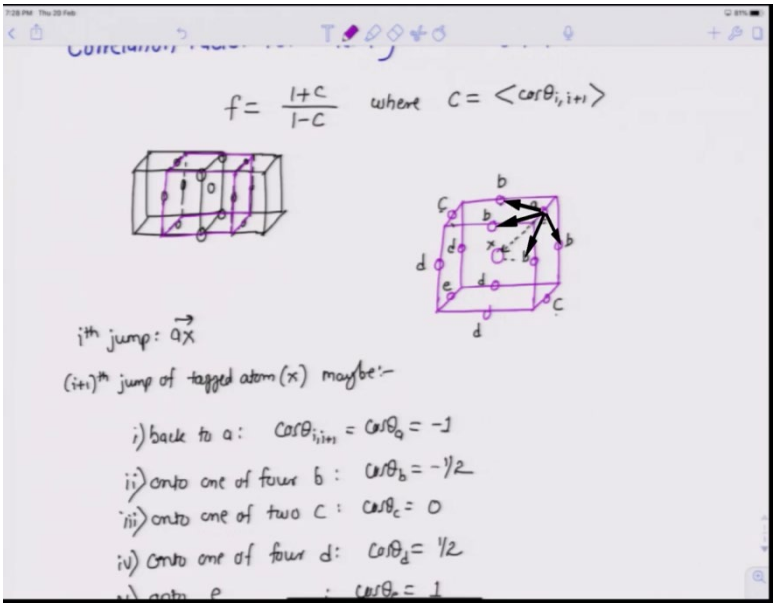
If you come back to this lattice here, the vacancy at a can either exchange with x itself or it can exchange with one of these four b atoms which are also the nearest neighbour of x or it can exchange with other solvent atoms which are not the nearest neighbour of x. So, we can define at least three different types of frequencies when the atom x is a different type of atom or when it is an impurity.

It is because the frequency of exchange with the impurity atom is not same as the frequency of exchange of the vacancy with a solvent atom. Again, the frequency of exchange with solvent atoms may not be the same for two different cases one with the solvent atom which is seated at one of the b sites because, these b sites are also the nearest neighbour of x and there may be an impurity solvent atom binding. The frequency of exchange of the solvent atom at b is not same as the frequency of exchange with other solvent atoms which are not nearest neighbour of x. So, we define three types of frequencies here.

(Refer Slide Time: 17:05)







$$\omega_2 = frequency\ of\ exchange\ of\ vacancy\ with\ X$$

$$\omega_1 = frequency\ of\ exchange\ of\ vacancy\ with\ a\ solvent\ atom\ that\ is\ also\ a\ NN\ of\ X$$

$$k_1 = frequency\ of\ exchange\ of\ vacancy\ with\ a\ solvent\ atom\ that\ is\ not\ a\ NN\ of\ X$$

Now, if we go back to this lattice there is only one atom with which vacancy can make an ω_2 type of jump, there are four sites onto which the vacancy can make an ω_1 type of jump and the remaining 7 sites which are nearest neighbour of the vacancy are the ones onto which the vacancy can make a k_1 type of jump. With this, the probability that the vacancy exchanges with x, f_1, can be expressed as:

$$f_1 = \frac{\omega_2}{\omega_2 + 4\omega_1 + 7k_1}$$

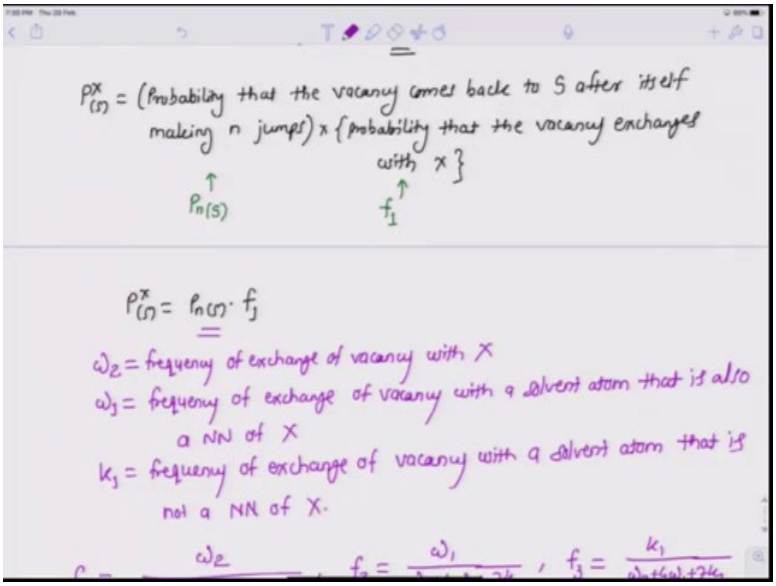
Similarly, f_2 can be expressed as:

$$f_2 = \frac{\omega_1}{\omega_2 + 4\omega_1 + 7k_1}$$

This is the probability that the vacancy exchanges with a solvent atom which is also a nearest neighbour of x. Let us call f_3 as the probability that the vacancy exchanges with a solvent atom which is not a nearest neighbour of x:

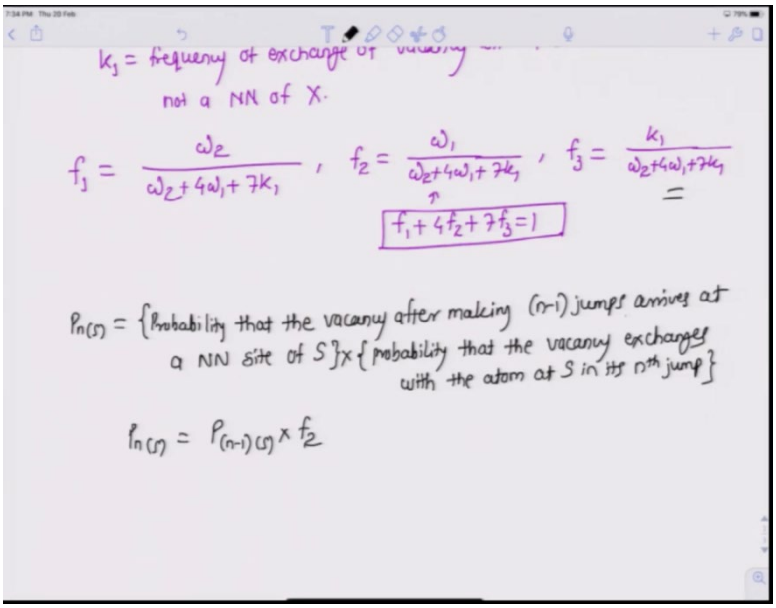
$$f_3 = \frac{k_1}{\omega_2 + 4\omega_1 + 7k_1}$$

(Refer Slide Time: 20:04)



Now, once we define this let us come back to evaluation of the second factor here that is $P_{n(s)}$. $P_{n(s)}$ is again the probability that the vacancy comes back to S after itself making n jumps.

(Refer Slide Time: 20:26)



To get the value of $P_{n(s)}$we can write this as the probability that the vacancy after making $n-1$ jump comes to a site which is nearest neighbour of S times the probability that the vacancy on its n^{th} jump exchanges with the atom on S:

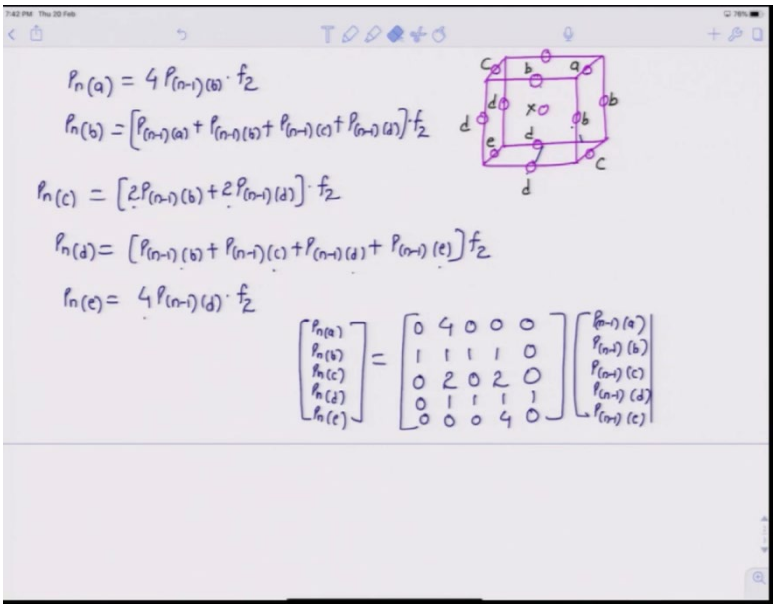
$P_{n(s)}$
$= (probability\ that\ the\ vacancy\ after\ making\ (n-1)\ jumps\ arrives\ at\ a\ NN\ site\ of\ S)$
$\times \left(probability\ that\ the\ vacancy\ exchanges\ with\ the\ atoms\ at\ S\ in\ its\ n^{th}\ jump\right)$

We know the second part of the probability that the vacancy exchanges with atom at S would be f_2 because this jump would be an ω_1 type of jump as this is a solvent atom which is nearest neighbour to atom x and the first probability we can write it as $P_{(n-1)(s)}$:

$$P_{n(s)} = P_{(n-1)(s)} \times f_2$$

Now, to proceed further we will make an assumption that any vacancy which makes a k_1 type of jump is lost permanently. It means if the vacancy makes a k_1 type of jump then, we are not considering it anymore for the correlation. In other words we are assuming that if a vacancy makes a k_1 type of jump then the probability that it will arrive back on one of the nearest neighbour sites of x would be much less than the probability that a fresh vacancy would randomly arrive at the nearest neighbour of x. Because of this assumption we will have to only consider the jumps of the vacancy which are on the nearest neighbour of x. So, we need to only consider the ω_1 type of jumps of the vacancy before the ω_2 type of jump occurs. If the vacancy makes a k_1 type of jump, then the correlation ends there, so the next vacancy which comes near to x is a random vacancy.

(Refer Slide Time 23:53)



In order to visualize properly let us draw this FCC cube again here. We need to consider only those jumps of the vacancy which are onto the nearest neighbour of x. If we want to evaluate

$P_{n(s)}$ that is the probability that the vacancy after making n jumps will arrive at site a then, it is the probability that the vacancy after $n-1$ jumps will arrive at any one of the common nearest neighbour sites of x and here, the common nearest neighbours of a and x are 4 b type of sites. This would be:

$$P_{n(a)} = 4P_{(n-1)(b)} \times f_2$$

Similarly for $P_{n(b)}$, if we consider any b atom here, the nearest neighbour of b and x contain one a site, one b type of site, one c site and one d site. So, this would be:

$$P_{n(b)} = \left[P_{(n-1)(a)} + P_{(n-1)(b)} + P_{(n-1)(c)} + P_{(n-1)(d)}\right]f_2$$

Similarly for $P_{n(c)}$, if we consider any c atom, the common nearest neighbour between c and x are 2 b atoms and 2 d atom. This should give:

$$P_{n(c)} = \left[2P_{(n-1)(b)} + 2P_{(n-1)(d)}\right]f_2$$

For $P_{n(d)}$, considering any d atom, it is nearest neighbours that are common nearest neighbour to x are b, c, d and e. We have:

$$P_{n(d)} = \left[P_{(n-1)(b)} + P_{(n-1)(c)} + P_{(n-1)(d)} + P_{(n-1)(e)}\right]f_2$$

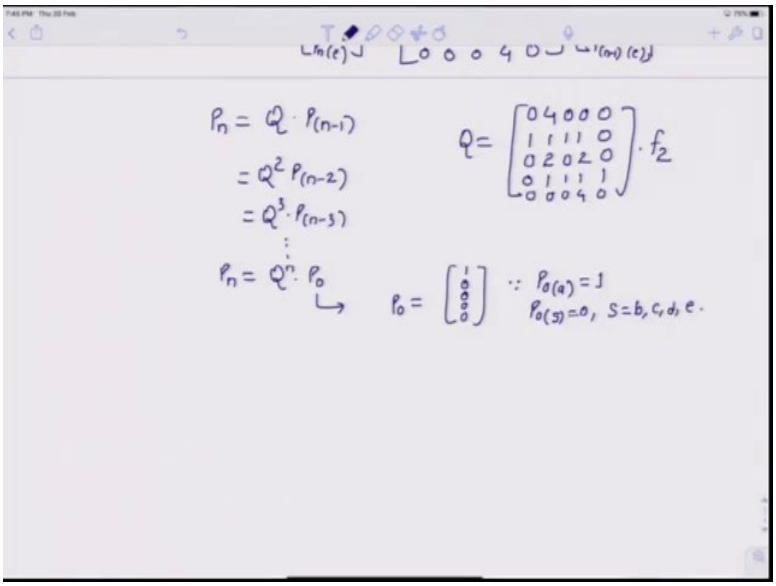
And for e atom, the common nearest neighbour of e and x are all 4 d types of sites. This would be:

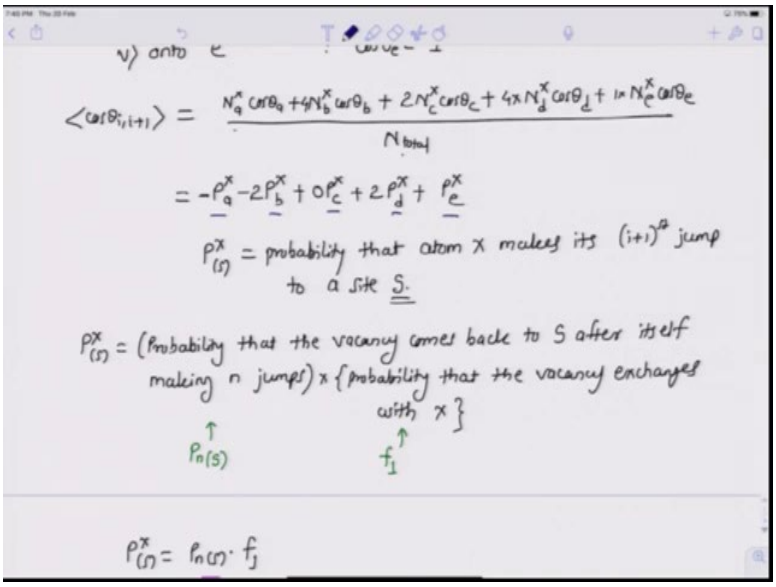
$$P_{n(e)} = 4P_{(n-1)(d)}f_2$$

If we write this in the form of a matrix, we will see:

$$\begin{bmatrix} P_{n(a)} \\ P_{n(b)} \\ P_{n(c)} \\ P_{n(d)} \\ P_{n(e)} \end{bmatrix} = \begin{bmatrix} 0 & 4 & 0 & 0 & 0 \\ 1 & 1 & 1 & 1 & 0 \\ 0 & 2 & 0 & 2 & 0 \\ 0 & 1 & 1 & 1 & 1 \\ 0 & 0 & 0 & 4 & 0 \end{bmatrix} \begin{bmatrix} P_{(n-1)(a)} \\ P_{(n-1)(b)} \\ P_{(n-1)(c)} \\ P_{(n-1)(d)} \\ P_{(n-1)(e)} \end{bmatrix} f_2$$

(Refer Slide Time: 29:14)





If we call the matrix on the left hand side as P_n, 5 x 5 matrix including factor f_2 as:

$$Q = \begin{bmatrix} 0 & 4 & 0 & 0 & 0 \\ 1 & 1 & 1 & 1 & 0 \\ 0 & 2 & 0 & 2 & 0 \\ 0 & 1 & 1 & 1 & 1 \\ 0 & 0 & 0 & 4 & 0 \end{bmatrix} . f_2$$

And column matrix on right hand side as $P_{(n-1)}$. So:

$$P_n = QP_{(n-1)}$$

With the similar logic we can express $P_{(n-1)}$ as:

$$P_{(n-1)} = QP_{(n-2)}$$

So, we can write this as:

$$P_n = QP_{(n-1)} = Q^2P_{(n-2)} = Q^3P_{(n-3)}$$

and if we keep writing this we can write:

$$P_n = Q^nP_0$$

Where P_0 is the probability matrix that the vacancy will be at the site S after making no jump. Now, after making 0 jump means we are considering the same situation which we stated with and we know after the first jump of x the vacancy is at a. The probability that there would be a vacancy after the vacancy had made 0 jump is 1 for site a and will be 0 for all other sites. We can write this matrix P_0 as simply:

$$P_0 = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

$$\because \; P_{0(a)} = 1$$

And:

$$P_{0(s)} = 0 \quad , \quad s = b, c, d, e$$

Now, let us try to work on it further. In the expression for C:

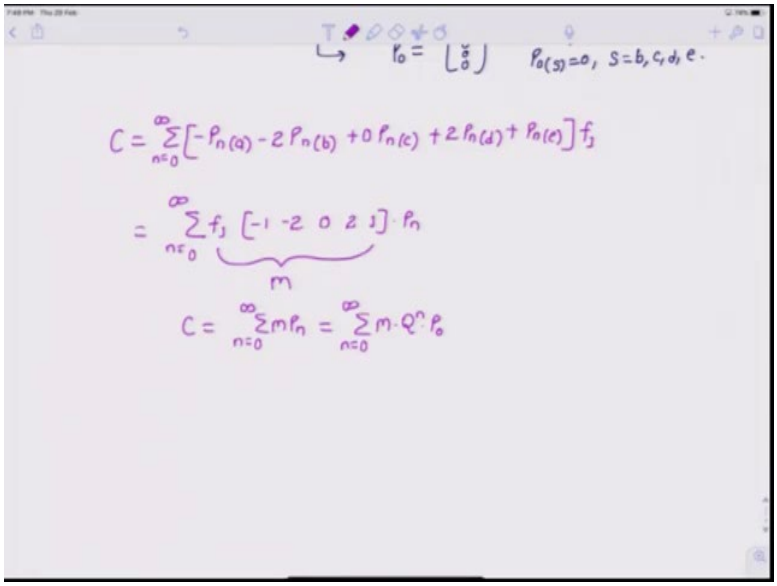
$$\langle \cos\theta_{i,i+1} \rangle = -P_a^x - 2P_b^x + 0P_c^x + 2P_d^x + P_e^x$$

if we substitute back the probabilities in terms of $P_{n(s)}$ we get:

$$C = \sum_{n=0}^{\infty} \left[-P_{n(a)} - 2P_{n(b)} + 0P_{n(c)} + 2P_{n(d)} + P_{n(e)} \right] f_1$$

Remember, this n may be different because some vacancies may just make two jumps and come back, some vacancies will make 10 jumps and come back, some vacancies will make 1000 jumps and come back. So n has to vary from 0 to infinity and we take this as a summation.

(Refer Slide Time 31:48)



We will get:

$$C = \sum_{n=0}^{\infty} f_1[-1 \quad -2 \quad 0 \quad 2 \quad 1]\, P_n$$

Now, let us denote matrix m as:

$$m = f_1[-1 \quad -2 \quad 0 \quad 2 \quad 1]$$

So, we have:

$$C = \sum_{n=0}^{\infty} m\, P_n$$

and we know P_n can be expressed as:

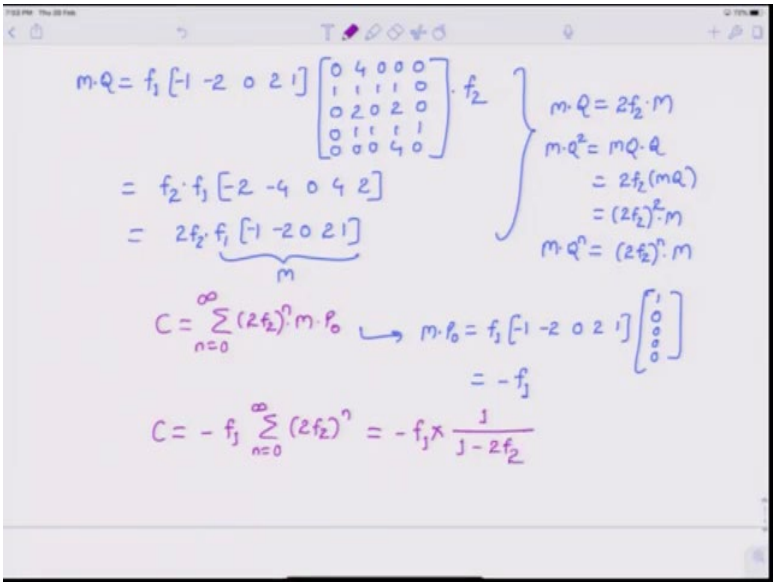
$$P_n = Q^n P_o$$

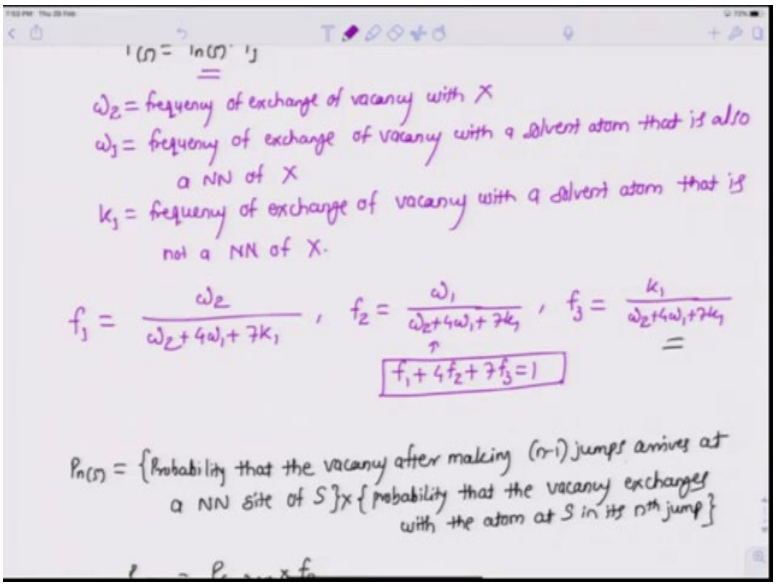
This should be equal to:

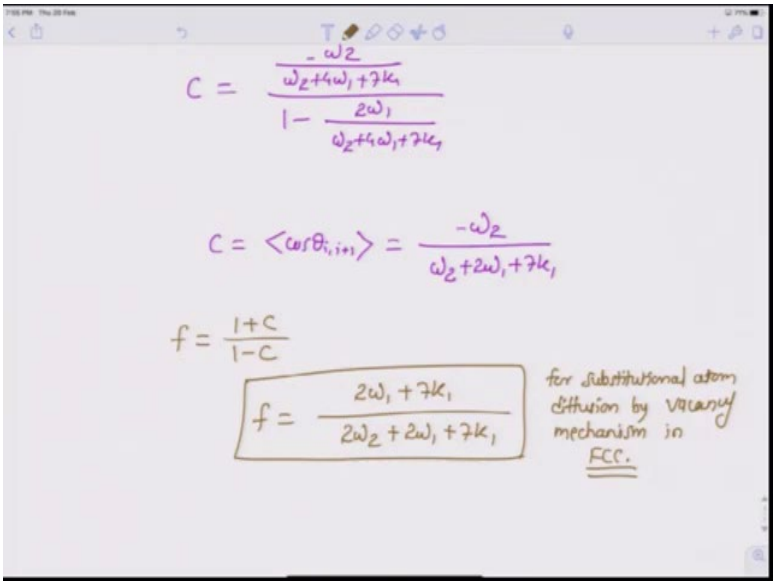
$$C = \sum_{n=0}^{\infty} m\, P_n = \sum_{n=0}^{\infty} m\, Q^n P_o$$

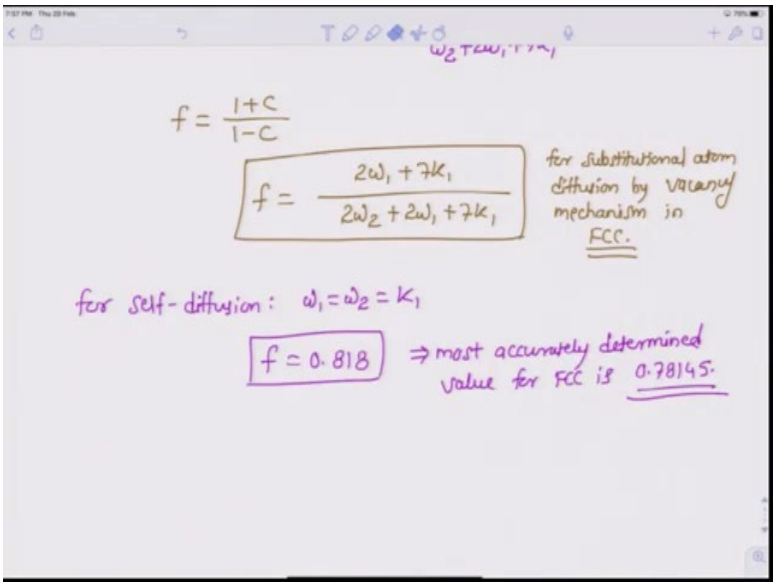
Let us try to evaluate the value of mQ^n.

(Refer Slide Time: 34:00)









Let us first try to evaluate the value of mQ. We will get:

$$mQ = f_1[-1 \quad -2 \quad 0 \quad 2 \quad 1]\begin{bmatrix}0 & 4 & 0 & 0 & 0\\ 1 & 1 & 1 & 1 & 0\\ 0 & 2 & 0 & 2 & 0\\ 0 & 1 & 1 & 1 & 1\\ 0 & 0 & 0 & 4 & 0\end{bmatrix} f_2$$

On solving:

$$mQ = f_2.f_1[-2 \quad -4 \quad 0 \quad 4 \quad 2] = 2f_2.f_1[-1 \quad -2 \quad 0 \quad 2 \quad 1]$$

and again this matrix and f_1 is nothing but what we defined as matrix m. So, we get:

$$mQ = 2f_2 m$$

$$mQ^2 = mQ.Q = 2f_2(mQ) = (2f_2)^2 m$$

If we write mQ^n that should be equal to:

$$mQ^n = (2f_2)^n m$$

And, if we substitute back in the expression for$C$ we get:

$$C = \sum_{n=0}^{\infty} m\,P_n = \sum_{n=0}^{\infty} m\,Q^n P_o = \sum_{n=0}^{\infty} (2f_2)^n m\,P_o$$

Again, if you evaluate mP_o that should be equal to:

$$mP_o = f_1[-1 \quad -2 \quad 0 \quad 2 \quad 1]\begin{bmatrix}1\\0\\0\\0\\0\end{bmatrix} = -f_1$$

and C becomes:

$$C = -f_1 \sum_{n=0}^{\infty} (2f_2)^n = -f_1 \times \frac{1}{1-2f_2}$$

and if we substitute for f_1 and f_2 as defined earlier:

$$f_1 = \frac{\omega_2}{\omega_2 + 4\omega_1 + 7k_1} \quad , \quad f_2 = \frac{\omega_1}{\omega_2 + 4\omega_1 + 7k_1}$$

If, we substitute we get :

$$C = \langle \cos\theta_{i,i+1} \rangle = \frac{-\dfrac{\omega_2}{\omega_2 + 4\omega_1 + 7k_1}}{1 - \dfrac{2\omega_1}{\omega_2 + 4\omega_1 + 7k_1}}$$

and if we substitute in the expression for correlation factor which we know:

$$f = \frac{1+C}{1-C} = \frac{2\omega_1 + 7k_1}{2\omega_2 + 2\omega_1 + 7k_1}$$

So, we get expression for correlation factor in FCC for the diffusion of substitutional atom by vacancy mechanism. Now, for self-diffusion this expression can be simplified because for self-diffusion there is no binding involved between the impurity and vacancy and all the jump frequencies of the vacancy should be same, which means for self-diffusion:

$$\omega_1 = \omega_2 = k_1$$

and if we substitute these equalities in previous expression of f we get:

$$f = 0.818$$

which is very close to the most accurate determination of correlation factor in FCC which is:

$$f = 0.78145$$

Now, there is a difference between the most accurately determined value and the value that we determined here and this difference is because of our simplistic assumption. We assumed that any vacancy that made a k_1 type of jump is permanently lost. So, we did not consider that vacancy in the correlation effect if it made a k_1 type jump. But in reality the vacancy can go on to the second coordination shell of the tagged atom and still come back. Similarly, it can go onto the third coordination shell and come back from there and on. Since we ignored those jumps we get a little bit different values here, but still we could roughly estimate the correlation factor for FCC even with this simplistic assumption.

So, this was for FCC, we will also see how we can estimate the correlation factor for other cubic structure like BCC or diamond cubic, that would be in the next class. Thank you.