Heat Treatment and Surface Hardening (Part–1)
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Lecture Number 36
Diffusion in Solids - 1

In this lecture we will talk about diffusion.

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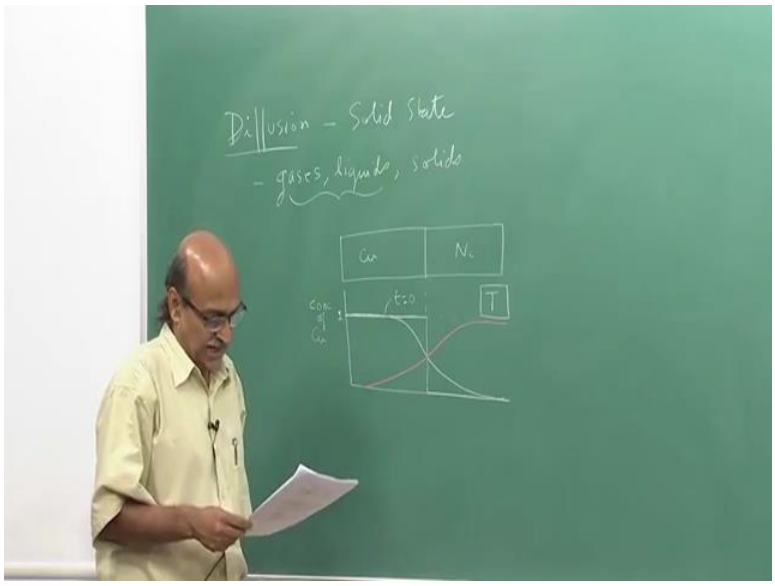

So far we had been we are mentioned diffusion on and of in the earlier lectures. Essentially diffusion is migration of atoms whether it is in the in a gas or migration of atoms in a liquid or migration if atoms in a solid. So, diffusion takes place or movement of atoms takes place in gases, liquids as well as solids, regarding gases and liquid we have an intuitive idea of movement of atoms because from our everyday experience we are able to tell that atoms do migrate very easily in gases and liquids.

If you drop a color die in water you will very quickly see the color spreading which means the the, the die, the atoms that make, make up the die very quickly move in the liquid medium. Same thing happens with gases if you you can easily smell any anything like a let say chemical bottle open, opened up in one corner of the room very quickly you will smell it at the other end of the

room. However it is solids we do not have direct experienced until we actually measure the movement of atoms inside a solid.

For example, if I take a block of copper and I weld it. Join it with a block of nickel. Let us say, so I have copper here pure copper I have pure nickel and if I look at how the copper atoms and nickel atoms are distributed across this couple copper and nickel couple. That is let us say here it is concentration of copper atoms then when I join it in the beginning I will have some 100 percent copper on this side so, I will have concentration of copper as let us say fraction of copper atoms is one and in the nickel side there will be zero fractions of copper atoms. So, this is at ley say time t is equal to 0.

If I measure it after sometime at but if it was that let us say room temperature that we would see no measurable change. However at an elevated temperature T if I measure it after sometime T if I expose this couple, put this couple inside the farness for some time and that take it out and then measure the copper concentration right across I may observe a concentration profile of copper like this basically see telling me they copper atoms have migrated to the nickel side.

Similarly if I want to make a concentration profile for nickel I will observe the reverse situation where nickel atoms may have migrated on the left hand side. So, this is what we would call as diffusion in the solid state. So, in this lecture and subsequent lectures we are going to be concerned with diffusion of atoms in the solid state, in fact it took several decades to really understand how diffusion was taking place in the solid state where atoms are high are very compact and there is hardly any place to move even then diffusion takes place.

So, the exact mechanism of movement of movement of atoms is now well understood and that is what we will be looking at. But before I go it to diffusion in the solid state, I would like to just in general if there was an atom which could migrate in any direction then and in fact if we does not have any (pre) preference to move in a particular direction then we have a problem which is called at the Random Walk Problem.

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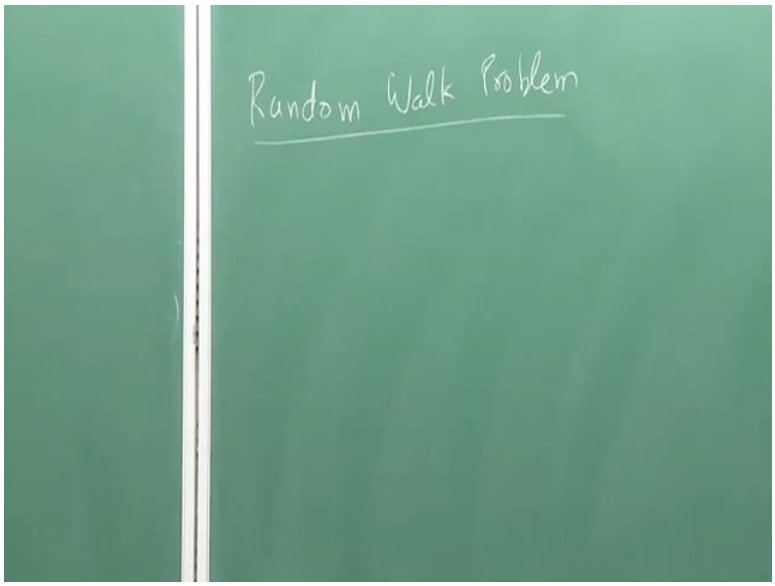

This is also often called as a Drunken Walk Problem or Brownian motion where partial could move in 3 dimensions in any direction. It can we can look at look at such a problem in 2 dimensions we can also look at such a problem in one dimension.

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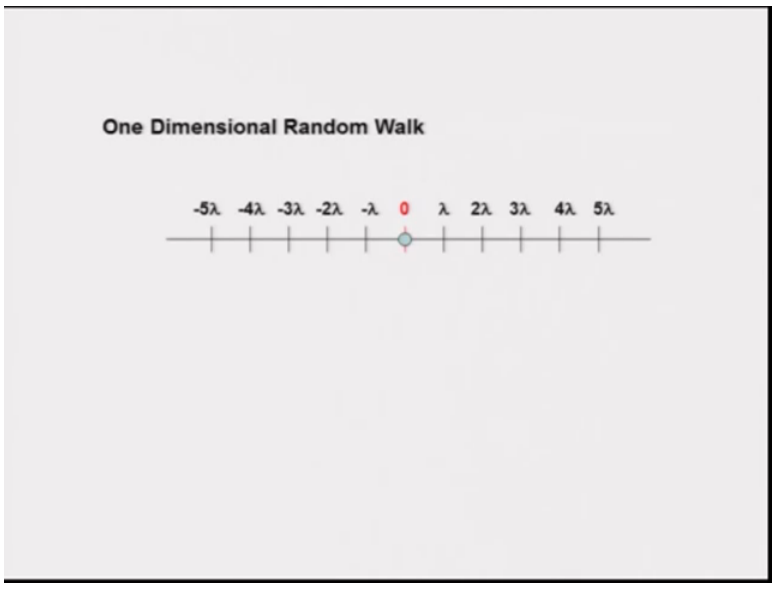

Just to show you a little bit of an animation consider a one dimension random walk where you have an atom located at the origin and it is constraint to move only along this axis in one dimension either in the plus direction or towards the left in the negative x direction. If we let this

atom move and at every step there is an equal probability for this atom either to move in the plus direction or the minus direction plus it moves in steps of lambda.

In that case as you can see these atoms as move 2 steps, 3 steps it can go back well it as gone forward to 4 steps and then it can reverse and the problem could be that after how many steps what would be the location of the atom after and x number of steps.

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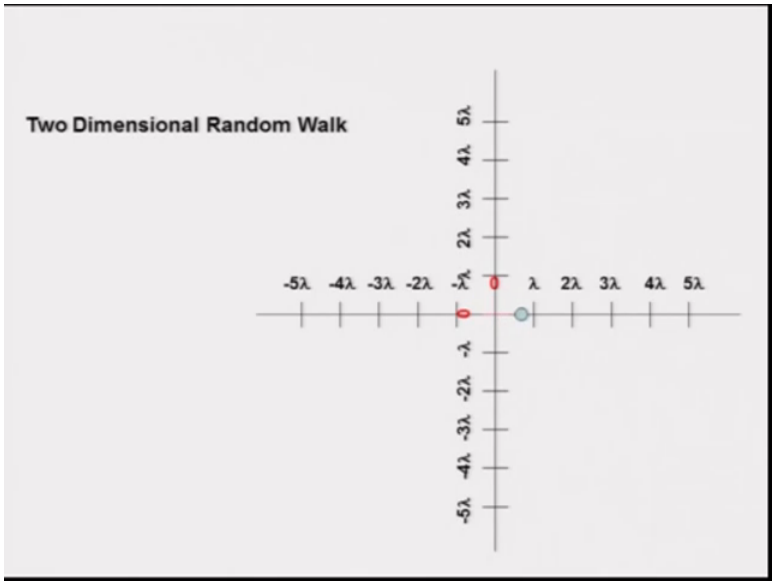

A similar situation one can also see in to dimension, where again the atom is now free to migrate in two dimensions. So, it can move up and down and left in right and the problem that we want to look at is that after it has traveled n number of steps where would these atoms be look at it. So, we will try to solve this problem as a 1 dimensional problems and see what is it is significance in the case for diffusion.

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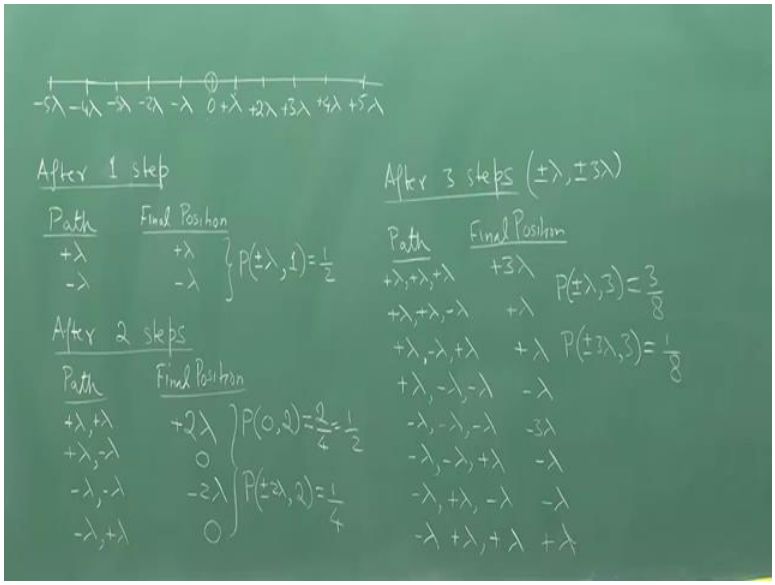

So, let us consider a 1 dimensional walk, so we will look at a 1 dimensional walk problem at this constraint to move on this horizontal axis towards the right or the left and let me break this axis up into steps of lambda. So, each time an atom located here can move in steps of lambda which would be for example it it is in atom simply an atomic step or the interatomic distance in solids.

Here on this side it is minus lambda, minus 2 lambda, minus 3 lambda, minus 4 lambda and minus 5 lambda. Let us say that I want to look at where will the atom B after one step. So, after one step it I have to look at this problem after one step, I want to see what path it will take and what will be it is final location or final position and the path it takes we will determine what would be the position of this atom after 1 step.

So, very clearly one possible path is it moves a step of plus lambda which means this moves in the right direction. The final position clearly would be over here which is simply plus lambda. It could move also in the negative direction by a step of lambda, so the path it will be taking would be minus lambda and the final position would be minus lambda. Since you have assumed that there is an equal probability at any stage for this atom either to move in the right direction or the left direction which means probability P of this atom being located at either plus lambda or minus lambda after one step is simply equal to half.

That is the probability of it being located at plus lambda is half probability of the atom being located after one step at minus lambda location is also half. Now let us take this problem is step further and say what would be the atom position after two steps. Well after two step again let us consider the path as before and the final position for each path. One possible path is plus lambda, so atoms move from here towards the right one step and again plus lambda so, it moves another step of lambda reaching the final position of two lambda.

The second possible path plus lambda in so it is moves here and then takes here it moves to the left by minus lambda very clearly it will come back to it is starting point of zero position so the final position is zero. Now third possibility it first moves towards the left by a step of minus lambda and another step of minus lambda, so it reaches minus 2 lambda. Now forth possibility takes a minus lambda step and takes a plus lambda step reaching the final position of zero again.

If I look at what is the probability of this particle would be at it is starting position or the position zero after two steps. So, there are two possible paths in which, which lead to the position of zero. So, there are two paths and there are total of four possible paths for two steps. So, the probability would be 2 upon 4 for simply half. Probability that the atom would be at plus 2 lambda and minus 2 lambda after 2 steps for each of them. So, for the (prob) particle to be at plus 2 lambda position the there is only one possible path out of 4 possibilities hence, it is 1 upon 4 and similar is the case for the final position of minus 2 lambda.

So, for plus 2 lambda or minus 2 lambda the probability is 1 upon 4. Extend this further what happens after 3 steps, again we have, we have to list down all possible path and clearly as we increase the number. The number of paths possible paths also increased. So, one the first possibility let me write down plus lambda step another plus lambda step or third plus lambda step clearly the final position would be plus 3 lambda.

Second, plus lambda plus lambda minus lambda, so it moves 1 lambda another lambda reaches 2 lambda but then it returns back by a negative lambda. So, the final position is plus lambda, third one plus lambda minus lambda plus lambda. So, it is starts from zero it goes plus lambda then comes back minus lambda it goes back to plus lambda. So, the final position is plus lambda, forth possibility plus lambda, minus lambda, minus lambda. So, moves lambda then it returns back and then goes further to the left by another step of lambda reaching to minus lambda.

Are there any other possibilities? Yes, all our (possible) first 4 paths started with the steps towards the right. Now I can just repeat this whole exercise for all steps beginning with minus lambda or the particle moving to the left, thus the first step. So, minus lambda again minus lambda again minus lambda that gives me the final position as minus 3 lambda. Then I have minus lambda minus lambda and a plus lambda, this will give me the final position to be minus lambda.

Another possibility minus lambda plus lambda and let say minus lambda so, minus lambda, plus lambda minus lambda giving me final position of minus lambda. Then I can have minus lambda plus lambda and plus lambda. So, minus lambda, plus lambda plus lambda takes me to the final position of lambda. If I look at it basically after 3 steps the only possible positions for the particles are plus or minus lambda and plus and minus 3 lambda. So, probability for the particle to be at plus or minus lambda after 3 steps would turn out to be well let see for plus lambda there are total of 3 paths.

So, which will lead to the plus lambda position, how many paths are there if I count them 1, 2, 3, 4, 5, 6, 7, 8. There are 8 paths hence the probability is 3 by 8 to be at plus 3 lambda in the same or to be at plus lambda the same would be the case for minus lambda the probability would be 3 upon 8. Similarly probability for the, the particle to be at plus or minus 3 lambda after 3 steps, well there is only one path which can take me to plus 3 lambda, there is only one path which can take me to minus 3 lambda. Hence the probability is simply 1 upon 8 for each of the two cases of plus 3 lambda and minus 3 lambda.

Similarly, one can determine for higher number of steps and in fact one will can generalize this two end steps. Now what do we do with this, well I want to have an idea where would the particle will be located after a given number of steps have been executed.

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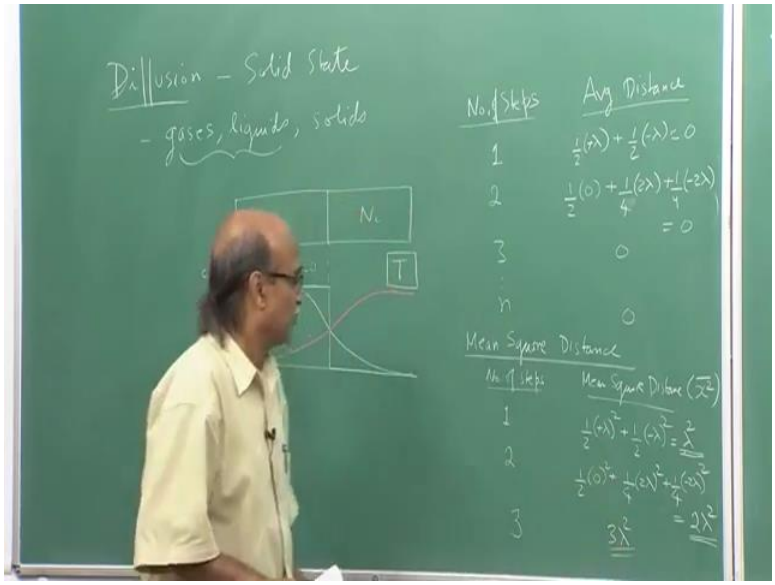

So, let us look at it, let me write down make a table here number of step and average distance. Average distance move by the particle from it is starting location. So, if I calculate for just a one, then what I have to do is the atom moves by a in this final position is plus lambda therefore the distance moved is plus lambda.

So, in order to calculate the average distance I would multiply by the probability multiplied by plus lambda, plus it can also move to minus lambda. So, again it has a probability of half multiplied by minus lambda, very clearly this just simply gives me zero. If I repeat this with the number of steps being 2, well the particle gets located at zero with the probability of half. So, half multiplied by zero distance travelled, plus half 1 forth there is a probability of 1 forth that it will be located at plus 2 lambda giving from here.

So, it is how 1 forth plus 2 lambda plus 1 forth into minus 2 lambda, clearly this is again it gives me a result of zero. In fact if I repeat this exercise for 3 steps also the average distance moved would be zero. Similarly if I go n steps the average distance is zero. Now what does this mean, all this is telling me is, that this only gives me an average distance travelled. But this does not mean that the atom will remain at zero location. In fact there would a distribution of atom positions around the mean of zero.

So, the mean of the distribution is zero but after any after the certain number of steps this particle can be located at any position around the mean with the certain probability. So, what in order to take care of this problem, what we need to concern ourselves is with the mean square distance? So, we should concern ourselves with the mean square distance and what is the mean square distance. So, let us calculate again if I have here number of steps and the mean square distance which is x square bar.

So, after one step what is the mean square distance? It is half plus lambda square, square of the distance moved plus probability of half that it can be located at minus lambda. So, it will square of minus lambda and this will give me a mean square distance of lambda square. After two steps we repeat this there is a probability of half that it is back to it is starting position. So, half times zero square plus 1 forth times 2 lambda square because that is the probability of 1 forth that the particle will be located that 2 lambda distance of A from the starting point.

Similarly again the probability of 1 forth that it is located minus 2 lambda from the starting point. So, it is minus 2 lambda square times the probability 1 upon 4, if I add all this up I will get 2 lambda square. So, here I have lambda square, I have here 2 lambda square, after 3 steps I leave it to you to calculate from these probabilities and these locations of plus minus lambda and plus minus 3 lambda I will get 3 lambda square.

So this tends you suggest the sequence after one step I have a mean square distance of lambda square after 2 steps I have a distance of 2 lambda square after 3 steps I have a mean square distance of 3 lambda square therefore after n steps the mean square distance would be n times lambda square.

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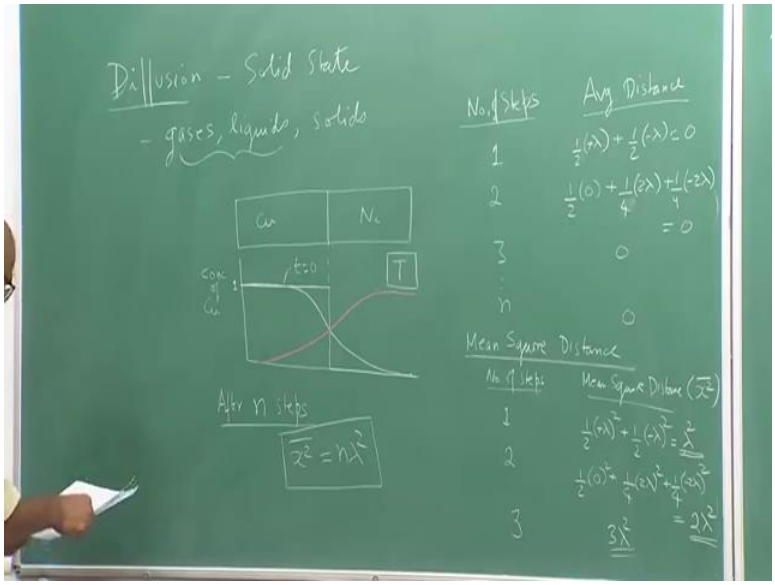

In fact what this quantity that we have calculated is actually the variance of the distribution of positions, since the mean is zero x square bar represents the variance of this distribution from this I can also calculate what is the root mean square distance.

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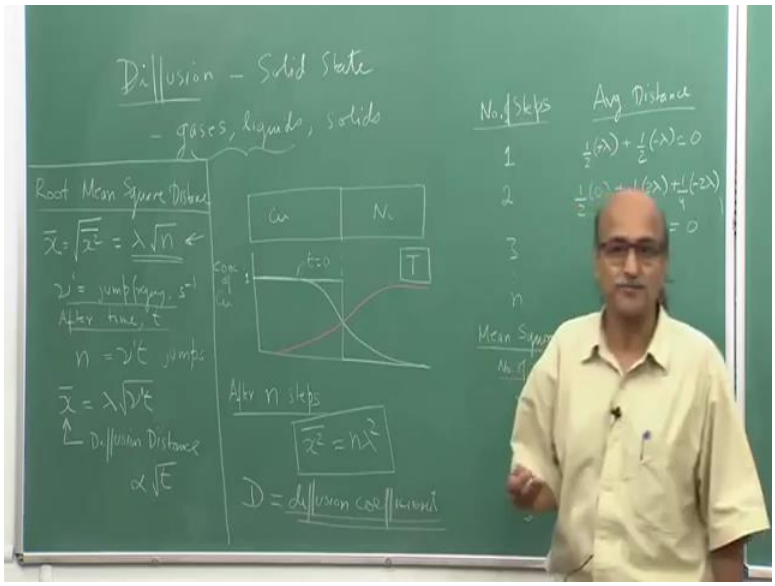

The root mean square distance is simply I will call this as a x bar which is square root of the root of the mean square distance x square bar which take the square root of this and this would give

me lambda times this square root of n. So, this is the root mean square distance that after n steps the particle is at a root means root mean square distance of lambda square root n.

Now if we assume that the jump frequency of the atom, after all if I want to understand after how much time what would be the root mean square distance I should know at what frequency the particle is jumping from one location to another location in steps of lambda. So, let us say that new prime is equal to the jump frequency. So, it has units of per second that so many jump it is would takes place every second.

So, after time t the number of jumps that would of taking place is new prime t jumps. Now this is nothing but n steps that a particular particle or an atom is taking. So, n is equal to new prime t which I can now substitute here giving me the root mean square distance of lambda square root of new prime t. This x bar is like a diffusion distance and one notable thing from this relation is that diffusion distance is proportional to square root of time.

At this is at interesting conclusion that has been drawn here, the diffusion distance is proportional to square root of time and in fact large number of in in fact in all diffusion problems you are going to get this that diffusion distance is related to or directly related to square root of time. This is one peculiar nature of diffusion. We will we do not eventually relate this diffusion distance to what is called as the diffusion coefficient. If you remember if you go back a few lectures back I had talked about diffusional growth, in diffusional growth I had Broughton what was called is the diffusion coefficient D.

And in fact we would spend sometimes in the subsequent (lec) lectures on D and how this D is going to get related to this jump frequency. That means we will also have to understand this jump frequency it is nature what all factors it is going to determinant, in fact one of the factors that this jump frequency will determine all is again that when I when I jump takes place atoms has to go through a energy hill. So, it has to just like in the case of nucleation a stable nuclei to form by climbing over an energy hills.

Similarly an atomic jump that take place also has to climb over energy hill and therefore each jump would have a certain probability which would be linked to this jump frequency as we would be seen in the subsequent lectures. So, in this lecture I have given you in idea of a diffusion I have not yet broughton how diffusion will takes place in the solid state. One has a

good feeling in liquid there is lot of space between atoms and therefore if I put in for an atom that atom can move in between the spaces. Now how exactly these jumps are going to takes place in the solid state would be the subject of the next lecture. So I will stop here