Diffusion in Multicomponent Solids
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Lecture 35
Derivation of Correlation Factor in Cubic Crystals by Vacancy Mechanism

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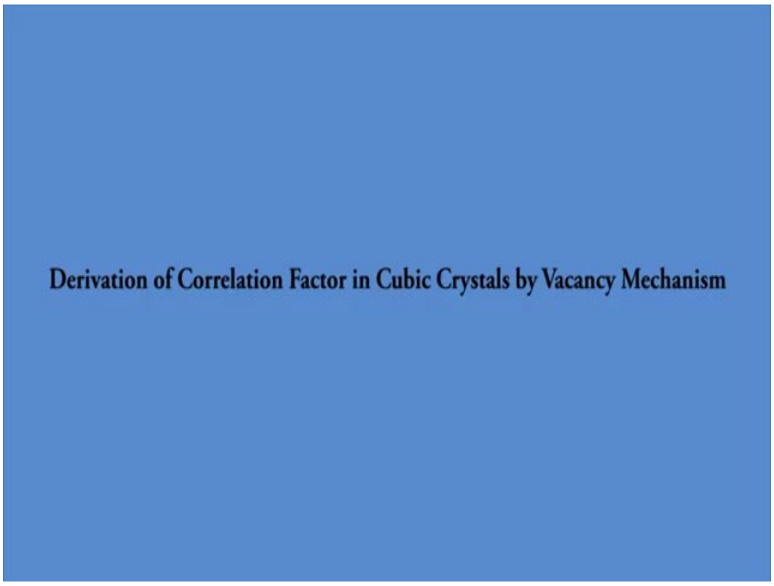

Derivation of Correlation Factor in Cubic Crystals by Vacancy Mechanism

Welcome to the 35th lecture in the open course on Diffusion in Multicomponent Solids. In this lecture, the concept of correlated jumps is introduced. It is shown that the diffusivity as defined by Einstein's equation needs to be modified by a correlation factor for diffusion of substitutional atoms guided by defects. A general expression is also derived for substitutional diffusion via vacancy mechanism in any cubic lattice.

Last couple of classes we went over the theory of random walk. Now we would like to apply it to derive expressions for diffusivity in crystalline solids, specifically in cubic lattices.

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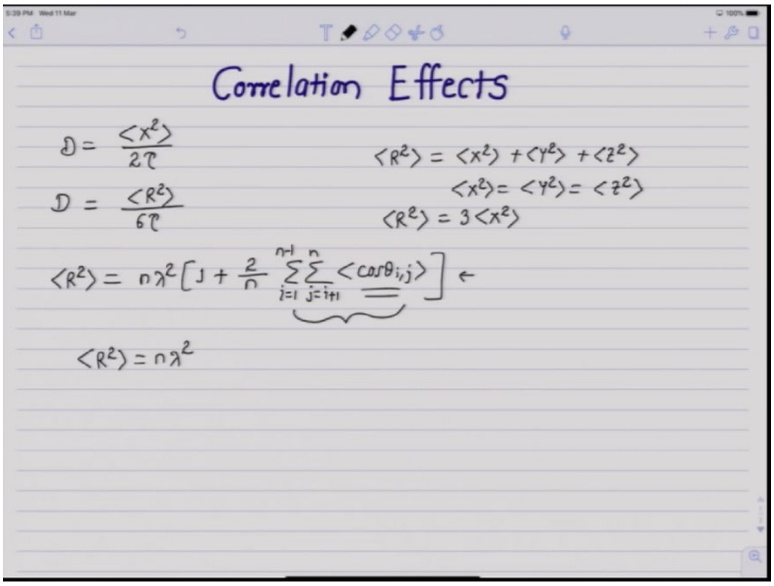


Correlation Effects

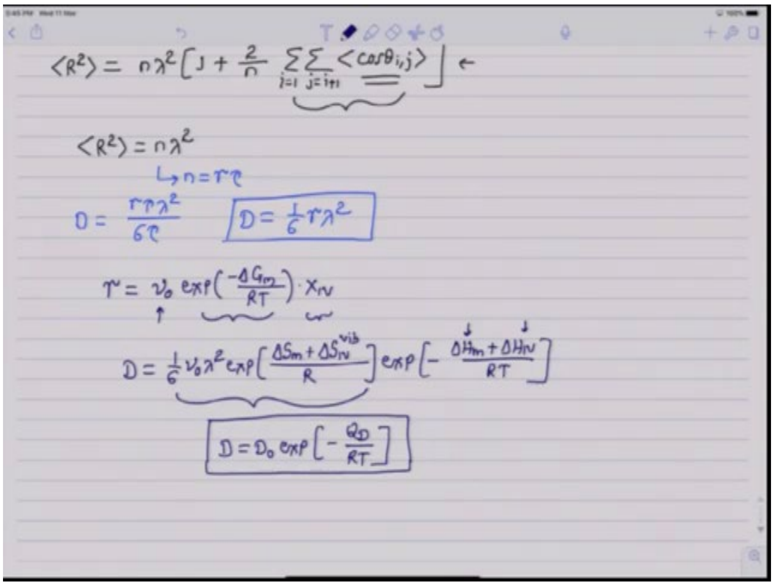
$$D = \frac{\langle x^2 \rangle}{2\tau} \qquad \langle R^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle$$

$$\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle$$

$$D = \frac{\langle R^2 \rangle}{6\tau} \qquad \langle R^2 \rangle = 3\langle x^2 \rangle$$

$$\langle R^2 \rangle = n\lambda^2 \left[1 + \frac{2}{n} \underbrace{\sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \langle \cos\theta_{i,j} \rangle}_{} \right] \leftarrow$$

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



$$\langle R^2 \rangle = n\lambda^2 \left[1 + \frac{2}{n} \underbrace{\sum_{i=1} \sum_{j=i+1} \langle \cos\theta_{i,j} \rangle}_{} \right] \leftarrow$$

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

$$\hookrightarrow n = \Gamma\tau$$

$$D = \frac{\Gamma\tau\lambda^2}{6\tau} \qquad \boxed{D = \frac{1}{6}\Gamma\lambda^2}$$

$$\Gamma = \underset{\uparrow}{\nu_0} \underbrace{\exp\left(\frac{-\Delta G_m}{RT}\right)}_{} \cdot \underbrace{X_v}_{}$$

$$D = \underbrace{\frac{1}{6}\nu_0\lambda^2 \exp\left[\frac{\Delta S_m + \Delta S_v^{vib}}{R}\right]}_{} \exp\left[-\frac{\overset{\downarrow}{\Delta H_m} + \overset{\downarrow}{\Delta H_v}}{RT}\right]$$

$$\boxed{D = D_0 \exp\left[-\frac{Q_D}{RT}\right]}$$

Just a recap over the last couple of lectures, we derived the expression for diffusivity in terms of mean square displacement as:

$$D = \frac{\langle X^2 \rangle}{2\tau}$$

where $\langle X^2 \rangle$ denotes the average of square of x projections of net displacements of all the atoms and τ is the small time interval. If we consider the mean square displacement, which is denoted as $\langle R^2 \rangle$, it can be given as:

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

X, Y, Z here denote the projections on x, y and z axis of the net displacement vector R. In isotropic diffusion, the distribution is spreading equally in all directions. So we have:

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

And we can write, average of R^2 that is the mean square displacement as:

$$\langle R^2 \rangle = 3\langle X^2 \rangle$$

If we substitute this in a previous equation, we get:

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

We also derived the expression for mean square displacement that is average of R^2, which we can write as:

$$\langle R^2 \rangle = n\lambda^2 \left[1 + \frac{2}{n} \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \langle \cos \theta_{i,j} \rangle \right]$$

Now, this expression for mean square displacement is valid for any type of jumps whether random or not. If the jumps are truly random, then we have seen that:

$$\langle \cos \theta_{i,j} \rangle = 0$$

and we get the expression as:

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

Now, if we consider the small time interval τ and if γ is the successful jump frequency of atoms, then in time interval τ the total number of jumps n will be:

$$n = \gamma\tau$$

If we substitute back in D we get:

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

This is the equation that we had already derived using the simple atomic jump model a few classes back. Now, in order to evaluate the successful jump frequency, we need to consider two contributions. For any successful jump of an atom, two conditions have to be satisfied. First, the atom has to gain energy equal or greater than the activation energy for migration and second, the next site or one of the nearest neighbor site has to be vacant so that the atom can jump onto that site.

When these two conditions are satisfied, a particular vibration will convert into a successful jump. We can write γ as:

$$\gamma = \nu_o \exp\left(-\frac{\Delta G_m}{RT}\right).X_{1V}$$

Here ν_o is the Debye frequency which is the number of times an average atom vibrates per unit time. The second exponential term basically represents the probability that a particular vibration will have an energy equal to or greater than the activation energy for migration that is ΔG_m, and X_{1V} represents the probability that a particular site is vacant. X_{1V} is basically the equilibrium concentration of vacancies. So, we are assuming all the vacancies are randomly distributed in the crystal, we can write X_{1V} as:

$$X_{1V} = \exp\left(-\frac{\Delta H_{1V} - T\Delta S_{1V}^{vib}}{RT}\right)$$

If we substitute for X_{1V} and then substitute for γ in D, we get the expression for D as:

$$D = \frac{1}{6}\gamma\lambda^2 = \frac{1}{6}\nu_o\lambda^2 \exp\left(\frac{\Delta S_m + \Delta S_{1V}^{vib}}{R}\right)\exp\left(-\frac{\Delta H_m + \Delta H_{1V}}{RT}\right)$$

This we get after combining the entropic and enthalpic terms together. Here ΔH_m is the activation enthalpy of migration, ΔH_{1V} is the enthalpy of mono vacancy formation, ΔS_m is the entropy of migration that is the difference in the entropy of equilibrium state and the state of saddle configuration and ΔS_{1V}^{vib} is the vibrational entropy change associated with a mono vacancy formation. Now, the first term including ν_o, λ and the entropic term are relatively independent of temperature. The second exponential term is strongly dependent on temperature. Usually the temperature independent terms are combined together and denoted as D_o, so we get the expression for D as:

$$D = D_o \exp\left(-\frac{\Delta Q_D}{RT}\right)$$

Where:

$$\Delta Q_D = \Delta H_m + \Delta H_{1V}$$

ΔQ_D is the activation energy for diffusion. And thus we get an Arrhenius type of equation or the Arrhenius type of temperature dependence for the diffusivity term which is obvious because diffusion is a thermally activated process.

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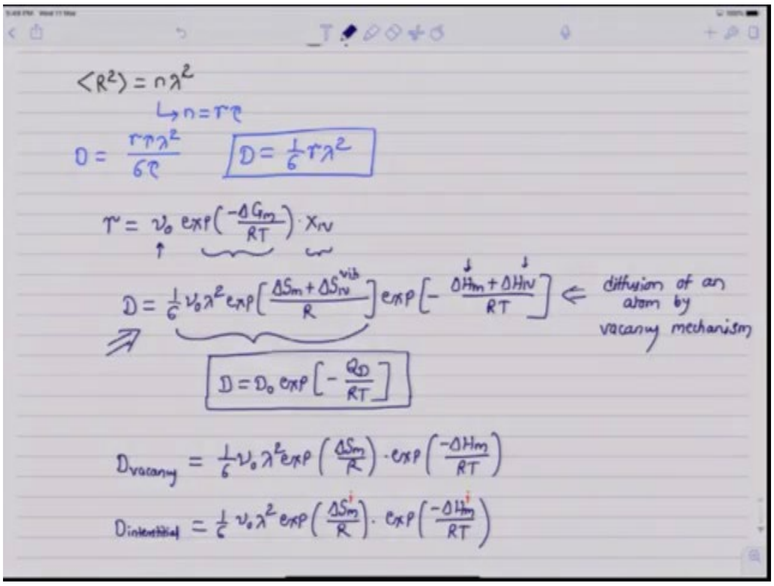

$$\langle R^2 \rangle = n\lambda^2$$

$$\hookrightarrow n = \Gamma\tau$$

$$D = \frac{\Gamma\tau\lambda^2}{6\tau} \qquad \boxed{D = \frac{1}{6}\Gamma\lambda^2}$$

$$\Gamma = \underset{\uparrow}{\nu_0}\, \underbrace{\exp\left(\frac{-\Delta G_m}{RT}\right)} \cdot \underbrace{X_{1V}}$$

$$D = \frac{1}{6}\nu_0\lambda^2 \underbrace{\exp\left[\frac{\Delta S_m + \Delta S_{1V}^{vib}}{R}\right]} \exp\left[-\frac{\overset{\downarrow}{\Delta H_m} + \overset{\downarrow}{\Delta H_{1V}}}{RT}\right] \Leftarrow \text{diffusion of an atom by vacancy mechanism}$$

$$\nearrow \qquad \boxed{D = D_0 \exp\left[-\frac{Q_D}{RT}\right]}$$

$$D_{vacancy} = \frac{1}{6}\nu_0\lambda^2 \exp\left(\frac{\Delta S_m}{R}\right) \cdot \exp\left(\frac{-\Delta H_m}{RT}\right)$$

$$D_{interstitial} = \frac{1}{6}\nu_0\lambda^2 \exp\left(\frac{\Delta S_m^i}{R}\right) \cdot \exp\left(\frac{-\Delta H_m^i}{RT}\right)$$

Now this expression is valid for diffusion of an atom by vacancy mechanism. Remember when an atom jumps into a vacancy, the vacancy is making a reverse jump. So, we can also consider diffusion of a vacancy. Let us consider the vacancy diffusion. Since the vacancy concentration is typically very low (less than 10^{-4}) at most temperatures, for any given vacancy all 12 nearest neighbors in FCC, for example, should be occupied by atoms. So the probability of finding a vacancy next to a vacancy is very-very low. At any given instance, the vacancy can jump on to any of the nearest neighbor site. So the diffusion of a vacancy truly represents random walk. When we consider the diffusion of a vacancy, we do not need to consider this term X_{1V} because the probability that the next site is vacant is 1 almost at all times. The only contribution to the activation energy for diffusion of a vacancy will be from the activation barrier for migration. For a vacancy we can write:

$$D_{vacancy} = \frac{1}{6}\nu_o\lambda^2 \exp\left(\frac{\Delta S_m}{R}\right). \exp\left(-\frac{\Delta H_m}{RT}\right)$$

Similarly, for an interstitial diffusion the jumps of an interstitial will represent true random walk because the equilibrium concentration of interstitial is typically very low. The probability that there will be an interstitial in the nearest neighbor interstitial site of an existing interstitial will be very, very low. So, at any instance the interstitial will have all of it's nearest neighbor site available for jumping. Therefore, the interstitial diffusion also represents true random walk.

In case of interstitial diffusion too, the only contribution to the activation energy for diffusion will be from the activation barrier for migration of the interstitial. Obviously, the migration barrier for interstitial will be different from that for substitutional diffusion. We can write the similar expression as vacancy for interstitial diffusion:

$$D_{interstitial} = \frac{1}{6}\nu_o\lambda^2 \exp\left(\frac{\Delta S_m^i}{R}\right). \exp\left(-\frac{\Delta H_m^i}{RT}\right)$$

We have put superscript i to denote interstitial. Now, coming back to the expression for diffusion of an atom by vacancy mechanism, this expression needs a little bit of correction because while deriving this expression we assumed that the atom is making random walk.

It comes from the expression for average of R^2 that is the mean square displacement which was $n\lambda^2$ for random walk. When the jumps are not random, then we need to use a more general expression here because:

$$\langle \cos\theta_{i,j} \rangle \neq 0$$

Let us see how.

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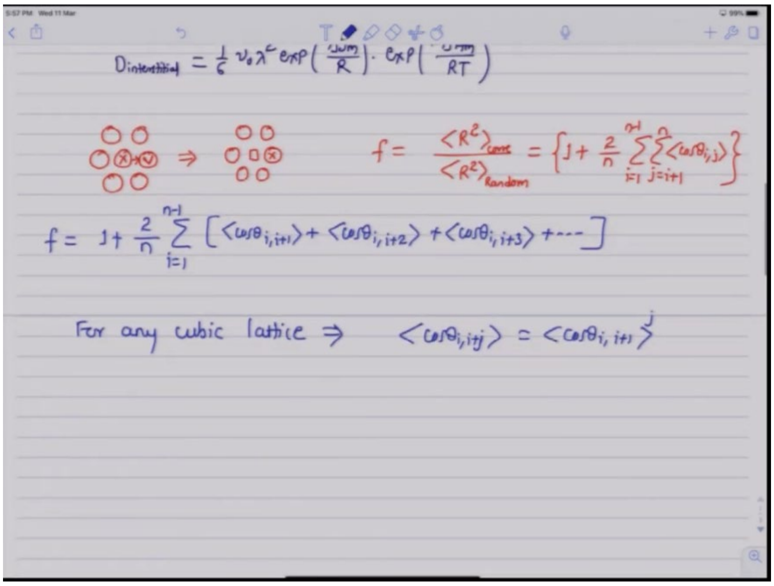
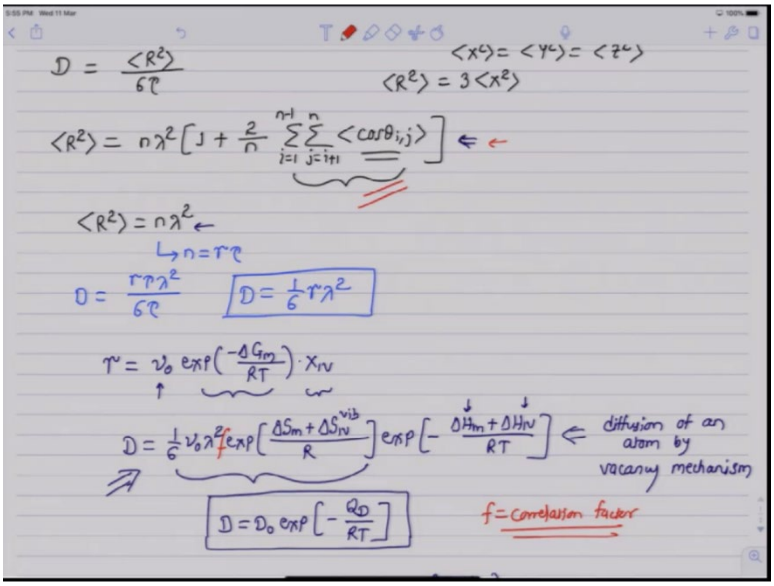


$D_{interstitial} = \frac{1}{6}\nu_o\lambda^2 \exp\left(\frac{\Delta S_m}{R}\right)\cdot \exp\left(\frac{\Delta H_m}{RT}\right)$

$f = \frac{\langle R^2\rangle_{corr}}{\langle R^2\rangle_{Random}} = \left\{1 + \frac{2}{n}\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\langle \cos\theta_{i,j}\rangle\right\}$

$f = 1 + \frac{2}{n}\sum_{i=1}^{n-1}\left[\langle \cos\theta_{i,i+1}\rangle + \langle \cos\theta_{i,i+2}\rangle + \langle \cos\theta_{i,i+3}\rangle + \cdots\right]$

For any cubic lattice $\Rightarrow$ $\langle \cos\theta_{i,i+j}\rangle = \langle \cos\theta_{i,i+1}\rangle^j$



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

$$\langle x^2\rangle = \langle y^2\rangle = \langle z^2\rangle$$

$$\langle R^2\rangle = 3\langle x^2\rangle$$

$$\langle R^2\rangle = n\lambda^2\left[1 + \frac{2}{n}\underbrace{\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\langle\cos\theta_{i,j}\rangle}\right] \Leftarrow \leftarrow$$

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

$$\hookrightarrow n = \Gamma\tau$$

$$D = \frac{\Gamma\tau\lambda^2}{6\tau} \qquad \boxed{D = \frac{1}{6}\Gamma\lambda^2}$$

$$\Gamma = \underset{\uparrow}{\nu_0}\underbrace{\exp\left(\frac{-\Delta G_m}{RT}\right)}\cdot\underbrace{X_{IV}}$$

$$D = \frac{1}{6}\nu_0\lambda^2 f\underbrace{\exp\left[\frac{\Delta S_m + \Delta S_{IV}^{vib}}{R}\right]}\exp\left[-\frac{\overset{\downarrow}{\Delta H_m} + \overset{\downarrow}{\Delta H_{IV}}}{RT}\right] \Leftarrow$$

diffusion of an atom by vacancy mechanism

$$\boxed{D = D_0\exp\left[-\frac{Q_D}{RT}\right]}$$

f = correlation factor

Let us consider for example, the (111) plane in an FCC lattice. Suppose, we are considering the diffusion of this atom X. The first time a vacancy arrives at any of the nearest neighbor of this atom X, it is a random process. A vacancy will randomly arrive on any of the nearest neighbor of X and the atom X will make a random jump into that site. Let us say the first random jump was from X to this site V here.

After the jump the vacancy is in the middle here and the atom is at X. Now, the second jump of X would no more be random, because now there exists more than random probability that the vacancy exists as the nearest neighbor of X, because the X have just exchanged with this vacancy. What would be that probability? Of course, it would not be unity, but it will be more than random. Why is it not unity? Because vacancy itself is making random jumps and for vacancy, there is no barrier for vacancy formation as for the diffusion of X. The only barrier for vacancy diffusion is the migration barrier. The number of successful jumps of a vacancy per unit time will be much higher than that for the atom X. The vacancy itself will make n number of jumps and after making n number of jumps, it can come back to one of the nearest neighbor site of X. Then this X will make its second jump into that same vacancy, then that jump will no more be random because X is exchanging with the same vacancy.

The extreme case would be after the first jump, X will immediately jump back onto the same vacancy. So, it will be a reverse jump. This reverse jump will nullify the contribution to the diffusion from the previous jump. So we need to apply certain factor to this expression for D which will take into account this correlation effect and it is done by applying a factor f in the expression for D.

f is called correlation factor because the next jump of the atom X is no more random, it depends upon the previous jump. These are called correlated jumps. Now the same vacancy can exchange with atom X multiple times and such a sequence of jumps of an atom into the same vacancy again and again it is called correlation chain or correlation sequence. If a fresh vacancy arise on nearest neighbor shell of X and then X exchanges with that fresh vacancy, the first correlation sequence is broken and the new correlation sequence will start with the new vacancy and it is important to determine this correlation effect. The correlation factor, f accounts for this correlation effect.

The correlation factor is defined as mean square displacement when the jumps are correlated divided by mean square displacement assuming completely random jumps. If we look into this expression for R^2 again, when the jumps are completely random:

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

And in a sense, this summation of $\langle \cos\theta_{i,j} \rangle$ gives the contribution from the correlated jumps. f is essentially:

$$f = \frac{\langle R^2 \rangle_{corre}}{\langle R^2 \rangle_{Random}} = \left\{ 1 + \frac{2}{n} \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \langle \cos\theta_{i,j} \rangle \right\}$$

So, we need to determine $\langle \cos\theta_{i,j} \rangle$ and we need to consider the combination of each jump with every other jump that occurred after it in order to evaluate the correlation factor f. Now, let us try to determine this correlation factor here, we expand the summation inside, so we can write:

$$f = 1 + \frac{2}{n} \sum_{i=1}^{n-1} \left[\langle \cos\theta_{i,i+1} \rangle + \langle \cos\theta_{i,i+2} \rangle + \langle \cos\theta_{i,i+3} \rangle + \cdots \right]$$

Fortunately, we do not need to consider the pair of each jump with another jump that occurred after it because for any cubic lattice, we can show:

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

We can illustrate this for the case of simple cubic.

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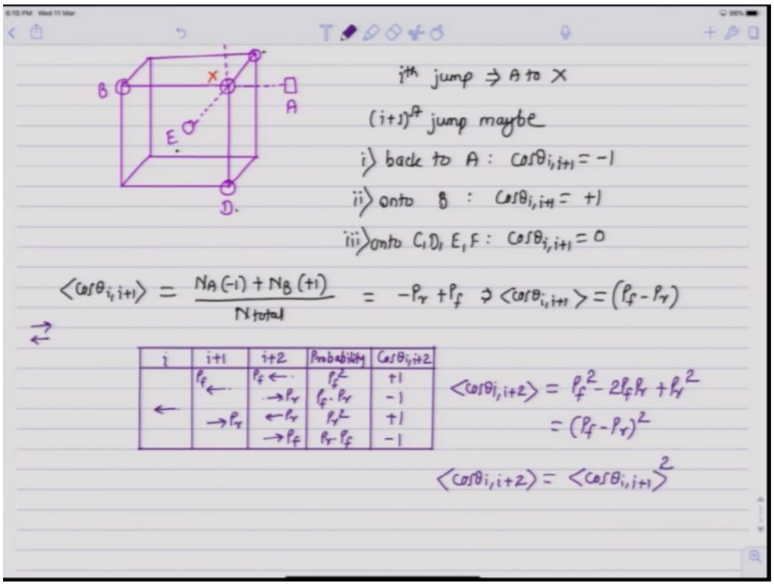


i^{th} jump $\Rightarrow$ A to X

$(i+1)^{th}$ jump maybe

i) back to A : $\cos\theta_{i,i+1} = -1$

ii) onto B : $\cos\theta_{i,i+1} = +1$

iii) onto C, D, E, F : $\cos\theta_{i,i+1} = 0$

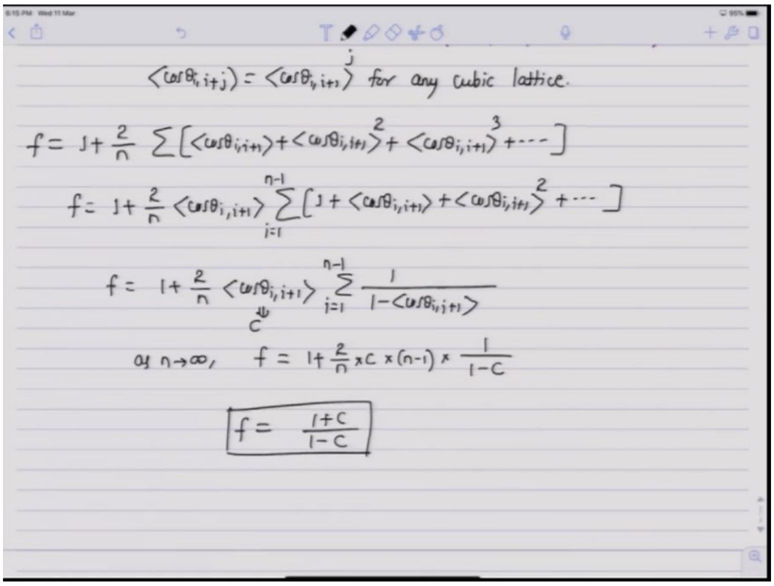
$$\langle\cos\theta_{i,i+1}\rangle = \frac{N_A(-1) + N_B(+1)}{N_{total}} = -\rho_r + \rho_f \Rightarrow \langle\cos\theta_{i,i+1}\rangle = (\rho_f - \rho_r)$$

$\rightleftarrows$

i	i+1	i+2	Probability	$\cos\theta_{i,i+2}$
$\leftarrow$	$\rho_f \leftarrow$	$\rho_f \leftarrow$	ρ_f^2	+1
		$\rightarrow \rho_r$	$\rho_f \cdot \rho_r$	−1
	$\rightarrow \rho_r$	$\leftarrow \rho_r$	ρ_r^2	+1
		$\rightarrow \rho_f$	$\rho_r \cdot \rho_f$	−1

$$\langle\cos\theta_{i,i+2}\rangle = \rho_f^2 - 2\rho_f\rho_r + \rho_r^2$$
$$= (\rho_f - \rho_r)^2$$

$$\langle\cos\theta_{i,i+2}\rangle = \langle\cos\theta_{i,i+1}\rangle^2$$



$\langle\cos\theta_{i,i+j}\rangle = \langle\cos\theta_{i,i+1}\rangle^{j}$ for any cubic lattice.

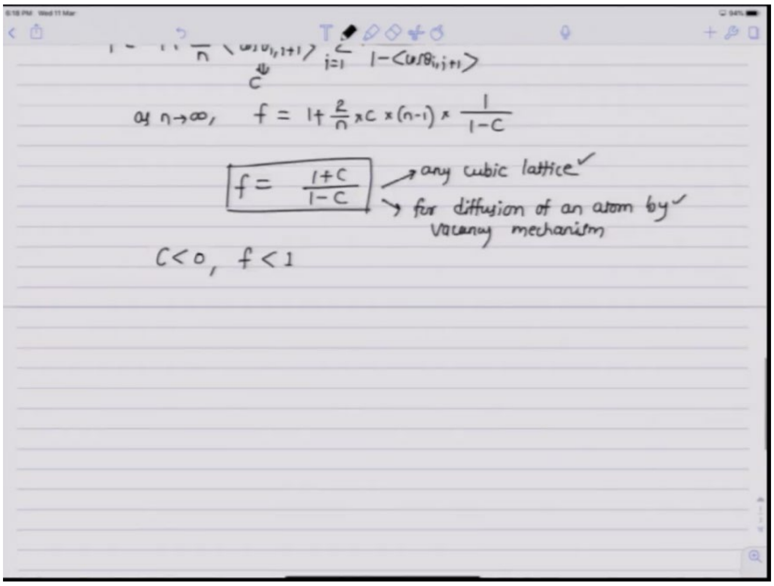
$$f = 1 + \frac{2}{n}\sum\left[\langle\cos\theta_{i,i+1}\rangle + \langle\cos\theta_{i,i+1}\rangle^2 + \langle\cos\theta_{i,i+1}\rangle^3 + \cdots\right]$$

$$f = 1 + \frac{2}{n}\langle\cos\theta_{i,i+1}\rangle\sum_{i=1}^{n-1}\left[1 + \langle\cos\theta_{i,i+1}\rangle + \langle\cos\theta_{i,i+1}\rangle^2 + \cdots\right]$$

$$f = 1 + \frac{2}{n}\underset{\underset{C}{\Downarrow}}{\langle\cos\theta_{i,i+1}\rangle}\sum_{i=1}^{n-1}\frac{1}{1-\langle\cos\theta_{i,i+1}\rangle}$$

as $n\to\infty$, $f = 1 + \frac{2}{n} \times C \times (n-1) \times \frac{1}{1-C}$

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

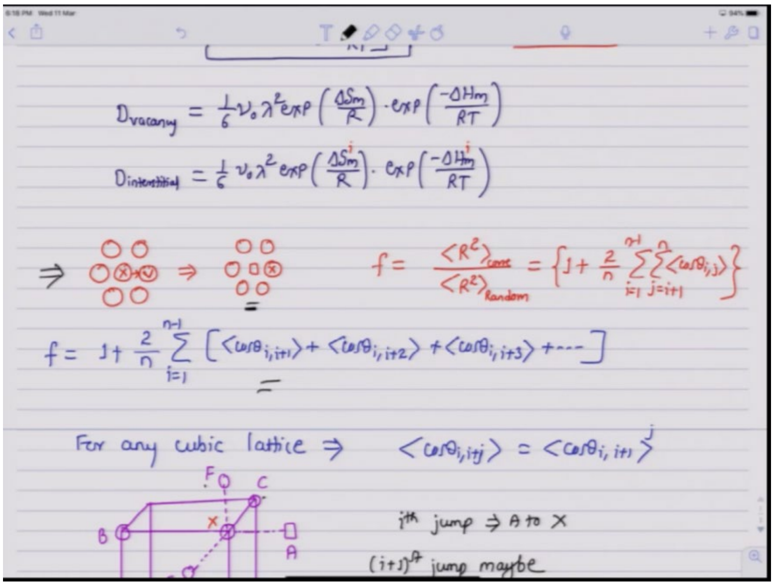


$\frac{2}{n}\underset{\underset{C}{\Downarrow}}{\langle\cos\theta_{i,i+1}\rangle}\sum_{i=1}\frac{1}{1-\langle\cos\theta_{i,i+1}\rangle}$

as $n\to\infty$, $f = 1 + \frac{2}{n} \times C \times (n-1) \times \frac{1}{1-C}$

$\boxed{f = \frac{1+C}{1-C}}$ → any cubic lattice ✓ → for diffusion of an atom by vacancy mechanism ✓

$C < 0$, $f < 1$



$$D_{vacancy} = \frac{1}{6}\nu_0 \lambda^2 \exp\left(\frac{\Delta S_m}{R}\right) \cdot \exp\left(\frac{-\Delta H_m}{RT}\right)$$

$$D_{interstitial} = \frac{1}{6}\nu_0 \lambda^2 \exp\left(\frac{\Delta S_m^i}{R}\right) \cdot \exp\left(\frac{-\Delta H_m^i}{RT}\right)$$

$$f = \frac{\langle R^2 \rangle_{corr}}{\langle R^2 \rangle_{Random}} = \left\{1 + \frac{2}{n}\sum_{i=1}^{n-1}\sum_{j=i+1}^{n}\langle \cos\theta_{i,j} \rangle\right\}$$

$$f = 1 + \frac{2}{n}\sum_{i=1}^{n-1}\left[\langle \cos\theta_{i,i+1}\rangle + \langle \cos\theta_{i,i+2}\rangle + \langle \cos\theta_{i,i+3}\rangle + \cdots\right]$$

For any cubic lattice ⇒ $\langle \cos\theta_{i,i+j}\rangle = \langle \cos\theta_{i,i+1}\rangle^j$

i^{th} jump ⇒ A to X

$(i+1)^{th}$ jump maybe

Let us consider the simple cubic lattice unit cell here. Suppose the atom X has made its i^{th} jump from A to X and the atom is now at position X and the vacancy is on A. X has 6 nearest neighbor sites, which are denoted as A, B, C, D, E, F. Now on its $(i+1)^{st}$ jump, atom X can either jump:

1) *back to A* : $\cos\theta_{i,i+1} = -1$ (*reverse jump*)
2) *onto B* : $\cos\theta_{i,i+1} = +1$ (*forward jump*)
3) *onto C, D, E, F* : $\cos\theta_{i,i+1} = 0$

For the last case, jump vector would make an angle of 90 degree with the first jump vector $\overrightarrow{AX}$. If you find the average, $\langle \cos\theta_{i,i+1}\rangle$ it would be the number of atoms N_A that make this reverse jump to A times $\cos\theta_{i,i+1}$ corresponding to that jump (which is -1) plus number of atoms that make jump onto site B times $\cos\theta_{i,i+1}$ corresponding to that jump (which is +1) divided by total number of atoms:

$$\langle \cos\theta_{i,i+1}\rangle = \frac{N_A(-1) + N_B(+1)}{N_{total}}$$

We do not need to consider other 4 jumps because $\cos\theta$ for those would be 0. Now $\frac{N_A}{N_{total}}$ is the fraction of atoms which have made the reverse jump back to A. It can be considered as the probability that an atom makes a reverse jump. Let us denote it as P_r. Similarly, $\frac{N_B}{N_{total}}$ is the probability that an atom makes a forward jump. Let us denote it by P_f, so we get:

$$\langle \cos \theta_{i,i+1} \rangle = \frac{N_A(-1) + N_B(+1)}{N_{total}} = -P_r + P_f$$

$$\langle \cos \theta_{i,i+1} \rangle = \left(P_f - P_r\right)$$

Now let us consider the combination of i^{th} and $(i + 2)^{nd}$ jump. For that, we need to consider all the sequences $i^{th}, (i + 1)^{st}$ and $(i + 2)^{nd}$, because $(i + 2)^{nd}$ jump will depend upon $(i + 1)^{st}$ as well as well as i^{th} jump. Let us denote the jump of X from left to right by right arrow and from right to left by a left arrow. Let us look at the table here:

$\boldsymbol{i}$	$\boldsymbol{i+1}$	$\boldsymbol{i+2}$	**Probability**	$\boldsymbol{\cos \theta_{i,i+2}}$
←	P_f ←	P_f ←	P_f^2	+1
		→ P_r	$P_f.P_r$	-1
	→ P_r	← P_r	P_r^2	+1
		→ P_f	$P_r.P_f$	-1

Now, a left arrow may indicate reverse jump or a forward jump, depending upon the previous jump, because these are correlated jumps. i^{th} jump of atom X here was from A to X and let us denote the i^{th} jump as left arrow. Now, $(i + 1)^{st}$ jump maybe a reverse jump or a forward jump. If $(i + 1)^{st}$jump was from right to left, it would be a forward jump, the probability of which would be P_f. And if it was from left to right, it would be a reverse jump, the probability of which would be P_r.

There will be 4 possibilities for $(i + 2)^{nd}$ jump depending upon what was the $(i + 1)^{st}$ jump. The $(i + 2)^{nd}$ jump might be again from right to left, the probability of which would be P_f because it is a forward jump with respect to the $(i + 1)^{st}$ jump, the first possible $(i + 1)^{st}$ jump or it can be from left to right the probability of which would be P_r. For the other possibility of $(i + 1)^{st}$ jump, the $(i + 2)^{nd}$ jump again would be if it was from left to right, the probability would be P_r because it is a reverse jump with respect to the previous jump. And if it is from left to right, the probability would be P_f. The probabilities for all the four sequences are given in the above Table. And if we see the combinations of i^{th} and $(i + 2)^{nd}$ jump, for the first combination the 2 jumps are in the same direction, for second the 2 jumps are in the opposite direction, for the third one again the 2 jumps are in the same direction and for the last one it will be again opposite jumps. The corresponding $\cos \theta_{i,i+2}$ for the four sequences are given in above Table.

The average of cosine $\langle \cos \theta_{i,i+2} \rangle$ would be:

$$\langle\cos\theta_{i,i+2}\rangle = P_f^2 - 2P_fP_r + P_r^2 = \left(P_f - P_r\right)^2$$

We can show that:

$$\langle\cos\theta_{i,i+2}\rangle = \langle\cos\theta_{i,i+1}\rangle^2$$

We can keep doing this for $(i+3)^{rd}$, $(i+4)^{th}$ jump and we can show that for any cubic lattice:

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

This is important because when I have to calculate $\cos\theta_{i,i+j}$ I don't have to consider combination of every jump with every other jump that occurred after it, but I have to know only $\cos\theta_{i,i+1}$ or only successive jumps of the atom. And when number of jumps n tends to infinity, average of cosine between the successive jumps or $\langle\cos\theta_{i,i+1}\rangle$ will be independent of i and that is why this result is important.

Let us substitute this back into the expression for f here and let us try to derive the expression for f. f is equal to:

$$f = 1 + \frac{2}{n}\sum_{i=1}^{n-1}\left[\langle\cos\theta_{i,i+1}\rangle + \langle\cos\theta_{i,i+1}\rangle^2 + \langle\cos\theta_{i,i+1}\rangle^3 + \cdots\right]$$

If we take average of $\langle\cos\theta_{i,i+1}\rangle$ common, we get:

$$f = 1 + \frac{2}{n}\langle\cos\theta_{i,i+1}\rangle\sum_{i=1}^{n-1}\left[1 + \langle\cos\theta_{i,i+1}\rangle + \langle\cos\theta_{i,i+1}\rangle^2 + \cdots\right]$$

Now this series can be approximated to:

$$f = 1 + \frac{2}{n}\langle\cos\theta_{i,i+1}\rangle\sum_{i=1}^{n-1}\frac{1}{1 - \langle\cos\theta_{i,i+1}\rangle}$$

Now, as I said earlier as $n \rightarrow \infty$ or for large values of n, $\langle\cos\theta_{i,i+1}\rangle$ would be independent of i that means, it should not matter which pair of successive jumps we are considering the average of cosine between the 2 successive jumps will be same for any pair, the average being taken over all the atoms.

If I substitute:

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

And as $\langle \cos\theta_{i,i+1} \rangle$ will be the same for any i, the expression for correlation factor will boil down to:

$$f = 1 + \frac{2}{n} \times C \times (n-1) \times \frac{1}{1-C}$$

Since n is large:

$$\frac{n-1}{n} \sim 1$$

And we get the expression for f as:

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

We derived the expression for correlation factor f and this is valid for any cubic lattice and for diffusion of an atom by vacancy mechanism. The correlation factor depends upon 2 factors, the geometry which is given by the crystal structure and the mechanism of diffusion. In this case, the expression is for diffusion of atom by vacancy mechanism. In cubic lattice if the diffusion is occurring by interstitialcy mechanism in which the atom diffuses by forming its self-interstitials then the expression for correlation factor will be different. Similarly, the correlation factor for vacancy mechanism in a tetragonal lattice would be different.

Next couple of classes we will look into the specific expression for f in different cubic lattices FCC, BCC, diamond cubic etc. And we will consider specifically the vacancy mechanism of diffusion. Now it should be noted that for the cubic lattice:

$$\langle \cos\theta_{i,i+1} \rangle \; or \; C < 0$$

And:

$$f < 1$$

This is because, as illustrated here considering the jumps in (111) plane of an atom X, the second jump of atom X here will most probably be back into the same vacancy. That is the most possible sequence and this nullifies the contribution to diffusion from the previous jump. Since this reverse jump is most possible, it kind of indicates that C has to be less than 0. We will stop here for today. Thank you.