Diffusion in Multicomponent Solids

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Lecture 38

Defects Structures

Welcome back. Today, we are going to go over two of the problems which appeared there in the last assignment. The first problem is related to finding out the average of cosine of angle between successive jumps in a BCC crystal structure. So, let us try to evaluate average of $\cos\theta_{i,i+1}$ in BCC.

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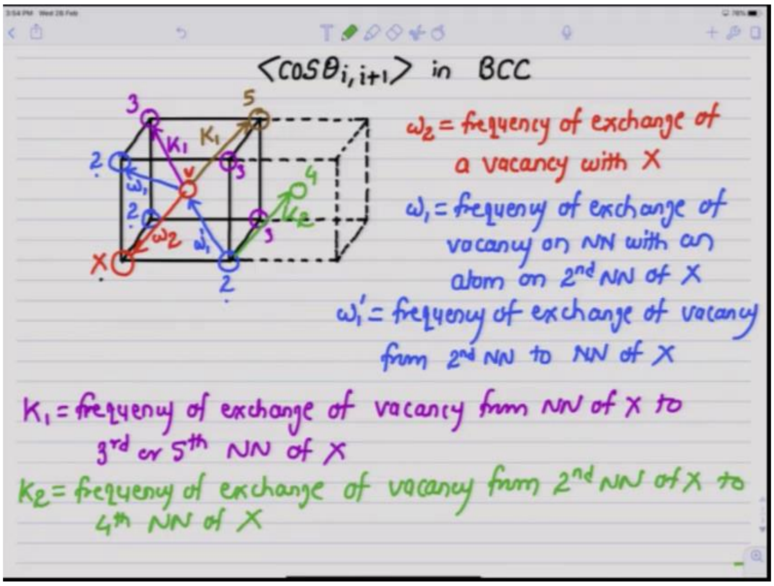

Just a recap of how manning defined various jump frequencies of vacancy in a BCC structure. This is what we have already seen in one of the previous lectures. I have shown two adjacent BCC unit cells here. On the left side at the body centre here, the vacancy is located and our tagged atom X is at the leftmost corner here. Manning defined the frequencies as follows. Now, there are 8 nearest neighbour for the vacancies all of which lie on 8 corners of this cube. One of them is of course the tagged atom X and:

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

Then, there are three nearest neighbour of the vacancy which are second nearest neighbour of the tagged atom and are denoted by number 2 here.

$$\omega_1 = frequency\ of\ exchange\ of\ \ vacancy\ on\ NN\ with\ an\ atom\ on\ 2^{nd}\ NN\ of\ X$$

Then, reverse frequency can be defined as:

$$\omega_1' = frequency\ of\ exchange\ of\ \ vacancy\ from\ 2^{nd}\ NN\ to\ NN\ of\ X$$

Then, there are third nearest neighbour and one fifth nearest neighbour which lie in the same cube, the frequency of exchange with them is denoted as k_1.

$$k_1 = frequency\ of\ exchange\ of\ \ vacancy\ from\ NN\ of\ X\ to\ \ 3^{rd}\ or\ 5^{th}\ \ NN\ of\ X$$

Then the vacancy can escape the 1st or 2nd coordination shell of X by jumping from the 2nd nearest neighbour on to the 4th nearest neighbour. 4th nearest neighbour does not actually lie in the 1st or 2nd coordination shell of X. It lies at the body centre of the next cube which is on the right hand side. I have shown it by number 4. So:

$$k_2 = frequency\ of\ exchange\ of\ \ vacancy\ from\ 2^{nd}\ NN\ of\ X\ to\ \ 4^{th}\ \ NN\ of\ X$$

Remember in BCC, there is no common nearest neighbour for X and vacancy. The 1st coordination shell of vacancy is either the 2nd nearest neighbour or 3rd and 5th nearest neighbour of X. This is important as we go further and any other frequency is denoted as ω_o. With this, let us try to evaluate $\langle cos\ \theta_{i,i+1}\rangle$.

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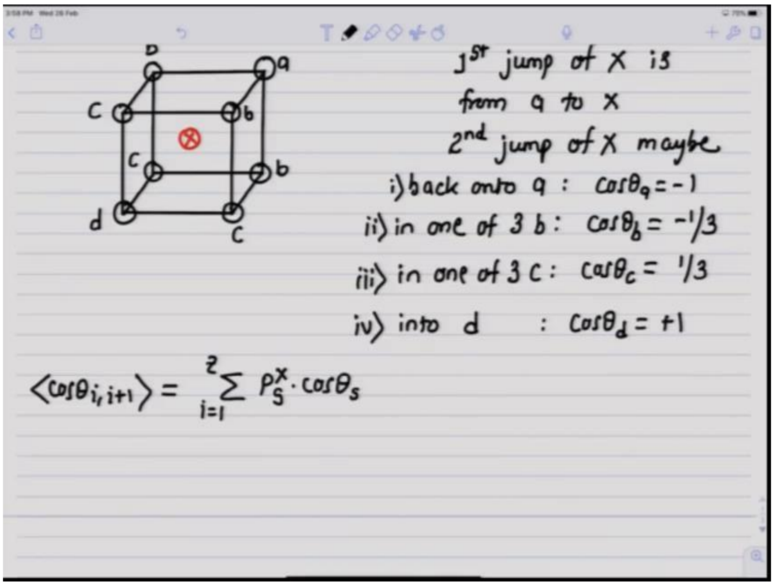


Let us redraw this BCC unit cell again and now in this cell I have shown the tagged atom at X at the body centre of this cube. Suppose the 1st jump of the atom X is from this site a to X. the 1st jump of tagged atom X is from a to X. The second jump of X maybe on one of the eight sites and those eight sites, the nearest neighbour of X can be divided into sites of the types $a, b, c\ or\ d$. a is from where the X has just jumped during the 1st jump. So:

$$2^{nd}\ jumpof\ X\ \ may\ be:$$

$$1)\ back\ onto\ site\ a\ \ : cos\ \theta_a = -1$$

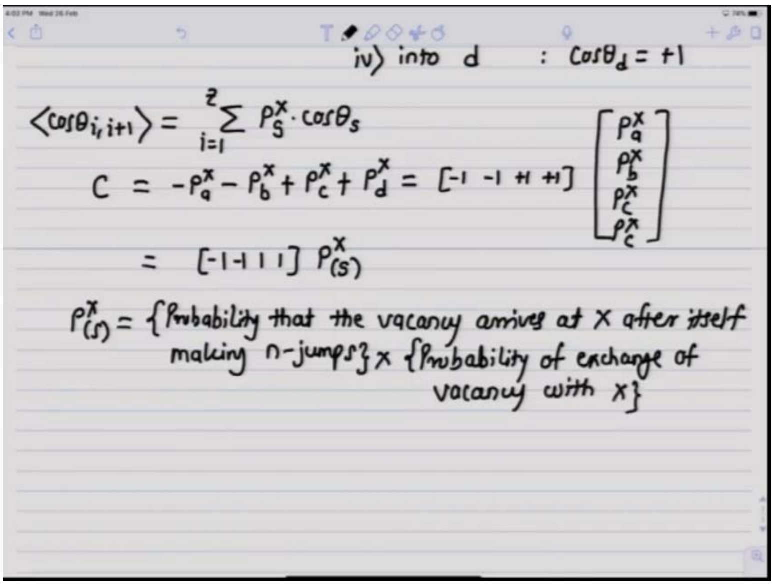
$$2)\ onto\ one\ of\ 3\ b\ \ : cos\ \theta_b = -\frac{1}{3}$$

$$3)\ onto\ one\ of\ 3\ c\ \ : cos\ \theta_c = +\frac{1}{3}$$

$$4)\ into\ d\ \ : cos\ \theta_d = 1$$

If you want to evaluate average of $cos\ \theta_{i,i+1}$, this can be given as:

$$\langle cos\ \theta_{i,i+1} \rangle = \sum_{i=1}^{Z} P_S^X . cos\ \theta_S$$



P_S^X is here is the probability that the 2nd jump of atom X is into the site S. $cos\,\theta_S$ is the cosine of the angle between the 2nd jump vector and the 1st jump vector which was aX. Now there are 1a type of site, 3b types, 3c types and 1d type.

We can expand this as:

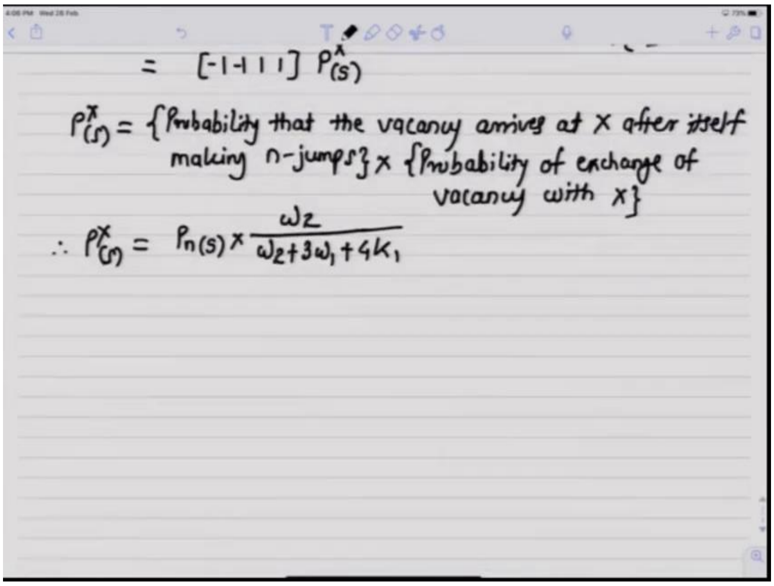
$$\langle cos\,\theta_{i,i+1}\rangle = C = -P_a^X - P_b^X + P_c^X + P_d^X$$

This is because $cos\,\theta_a = -1$ for 1 a site, there are 3b type of site and $cos\,\theta_b = -\frac{1}{3}$ for each, again 3 c types of sites for which $cos\,\theta_c = +\frac{1}{3}$ and there is only 1d site for which $cos\,\theta_d = 1$. Now, we need to evaluate this P_a^X, P_b^X and on. This can further be written as:

$$C = -P_a^X - P_b^X + P_c^X + P_d^X = [-1 \quad -1 \quad +1 \quad +1]\begin{bmatrix} P_a^X \\ P_b^X \\ P_c^X \\ P_d^X \end{bmatrix} = [-1 \quad -1 \quad +1 \quad +1].P_{(S)}^X$$

Now, we need to evaluate $P_{(S)}^X$. $P_{(S)}^X$ is the probability that the atom X jumps into site S for its 2nd jump. it can be written as

$$P_{(S)}^X = \{Probability\ that\ the\ vacancy\ arrives\ at\ X\ after\ itself\ making\ n\ jumps\} \times \{Probability\ of\ exchange\ of\ vacancy\ with\ X\}$$



Now, let us recall this probability that the vacancy arrives at X after itself making n jumps as $P_{n(S)}$ and the probability of exchange of vacancy with X is ω_2 divided by total number of jumps per second that the vacancy can make. So:

$$P_{(S)}^{X} = P_{n(S)} \cdot \frac{\omega_2}{\omega_2 + 3\omega_1 + 4k_1}$$

Now, let us try to evaluate $P_{n(S)}$ for different types of sites. For example, $P_{n(a)}$ here is the probability that the vacancy after itself making n jumps will arrive on site a. Remember, when I am talking about exchange of vacancy, Iam considering the same vacancy with which atom X has exchanged during the first jump. That vacancy itself can make number of jumps and arrive again on one of the nearest neighbour sites of X and the X can exchange with it again. Those are the correlated jumps which will contribute to $\langle cos\,\theta_{i,i+1}\rangle$.

If at any time, the vacancy goes far away and another vacancy comes as nearest neighbour of X, and then if X exchanges with that new vacancy then the correlation sequence with the first vacancy is broken. In this particular problem, to make it simple, we are assuming that the vacancy is considered as escaped if it leaves its first or second coordination shell. That means, the vacancy is assumed to be escaped if the vacancy is not on either 1st, 2nd, 3rd or 5th nearest neighbour of X. Everywhere else if the vacancy jumps then we assume that the vacancy has escaped.

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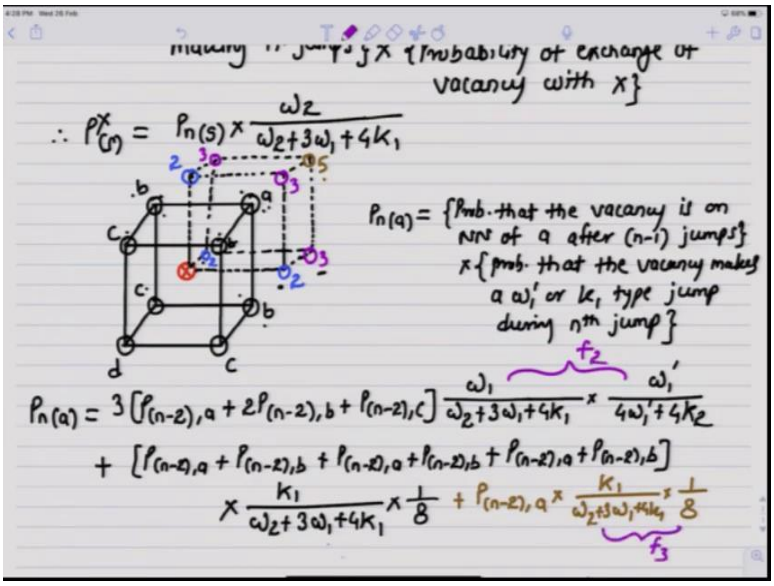

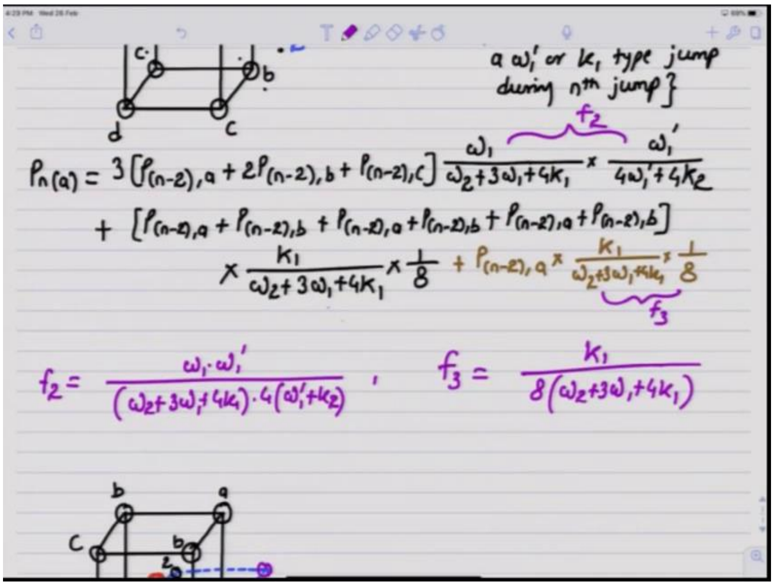

Similarly, if from the outside vacancy arrives at any of the sites on first or second coordination shell of X, it will be taken as a random vacancy jump. For vacancy to exist at a after n number of jumps, the vacancy should have been on one of the nearest neighbours of a after $n-1$ jumps. Okay, I have redrawn the BCC cell here. But now I have also shown all of the nearest neighbour sites of a because we want to evaluate $P_{n(a)}$. After $n-1$ jumps, the vacancy should have been on one of these nearest neighbours of a and on its nth jump the vacancy will exchange with a. Now this nth jump maybe of ω_1' type of jump or k_1 type of jump. ω_1' type of jump is the jump from second nearest neighbour of X to the nearest neighbour of X. The k_1 type jump is the jump from 3rd or 5th nearest neighbour of X to the nearest neighbour of X. I have shown three second nearest of X here by number 2, third nearest neighbour by number 3 and the 5th nearest neighbour of X by number 5 here.

Let us consider these different types of jumps one by one. We consider ω_1' types of jumps and let us consider any of the nearest neighbour site of a which is 2^{nd} nearest neighbour of X. Now, $P_{n(a)}$ can be written as:

$$P_{n(a)} = \{Probability\ that\ the\ vacancy\ is\ on\ NN\ of\ a\ after\ (n-1) jumps\} \times \{Probability\ that\ the\ vacancy\ makes\ a\ \omega_1'\ or\ k_1\ type\ jump\ during\ n^{th}\ jump\}$$

Let us first evaluate the ω_1' type of jump that is from the second nearest neighbour and then the k_1 type of jump. Let us consider this atom 2 here which is the second nearest neighbour atom of X. Now, for the vacancy to exist on this site, after the $n-2$ jump, the vacancy should have been on one of the nearest neighbour sites of 2. Remember, after $n-2$ jumps, now the vacancy can only be on either this a site or one of these two b sites or on c site because the other four nearest neighbour of this atom 2 are outside the 1st and the 2nd coordination shell of X and we are not considering those because if the vacancy jumps from there, then it would be a random vacancy jump and will not be a part of this correlation effect. The only sites that the vacancy should have occupied after $n-2$ jumps are either a or one of the two b or c. This we can write as:

$$P_{n(a)} = P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}$$

where $P_{(n-2),S}$ denotes the probability that the vacancy arrives at site S after $n-2$ jumps. Now we consider each of these type 2 site here. After $n-2$ jump, the vacancy should have been either on a or these two b or on c and also for this 2 here, the vacancy after $n-2$ jumps should have been either on a or these two b or on c. So, we can multiply by 3 as follows:

$$P_{n(a)} = 3\left[P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}\right]$$

It should be multiplied by the probability that the vacancy exchanges with the type 2 atom on its $(n-1)^{st}$jump. This will be the jump from the nearest neighbour of X to the second nearest neighbour of X. So, this will be an ω_1 type of jump and the probability of that would be: $\frac{\omega_1}{\omega_2+3\omega_1+4k_1}$. So:

$$P_{n(a)} = 3\left[P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}\right]\frac{\omega_1}{\omega_2 + 3\omega_1 + 4k_1}$$

For its nth jump, vacancy has to jump from this type 2 to a and this is a jump from second nearest neighbour to the nearest neighbour, it is an ω_1' type of jump. When the vacancy is on 2, it can either make a jump on to the one of the four nearest neighbours of X or it will make a jump on to one of the fourth nearest neighbour of X which are not shown in this figure. Those will be k_2 type of jumps, so the probability of ω_1' type of jump would be $\frac{\omega_1'}{4\omega_1'+4k_2}$.

$$P_{n(a)} = 3\left[P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}\right]\frac{\omega_1}{\omega_2 + 3\omega_1 + 4k_1}\cdot\frac{\omega_1'}{4\omega_1' + 4k_2}$$

Now, the vacancy after $n-1$ jump could have been on the third nearest neighbour, that is, on one of these three type 3 sites. Let us first consider this type 3 site here first. After $n-1$ jump, the vacancy should have been on one of the nearest neighbours of this 3 atom only 2 of which that is $a\ and\ b$ lie on the 1st and 2nd coordination shell of X here. The others will be outside it and we will not consider those. This would give: $P_{(n-2),a} + P_{(n-2),b}$.

$$P_{n(a)} = 3\left[P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}\right]\frac{\omega_1}{\omega_2 + 3\omega_1 + 4k_1}\cdot\frac{\omega_1'}{4\omega_1' + 4k_2} + \left[P_{(n-2),a} + P_{(n-2),b}\right]$$

Then, for another type 3 atom after $n-2$ jump, vacancy should have been either on this a or on this b. Similarly for the the third 3 type atom. So we get:

$$P_{n(a)} = 3\left[P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}\right]\frac{\omega_1}{\omega_2 + 3\omega_1 + 4k_1}\cdot\frac{\omega_1'}{4\omega_1' + 4k_2} + \left[P_{(n-2),a} + P_{(n-2),b} + P_{(n-2),a} + P_{(n-2),b} + P_{(n-2),a} + P_{(n-2),b}\right]$$

times the probability that on the $n-1$ jump, the vacancy exchanges from, let us say this type a to type 3 atom. This is a jump from nearest neighbour on to the 3rd nearest neighbour, so this is a k_1 type of jump. The probability of that would be $\frac{k_1}{\omega_2+3\omega_1+4k_1}$ and on $n-1$ jump, the vacancy has to exchange from this 3 to a. Now this is from 3rd nearest neighbour to a nearest neighbour. This would be counted in any other kind of jump, this is basically a random jump because other jumps are much away from atom X and so the probability of jump from type 3 atom to any of the nearest neighbour is 1/8th because there are 8 nearest neighbour, this should be multiplied by 1/8th here.

$$P_{n(a)} = 3\left[P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}\right]\frac{\omega_1}{\omega_2 + 3\omega_1 + 4k_1}.\frac{\omega_1'}{4\omega_1' + 4k_2} + \left[P_{(n-2),a} + P_{(n-2),b} + P_{(n-2),a} + P_{(n-2),b} + P_{(n-2),a} + P_{(n-2),b}\right]\frac{k_1}{\omega_2 + 3\omega_1 + 4k_1}.\frac{1}{8}$$

Now, there is one more nearest neighbour of a which is type 5 or the 5th nearest neighbour of X. Now, for the vacancy to be at type 5 after $n-1$ jump, it should have been on a only after $n-2$ jump because that is the only nearest neighbour of type 5 which lies in first or second coordination shell of X. Any other vacancy would have been a lost vacancy and those will not be considered. For this we can write as:

$$P_{n(a)} = 3\left[P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}\right]\frac{\omega_1}{\omega_2 + 3\omega_1 + 4k_1}.\frac{\omega_1'}{4\omega_1' + 4k_2} + \left[P_{(n-2),a} + P_{(n-2),b} + P_{(n-2),a} + P_{(n-2),b} + P_{(n-2),a} + P_{(n-2),b}\right]\frac{k_1}{\omega_2 + 3\omega_1 + 4k_1}.\frac{1}{8} + P_{(n-2),a}$$

This will be a k_1 type of jump, probability will be:

$$\frac{k_1}{\omega_2 + 3\omega_1 + 4k_1}$$

times $\frac{1}{8}$ which will finally give:

$$P_{n(a)} = 3\left[P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}\right]\frac{\omega_1}{\omega_2 + 3\omega_1 + 4k_1}.\frac{\omega_1'}{4\omega_1' + 4k_2} + \left[P_{(n-2),a} + P_{(n-2),b} + P_{(n-2),a} + P_{(n-2),b} + P_{(n-2),a} + P_{(n-2),b}\right]\frac{k_1}{\omega_2 + 3\omega_1 + 4k_1}.\frac{1}{8} + P_{(n-2),a}.\frac{k_1}{\omega_2 + 3\omega_1 + 4k_1}.\frac{1}{8}$$

Let us define a factor f_2 as:

$$f_2 = \frac{\omega_1\omega_1'}{(\omega_2 + 3\omega_1 + 4k_1)4(\omega_1' + k_2)}$$

And f_3 as:

$$f_3 = \frac{k_1}{8(\omega_2 + 3\omega_1 + 4k_1)}$$

Let us now consider $P_{n(b)}$ that is the probability that the vacancy arrives at site b after itself making n jumps.

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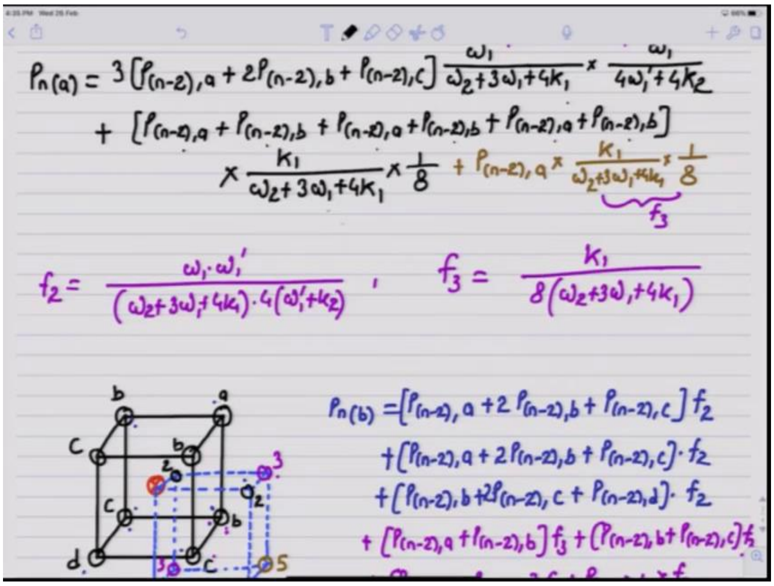

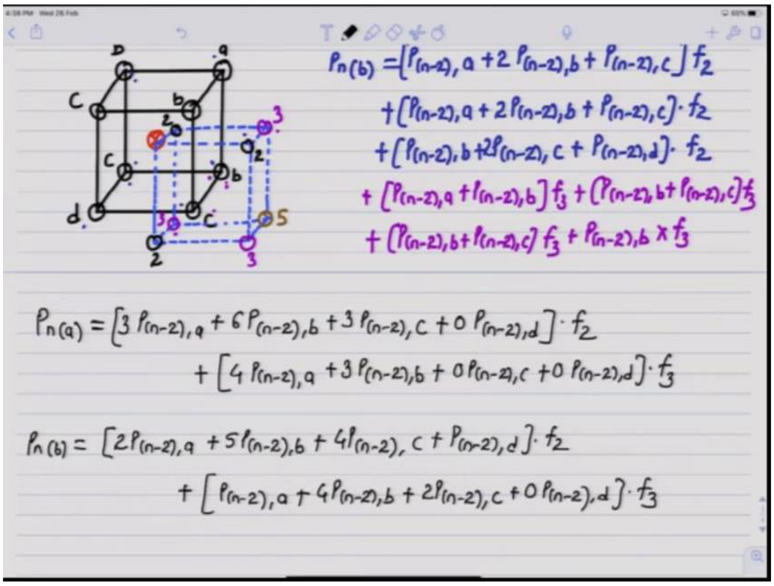

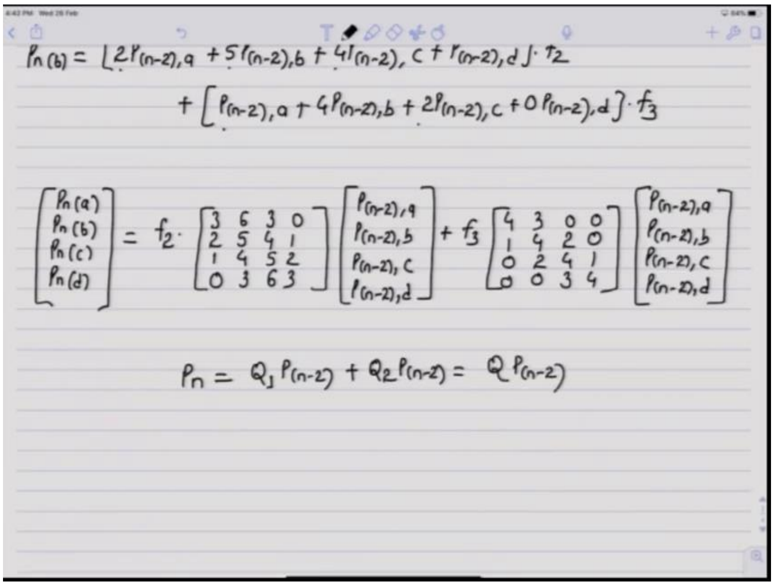

I have shown type b site, let us consider this type b site here, I have also shown all the nearest neighbour of this type b site here out of which there are three 2nd second nearest neighbour of X denoted by number 2, 3 third nearest neighbour of X which are shown by number 3 and one fifth nearest neighbour that is shown by number 5 here. 1st type of jump if we consider for b, we can write, $P_{n(b)}$ is equal to, the jump from second nearest neighbour to the nearest neighbour. This will be an ω_1' type of jump and for being on type 2 site after $n-1$ jump, the vacancy should have been either on $a\ or\ \ two\ b\ sites\ or\ \ one\ c$ site after $n-1$ jumps. We can write:

$$P_{n(b)} = [P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}]f_2$$

If we consider another type 2 site, again after $n-2$ jump, the vacancy should have been on either these two b sites or on this a site or on this c site. So:

$$P_{n(b)} = [P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}]f_2 + [P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}]f_2$$

If I consider third type 2 site, then the vacancy after $n-2$ jumps should have been either on this site b or one of these two sites c or on site d. This would be:

$$P_{n(b)} = [P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}]f_2 + [P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}]f_2 + [P_{(n-2),b} + 2P_{(n-2),c} + P_{(n-2),d}]f_2$$

Then, lets consider the third nearest neighbour type of sites. After $n-2$ jumps, the vacancy should have been either on $a\ or\ b$, this should be:

$$P_{n(b)} = \left[P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}\right]f_2 + \left[P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}\right]f_2 + \left[P_{(n-2),b} + 2P_{(n-2),c} + P_{(n-2),d}\right]f_2 + \left[P_{(n-2),a} + P_{(n-2),b}\right]f_3$$

For second type 3, the vacancy should have been on either this b or this c:

$$P_{n(b)} = \left[P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}\right]f_2 + \left[P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}\right]f_2 + \left[P_{(n-2),b} + 2P_{(n-2),c} + P_{(n-2),d}\right]f_2 + \left[P_{(n-2),a} + P_{(n-2),b}\right]f_3 + \left[P_{(n-2),b} + P_{(n-2),c}\right]f_3$$

For last type 3, the vacancy should have been either on this b or this c:

$$P_{n(b)} = \left[P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}\right]f_2 + \left[P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}\right]f_2 + \left[P_{(n-2),b} + 2P_{(n-2),c} + P_{(n-2),d}\right]f_2 + \left[P_{(n-2),a} + P_{(n-2),b}\right]f_3 + \left[P_{(n-2),b} + P_{(n-2),c}\right]f_3 + \left[P_{(n-2),b} + P_{(n-2),c}\right]f_3$$

For 5th nearest neighbour site, after $n-2$ jump, the vacancy could have been only on site b here because any other jump would have been a random jump because it would be from outside the coordination shells of X, this would be:

$$P_{n(b)} = \left[P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}\right]f_2 + \left[P_{(n-2),a} + 2P_{(n-2),b} + P_{(n-2),c}\right]f_2 + \left[P_{(n-2),b} + 2P_{(n-2),c} + P_{(n-2),d}\right]f_2 + \left[P_{(n-2),a} + P_{(n-2),b}\right]f_3 + \left[P_{(n-2),b} + P_{(n-2),c}\right]f_3 + \left[P_{(n-2),b} + P_{(n-2),c}\right]f_3 + \left[P_{(n-2),b}\right]f_3$$

On simplifying we can write:

$$P_{n(a)} = \left[3P_{(n-2),a} + 6P_{(n-2),b} + 3P_{(n-2),c} + 0P_{(n-2),d}\right]f_2 + \left[4P_{(n-2),a} + 3P_{(n-2),b} + 0P_{(n-2),c} + 0P_{(n-2),d}\right]f_3$$

$$P_{n(b)} = \left[2P_{(n-2),a} + 5P_{(n-2),b} + 4P_{(n-2),c} + P_{(n-2),d}\right]f_2 + \left[P_{(n-2),a} + 4P_{(n-2),b} + 2P_{(n-2),c} + 0P_{(n-2),d}\right]f_3$$

Now for c and d type, we can apply the similar treatment and in fact, we can get it by applying this inverted symmetry here because this cube is has an inverted symmetry about point X. whatever we apply for a and b type sites, by inverted symmetry, we can apply to type c and d sites. Now, we can also get the equations for $P_{n(c)}$ and $P_{n(d)}$and we can write those in the form of matrices.

$$\begin{bmatrix} P_{n(a)} \\ P_{n(b)} \\ P_{n(c)} \\ P_{n(d)} \end{bmatrix} = f_2 \begin{bmatrix} 3 & 6 & 3 & 0 \\ 2 & 5 & 4 & 1 \\ 1 & 4 & 5 & 2 \\ 0 & 3 & 6 & 3 \end{bmatrix} \begin{bmatrix} P_{(n-2),a} \\ P_{(n-2),b} \\ P_{(n-2),c} \\ P_{(n-2),d} \end{bmatrix} + f_3 \begin{bmatrix} 4 & 3 & 0 & 0 \\ 1 & 4 & 2 & 0 \\ 0 & 2 & 4 & 1 \\ 0 & 0 & 3 & 4 \end{bmatrix} \begin{bmatrix} P_{(n-2),a} \\ P_{(n-2),b} \\ P_{(n-2),c} \\ P_{(n-2),d} \end{bmatrix}$$

Observe, that the the last two rows of 4x4 matrixwas obtained by inversion from the first two rows.

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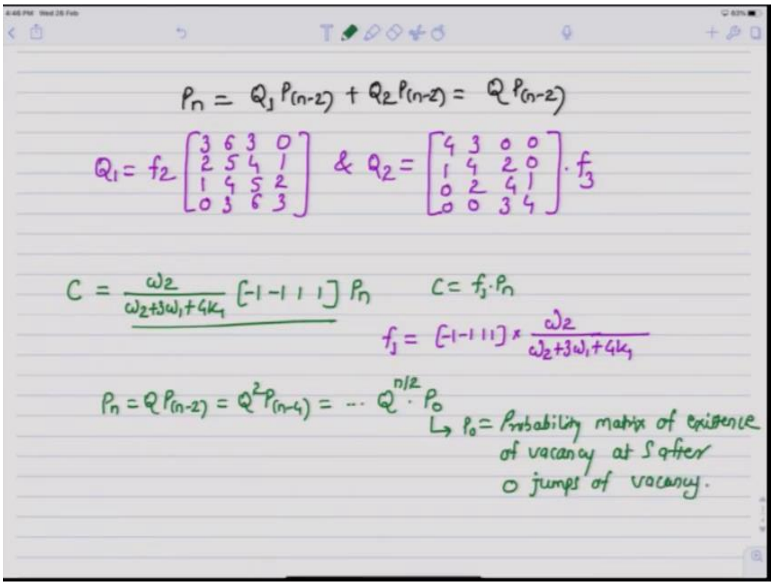

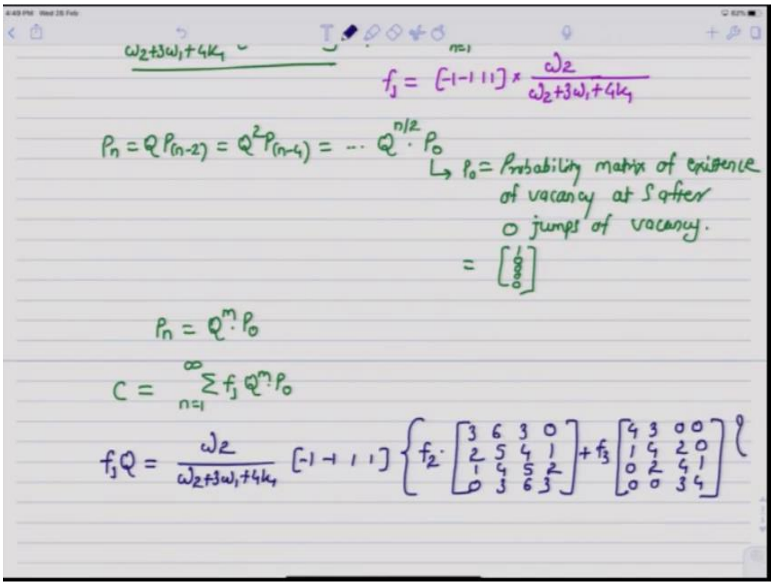

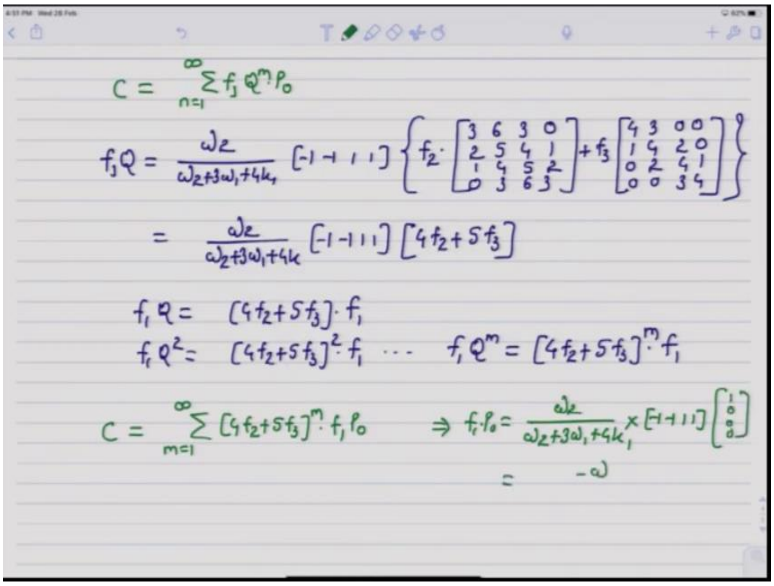

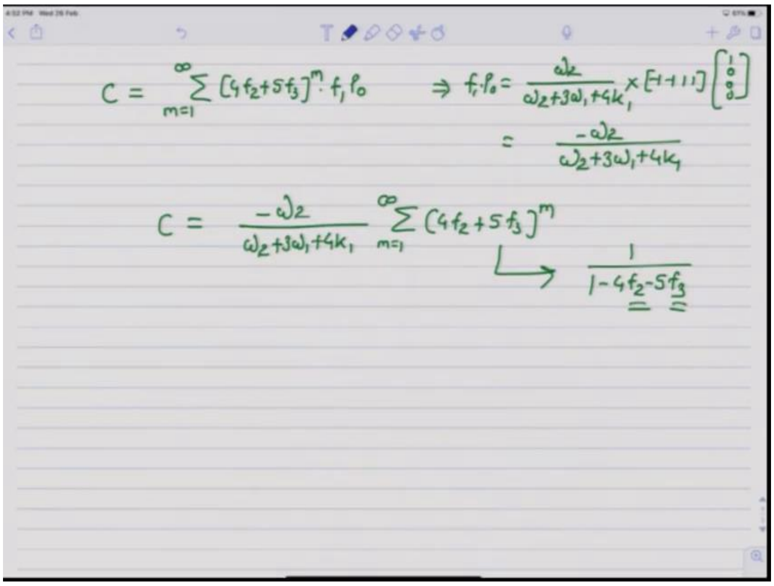

We can write this as:

$$P_n = Q_1 P_{(n-2)} + Q_2 P_{(n-2)} = Q P_{(n-2)}$$

Where:

$$Q_1 = f_2 \begin{bmatrix} 3 & 6 & 3 & 0 \\ 2 & 5 & 4 & 1 \\ 1 & 4 & 5 & 2 \\ 0 & 3 & 6 & 3 \end{bmatrix} \quad and \quad Q_2 = f_3 \begin{bmatrix} 4 & 3 & 0 & 0 \\ 1 & 4 & 2 & 0 \\ 0 & 2 & 4 & 1 \\ 0 & 0 & 3 & 4 \end{bmatrix}$$

Let us go back to the equation for C where:

$$C = [-1 \quad -1 \quad +1 \quad +1]. P_{(S)}^{X}$$

and we got:

$$P_{(S)}^{X} = P_{n(S)} \cdot \frac{\omega_2}{\omega_2 + 3\omega_1 + 4k_1}$$

We can denote a term f_1 as:

$$f_1 = [-1 \quad -1 \quad +1 \quad +1] \frac{\omega_2}{\omega_2 + 3\omega_1 + 4k_1}$$

And can write C as:

$$C = [-1 \quad -1 \quad +1 \quad +1] \frac{\omega_2}{\omega_2 + 3\omega_1 + 4k_1} P_n$$

So C is equal to:

$$C = f_1 P_n$$

Now, we can write $P_n$as:

$$P_n = QP_{(n-2)}$$

Now $P_{(n-2)}$ can be expressed as:

$$P_{(n-2)} = QP_{(n-4)}$$

So this becomes:

$$P_n = QP_{(n-2)} = Q^2 P_{(n-4)}$$

and if we continue this, we would get:

$$P_n = QP_{(n-2)} = Q^2 P_{(n-4)} = \cdots .. Q^{n/2} P_o$$

P_o here is the probability matrix that the vacancy exist at site S after zero jump, that is right after the first jump of X. And we know right after the first jump, the vacancy exist at a. So. P_o of only a is equal to 1 and P_o of all other sites should be 0. The matrix P_o essentially is:

$$P_o = Probability\ matrix\ of\ existence\ of\ vacancy\ at\ S\ after\ 0\ jumps\ of\ vacancy = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

In the equation of P_n,we can replace $\frac{n}{2}$with m and we can write:

$$P_n = Q^m P_o$$

Now when we write the expression for C, we are writing $f_1 P_n$ but n can vary from 1 to infinity because for some atom, the vacancy will arrive after making two jumps for some atoms it will arrive after making 10 jumps, for some atoms it will arrive after making 1000 jumps and we have to consider all such correlations and n has to vary from 1 to infinity. This we have to take actually summation for n equal to 1 to infinity.

We can write expression for C as:

$$C = \sum_{n=1}^{\infty} f_1 . Q^m P_o$$

Now, let us try to evaluate what is $f_1 Q^m$. If we first evaluate $f_1 Q$, that is going to be:

$$f_1 Q = \frac{\omega_2}{\omega_2 + 3\omega_1 + 4k_1} \begin{bmatrix} -1 & -1 & 1 & 1 \end{bmatrix} \left\{ f_2 \begin{bmatrix} 3 & 6 & 3 & 0 \\ 2 & 5 & 4 & 1 \\ 1 & 4 & 5 & 2 \\ 0 & 3 & 6 & 3 \end{bmatrix} + f_3 \begin{bmatrix} 4 & 3 & 0 & 0 \\ 1 & 4 & 2 & 0 \\ 0 & 2 & 4 & 1 \\ 0 & 0 & 3 & 4 \end{bmatrix} \right\}$$

Because

$$Q = Q_1 + Q_2$$

On simplifying we get:

$$f_1 Q = \frac{\omega_2}{\omega_2 + 3\omega_1 + 4k_1} \begin{bmatrix} -1 & -1 & 1 & 1 \end{bmatrix} [4f_2 + 5f_3]$$

Again this is nothing but f_1, so we get:

$$f_1 Q = [4f_2 + 5f_3] . f_1$$

So we can write:

$$f_1 Q^2 = [4f_2 + 5f_3]^2 . f_1$$

$$\dots \dots \quad f_1 Q^m = [4f_2 + 5f_3]^m . f_1$$

if we substitute in this series, we get equation for C as:

$$C = \sum_{m=1}^{\infty} [4f_2 + 5f_3]^m . f_1 P_o$$

As n is a very large number, we replaced $\frac{n}{2}$ by m.

If we evaluate $f_1 P_o$, this should be:

$$f_1 P_o = \frac{\omega_2}{\omega_2 + 3\omega_1 + 4k_1} \begin{bmatrix} -1 & -1 & 1 & 1 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} = \frac{-\omega_2}{\omega_2 + 3\omega_1 + 4k_1}$$

and we will end up getting:

$$C = \frac{-\omega_2}{\omega_2 + 3\omega_1 + 4k_1} \sum_{n=1}^{\infty} [4f_2 + 5f_3]^m$$

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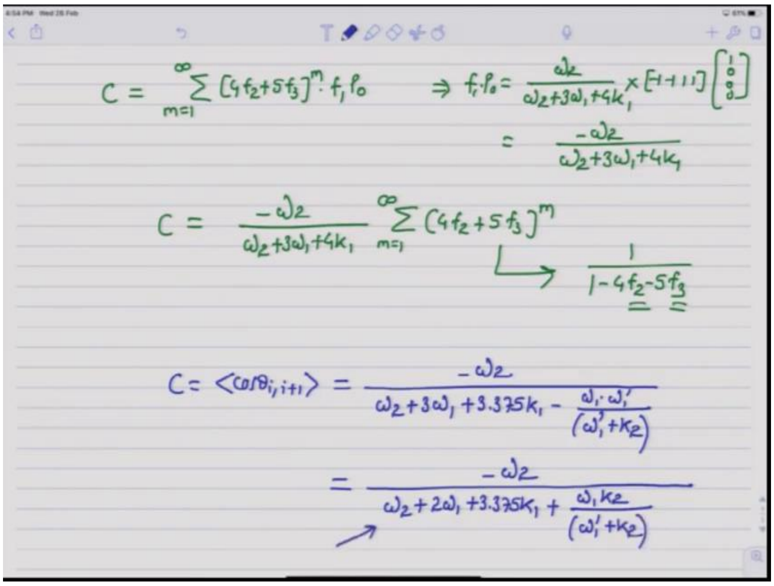

Now this series we can approximate as:

$$\sum_{n=1}^{\infty} [4f_2 + 5f_3]^m = \frac{1}{1 - 4f_2 - 5f_3}$$

If we substitute for f_2 and f_3 and simplify, we will get the expression for C which is nothing but $\langle cos\, \theta_{i,i+1} \rangle$for BCC as:

$$C = \langle cos\, \theta_{i,i+1} \rangle = \frac{-\omega_2}{\omega_2 + 3\omega_1 + 3.375k_1 - \frac{\omega_1 \omega_1'}{(\omega_1' + k_2)}}$$

which can also be written as:

$$C = \frac{-\omega_2}{\omega_2 + 2\omega_1 + 3.375k_1 + \frac{\omega_1 k_2}{(\omega_1' + k_2)}}$$

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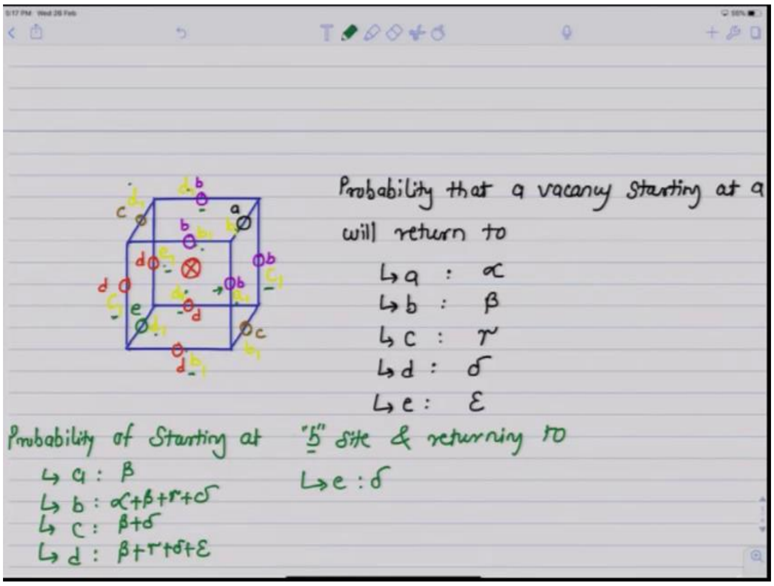

The second expression is the one which was derived by Manning. Note, there is a little bit of correction in Manning's paper this should have been ω_1' there. Okay, this is the expression for $\langle cos\,\theta_{i,i+1}\rangle$ in a BCC lattice. Now let us look into the second problem. In this problem, the probability of a vacancy starting at a and returning to one of a, b, c, d or e sites is given which are respectively:

$$\begin{array}{ll} a: & \alpha \\ b: & \beta \\ c: & \gamma \\ d: & \delta \\ e: & \varepsilon \end{array}$$

We have to find out the probability that a vacancy starting at one of the b sites returns to a, b, c, d or e type of site. To evaluate this, because of the symmetry we can reorient our cube which is shown here such that our b site now becomes an a site and we redistribute the other nearest neighbours of X in the types a, b, c, d and e. Let us call the new orientation as types $a1, b1, c1$ and $d1$. Let us say this site b is now type a1, I have shown the new distribution with the yellow colour here. The 4 b sites are each represented by $b1$, the two c sites are $c1$ c1, the four d sites are $d1$ $d1$ $d1$ and $d1$ and then e site is located here.

Now the probability that a vacancy starting at site b returns to a is same as probability of a vacancy starting at $a1$ and returning to a $b1$ type of site which should be equal to β and the probability of a vacancy stating at b returning to one of the b sites should be equal to the probability of a vacancy starting at a1 and returning to either one of the four $b1$types of sites which are originally $a\ b\ c\ and\ d$. This probability should be: $\alpha + \beta + \gamma + \delta$

Vacancy starting at b and returning to one of the c sites is same as vacancy starting at a1 and returning to either $b1$ and $d1$, which is $\beta + \delta$ and vacancy starting at b site and returning to one of the d sites is same as vacancy starting at $a1$ and returning to either $b1$ type, $c1$ type, $d1$ type or $e1$ type.

This should be equal to $\beta + \gamma + \delta + \varepsilon$ and vacancy starting at b and returning to an e site is same at vacancy starting at $a1$ and returning to $d1$. this should be equal to δ. Now this is ho`w we can find the new probabilities.

a: β
b: $\alpha + \beta + \gamma + \delta$
c: $\beta + \delta$
d: $\beta + \gamma + \delta + \varepsilon$
e: δ

Where is this useful? Remember when we derived the expression for correlation factor for FCC, we considered any vacancy moving out of the nearest neighbour coordination shell of the tagged atom as being escaped. But there is a finite probability that vacancy will return to anyone of the nearest neighbour site of X after making n jumps and it can return from 2nd coordination shell or 3rd or 4th or even from a far distance and if we want to be more accurate in calculating the correlation factor, then we need to know these probabilities. Once we know these probabilities, we can find the correlation factor more accurately and there we will need to convert from one starting position of the vacancy to another starting position based upon the knowledge of one set of probabilities. There this would be useful. These are the two problems we solved today. Thank you.