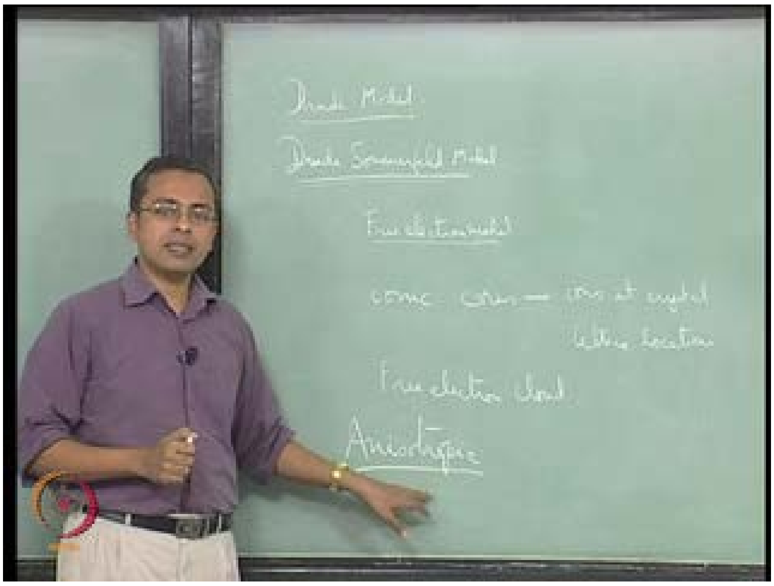
Physics of Materials
Prof. Dr. Prathap Haridoss
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Madras

Lecture No. # 21
Anisotropy and Periodic Potential in a Solid

Hello, welcome to this twenty first class of our physics of materials course, we have done lot of analysis on the various material properties that we are we are interested in trying to explain. And in particular we have focussed on the electronic and thermal properties that we can examine and record in in a macroscopic sense, and we have try to understand what is it that exist within the material in at microscopic level or even at a sub microscopic level. And try to see, what is the manner in which the phenomena that are occurring at those atomic and sub atomic scales, impact the property that we measure at the large scale right.

(Refer Slide Time: 01:07)



So, this is what we have done, we have already looked at a few couple of different models, we looked at the Drude model, and the Drude Sommerfeld model (No audio from 01:09 to 01:26) right. So, between them we have I have we have already looked at how you can, we have looked at the process first of all, so you are now become familiar with this process by which you know, you can look at a material a material property, and then attempt to build a set of rules and regulations that you can place on the constituents, and see how those rules and regulations impact the property that you are measuring. So that process, which it is which is itself I think a very important piece of understanding is something that we have now gone through right.

So, in future if you were to run in to models, which may be vastly more sophisticated may involve lot more concepts that that are of interest for that system, you at least will understand, how the process occurs right. So, there are different properties that people model, different systems that people model, and at least in general concept what we have done so for is the basic kind of approach that all of those models will take. The kind of computation they do may be different, the computational tools they use may be different, simply because the equations they put down, may be such that specific kinds of computation tools may become necessary.

It may not be straight forward for you to just write the equation and solve it in one goal right. So, the complexity of the equations may change and therefore, the mathematical approach that you may have to take may change, and this is where a lot of the mathematics that you learn as in the form of engineering mathematics becomes useful to you. So, you can find specific problems and find the appropriate mathematical tool, which will enable you to solve the equations that correspond to that problem or at least make plots of those phenomena. And examine how those trends strange as you go to one extreme or the other extreme of that of the experimental conditions.

So, this is something that I think, we at at this stage we need to pass and recognize, that you know we have come this for, we have an understanding of this process. So, that is itself an very important aspect that we need to recognize, over and above that specific to our discussion. We have looked at two models, we have looked at one model seen what prediction it makes, we have recognized that you know in fact it makes pretty good predictions, that it is able to do a lot of things that, we did not I mean at least upfront it feels like, it is a very simple model because you are just taking something that belongs to a gas employing it on a solid, that contains electrons and so upfront there is reason to be sceptical that, such a simplistic approach may actually work, but in fact it turns out that, it makes pretty good predictions.

And as I said at the beginning our whole purpose is to get away with this simplest theory that we can possibly use right. So, if there is a simple theory that works, there is absolutely no need for a more complicated theory. So, only when we find locations and reasons, why we feel that you know this theory that we are considering is actually not good enough, that we need to that there are specific aspects that, where it fails. We end up having to look at more sophisticated theories, so we did recognize that there were reasons why this the model was not good enough, that in fact it is making certain assumptions. And those assumptions some times are explicitly visible to us; sometimes in the equation we write it is simplicit.

And, in that process somewhere down the line, errors are creeping into the model and errors are creeping into the equation, which we do not realize, which is we simply write the equation because that equation is consistent with the rules we are assuming that the system is following. It is it simply that when you take a step back and examine whether whether or not in fact those rules are actually being followed by the system. Only when you do that, you recognize that in in fact that some of those rules are not correct for the situation that we are considering, some of the rules are not appropriate for the system that we are considering

And therefore, even though the equation is correct with respect to that rule, that rule itself is not appropriate for the system that we are looking at, and therefore the equation that we are writing is not appropriate for the system that we are looking at. So, you can do the calculation step by scept step correctly from there on, but fundamentally that equation was not appropriate, and therefore the result that you get is also not appropriate. So therefore, we had issues with the Drude model, we recognize the issues, we were able to pin it down to the fact that at at a very fundamental level since, we have assumed it is a classical particles we use Maxwell Boltzmann statistics, and that implies certain kinds of behaviour for the electrons with respect to energy with respect to temperature.

Then we recognize that you know, it needs to be modified, it needs to be improved and such an improvement was brought about by Sommerfeld many years ago in the 1920’s. So, we looked at that improvement what he had done, so he basically did not modified the model very significantly, at least in broad frame work he still treated it in a in a very similar manner to what Drude had done, except he recognize that the particle system that we had behaved somewhat differently, and it was not appropriate to just arbitrarily apply the rules of classical mechanics on to this particles.

So quantum mechanical behaviour and more specifically the Fermi Dirac statistics was appropriate for the system that that was being considered. So, he applied Fermi Dirac statistics to the Drude model, and immediately it showed an improvement, more specifically the specific phenomenon of property of specific heat, which is the in in our case we are looking at specific heat at constant volume. And, even more particularly we are looking at the electronic contribution to the specific heat at constant volume. It turns out that, if you compare the Maxwell Boltzmann statistics versus the Fermi Dirac statistics.

We are able to see how and why the Fermi Dirac statistics is actually able to correctly tell us, are at least significantly improve the ability to predict the electronic contribution to the specific heat at constant volume. Mainly because it it shows us that the rule that the particles are going to be a fermions, and therefore follow Pauli's exclusion principle and also the fact that there are fixed number of states at a given energy level, and therefore once they are full you have to moved higher energy level. Once you place that rule on the system, and therefore model the system and write the equations with respect to those rules. You find that naturally you reach a situation, where only some number of electrons can participates in this temperature increase process.

The fact that you significantly reduce this number of electrons that are able to participate in this increase in temperature, immediately also means you are significantly reducing the amount of energy that is required for this temperature increase process, and therefore you are significantly reducing the contribution of electrons or the electronic contribution to the specific heat at constant volume. So, this is how, so we see that you know that it is not enough, so this is the thing that we have to very cautious about, it is very easy to state a rule and then write the equations with respect to the rule and then continue solving.

It is very important for us to always step back and check whether that rule that we have imposed, is it reasonable, is it correct are the reasons to thing that in fact we should be imposing some other rule because otherwise, in fact the calculations for the Drude model are fine, the calculations for the Drude Sommerfeld model are also fine, So we we cannot simply say that the equations naturally leave to whatever solution they do, and therefore everything is fine. The only reason that Drude model is failing is because the original rule that we have imposing on the system itself is not appropriate, so that is the important thing that we need to recognize fine. So, from there we have come and we have found that the Drude Sommerfeld model is much more appropriate, and is able to do things that the Drude model is not able to do correctly, so that is the big piece of improvement that we have done.

Now, having come this part, we should also recognize that you know even as a as an improved model. The Drude Sommerfeld model is also effectively what we would call as a free electron model see in it is simplest form as is mentioned all it is doing is it is replacing Maxwell Boltzmann statistics by Fermi Dirac statistics. Almost all the other ideas, so to speak of the Drude model are largely left undisturbed, so largely where continuity use those ideas. So, what it means is because we are saying it is a free electron model, what it means is that as a system, we are saying that you know the electrons are largely free to move through that solid. And they are not really experiencing any differences in the potential that they experience from position to position as the move along, that the solid.

So, when you have such a possibility, I mean at once at one level as we mentioned earlier on, we can justify it in a loose sense, in the sense that you know for a for a given electron, if you take a particular electron that is moving through the solid, what it is going to experience is that, there are whole bunch of positive charges within that solid, which represents all those ionic course as I called it. (No audio from10:32 to 10:38) These are the ions at crystal lattice locations ions at crystal lattice location. So, these are the ionic course, so in our solid we have a frame work of this ionic course, ions sitting at crystal lattice location.

And we have an electron cloud that is around it, so free electron cloud. (No audio from 11:09 to 11:16) Now, if you have this combination of ionic course which are say, which are now positively charged, and free electron cloud which is negatively charged, and they are all sitting around the same region. We can make the approximation or we can we can sort of thing that it is to make the approximation that as an electron travels around. It is seeing a large positive charge, and a large negative charge sort of competing with each other, and since both the charges are essentially the same, I mean you have the same amount of negative charge, the same amount of positive charge, because they are not independent of each other with the solid is charge neutral. So, these positive charges at those ionic crystal locations are because those ions have released one electron per location to this free electron cloud.

So, for every electron in this free electron cloud, there is a positive ion in the in the crystal location, so there is a direct one to one correlation between these two, they are not independent of each other, this cloud did not appear from nowhere. So and neither did these ions, they were all initially neutral atoms each of them released one electron, so it got the atom became a positively charged ion plus one charge, and the cloud became negatively charged, electron cloud became negatively charged with minus one electron charge so to speak released into the cloud. So, there is a direct one to one correlation between these two, so the amount of negative charge you have here, in this free electron cloud is exactly equal to the amount of positive charge you have in this ionic core, the collection of ionic cores, all the ionic cores taken together fine.

So therefore, the approximation that we are making that, when an electron is moving along, it is not really seeing it is seeing a net neutralized charge, so to speak is reasonable from that perspective we can say that, there is a net the net positive charge versus the net negative charge is essentially zero, we can make such an assumption right. So therefore, at at that level of argument or understanding, it is not it does not appear that it is too wrong to think of it is a free electron model, where the electron freely moves around. It is not really seeing there are no features, in that potential, so the net potential, potential versus position is largely featureless.

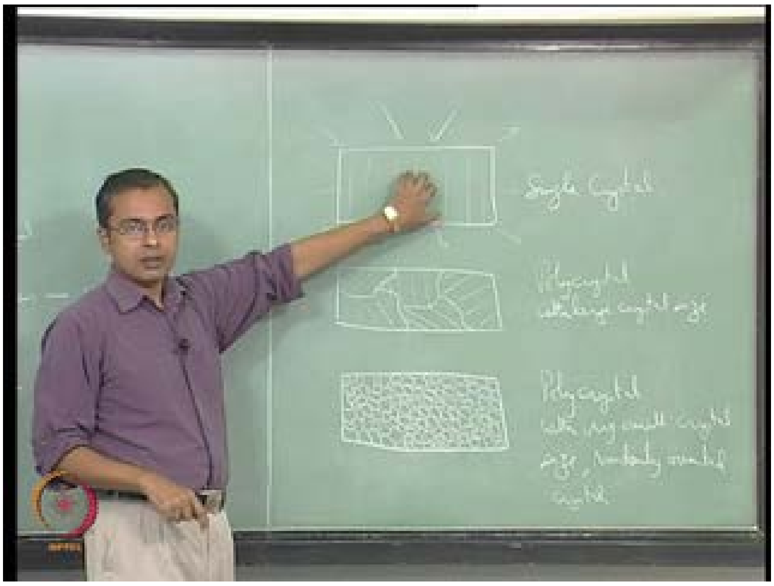
There is no higher potential at any one location, there is no significantly lower potential at any other location is largely featureless it is largely... So, the electron has no preference, it does not have any preference to be at any one location, there is no reason to believe that it will move faster at one location or it will get stuck at some location if it gets to that location and so on. Largely it is featureless, so whatever happens at one location is the exact same thing that the electron will experience at any other location within that solid, that is why, it is on it is on those grounds and that argument that we can say that, when you say it is a free electron model. It is not very for fetched, it is reasonable at least to start with, so that is how this is come above.

Now, the issue then therefore, is that we have so as we as we see this is not a bad assumption and also in terms of the values this does not seem to be bad assumption, because we are getting reasonable values, numbers are working out reasonably fine. So, from both those perspective, it is it is not too bad it is actually ok; we are in the right direction at least. The problem with this approach, which we can immediately recognize, is that if you take real material, so some you know silver metal you take or whatever it is, silver or copper or anything that you are measuring. We know for a fact from our general understanding of material science materials engineering and so on.

We know for a fact that many materials are anisotropic; many materials are typically anisotropic, what does it means? It means isotropic material means that the properties are the same regardless of the direction. So, in other words you have a solid, you measure the property in the x direction, you will get a value; you measure it in the y direction, you will get a you will get the same value; you measure it in the z direction, you will get exactly the same value. Any other coordinate, any other line that you draw through that solid, you draw the line, you make measure the property along that line, you should get exactly the same value, if it is an isotropic solid.

So, whatever the property you you are interested in you should end up with exactly the same value. Our experience is that typical solid is typically anisotropic, especially if you take a single crystal of that solid, if it is a poly crystal and sample, sometimes if the and if all the crystal are randomly oriented, then as an average overall solid, the solid may appear isotropic, simply because it is poly crystalline. And each and you have millions of such crystals, if a if it is poly crystal and the crystal size is small, and sample size is large right.

(Refer Slide Time: 16:13)



So, if you have, so I would say this is single crystal. (No audio from 16:17 to 17:06) So we have a three cases here, we have a single crystal, where and and a poly crystal with a large crystal size and, poly crystal with a very small crystal size relatively speaking. We just quickly draw this then we can compare this (No audio from 17:25 to 17: 37) we will just complete this diagram, so that way you have all the crystal and draw it here (No audio from 17:44 to 18:15) So, just for complete test, we have it now here, so you do not worry about the shapes here, but basically it is a poly crystal with very small crystal size. This is the poly crystal with very large crystal size and this is a single crystal.

In this, if we resize the single crystal what we mean is, the atomic planes are oriented correctly from this end to that end, correctly meaning in whatever sense, if if this is a 1 1 1 plane, all the way down this side also 1 1 1 plane. So it is all exactly the correct atomic orientation is perfect, atom to atom the order is correct from this end to that end, so that is a single crystal. This is a poly crystal in sample with large crystal size, so these are individual crystal, so you we only have 3 plus 2 5 crystals in this sample. In this sample we have only 5 crystals, here there is atomic order, here which is different from the atomic order, the direction of atomic order here.

So, this may be the 1 1 1 plane in this sample, that may be the 1 1 1 plane in the other sample, this may be the 1 1 1 plane in this in this I am sorry in this crystal, this may be the 1 1 1 plane, just quick a plane. We just arbitrarily I am showing you the 1 1 1 plane and we could have this as the 1 1 1 plane here. So, we have this is a poly crystal with large crystalied size, this is poly crystal with very small crystal size. So, the 1 1 1 plane could be in all all over the place in each of these crystals, so like that we can have it right.

So now, in a polycrystalline sample, when it gets more and more, when the crystal size keeps decreasing more and more too much smaller sizes, and therefore you have, you know huge number of small crystals within this within this within the dimension of that sample. Then when you take the measure a property from this side to that side of the sample, in which is a large sample you have something in your hand, which you can make measure measurement on, when you make the property measurement, what you are seeing is sort of the averaged property of all these crystals right, when you get to a single crystal, you are seeing a property that it is very specific to this particular direction.

So, this we measure a property like this and you say all the 1 1 1 planes are here, then you get the property in specific to that orientation. Here, since the 1 1 1 planes are in all possible directions and therefore, all the other planes are also in all the possible directions, I just speak 1 1 1 as an example. All the other planes are also in all possible directions, the the direction of the sample has no real link to the direction of any set of planes within this sample, whereas the direction of this sample, this direction in which we are making the measurement has a very unique orientation with respect to the orientation of planes within this crystal, because there are only one orientation of planes here, this direction in which we are making the measurement is specifically oriented with respect to those planes.

Here, there are so many such crystals here, that the planes are all over the place, there in there pointed in all different direction. So, when we pick one direction for making our measurement, it has no specific relationship to any one particular plane. This could be perpendicular to 1 1 1 plane in one crystal, it could be perpendicular to 1 1 0 plane in another crystal, it could be perpendicular to 1 3 2 plane in some other crystal and so on right. So what you see in this measurement is an average property across all possible planes, in fact the smaller the crystal size is the more more well average the properties plus assuming that the crystals are randomly oriented, that is also important.

So, very small crystal size randomly oriented crystals, (No audio from 21:48 to 21:58) very small crystal size and randomly oriented crystals and that depends on how you are made this sample, because you can have a small crystalline crystalline crystal size and still have highly oriented crystals, meaning even though the crystal size is small. Many of them have 1 1 1 direction in one particular direction, many of them. So therefore, that is not thus example we are looking at we are looking at small crystal size and randomly oriented crystals. If we take that combination, if you make a measurement this way, you will get a value, if you make the same measurement this way, you will get and you normalize it for the size of that sample.

So, I am let say conductivity or resistivity not resistance, resistivity if you measure, if you measure it this way or you measure it this way you should be a big difference, because the crystals are all randomly oriented, and there many of them. On this sample, even if it were randomly oriented, since it is a very large, the crystal size is large and only have five crystals from here to here, when you take a measurement this way, the on average there is greater orientation in a particular direction along this way and greater orientation some other direction along this way. And, it just so happens that for many for many materials, when you have such an orientation the property works out to be different.

And that is what we are referring to us anisotropic, which are aware of, so anisotropic is the fact that, if you measure a property in one direction, it will work out to be something different, then the same property measured in another direction. Such a thing is usually very glaringly visible when you look at a single crystal, so in a single crystal since there is only one possible orientation of all the planes of of any given particular plane except may be for the family of planes, a family may have some specific orientation with respect to each other, but in general there is there is orientation is what we are talking of, so that is why it is single crystal.

So it is very likely that a property measured this way is very significantly different from the same property measured different very likely, you just depends on by luck you may you may end up by just by chance you may end up with same family of planes on both direction, in which case it will work out to be the same number, but in general this is not going to be true. If you take any two random direction I just take the same measurement and measure it this way or this way right, any so I have any number of direction in which

I can measure the property. As long as, I can make connection to the sample in that appropriate manner and so on.

So, I have any number of direction in which I can measure this property, and if it is in a typical sample all those direction will give me different values for this for the property, almost all of them will give me different values. This will become a little less likely here, you there is a little greater chance that you may hit upon the same value more than ones, but still there is a is a very good chance that will get different values here, depending on direction in which make the measurement. Certainly when you go down to this, this kind of sample where you have a very small crystal size and all of them are randomly oriented crystals, when you do that in fact your values are work out to be same. So, this is the, this is our understanding of what we mean when we say properties isotropic or anisotropic.

In this sample the properties isotropic, simply because there is a very small crystal size they randomly oriented, so they average out the property across all direction. In this sample the properties anisotropic distingly anisotropic. So, from a from a purely material perspective, if you want to talk of you know, you want understand the property of a material and not just the property of a sample. This is the way of understanding material property. So here, the material in it is fundamental form, which is that single crystal, which has all the all the characteristic of the material or captured here, that you know the orientation what kind of atoms are there, where they are located, how they are located with respect to each other, in what direction are the bonds, in what direction are the other bonds.

All those all that information is well captured in a single crystal, when you go into a sample, which is a ploy crystal, you are sort of muddling of that information, you mixing of that information, because you have many particles pointed in different direction. So, when you look at a single crystal and make a measurement, you get something much more fundamental about that material. The actual behaviour of the original material is captured when you look at a single crystal, when you look at single crystal see of silver, copper any any of those materials, and large number of other materials also. In general, you will find that there is lot of anisotropic in the properties, you measure say electronic conductivity in one direction, you measure it another direction, they could be off by a marginal amount, they could be off by a significant amount.

A classic example of where you know the property could be of in a very significant way is say graphite. So, in graphite you have a layer structure, if you take a single crystal of graphite or well oriented graphite, then you will find that you know, if the planes of graphite are arranged one above the other. Planes it has a planar structure, so you you hexagonally bonded carbon atoms are there in each of those planes and you are and each each such plane is called a graphing sheet. If you take those graphing sheet an organize them exactly one one top of the other and get a well oriented graphite sample. You will find that conductivity perpendicular to those sheets is very poor, conductivity parallel to those sheets is very good.

So, this is the very significant difference is not just factor of 10 percent or 20 percent, it is a very significant difference, you conductivity perpendicular to the sheets could be negligible and conductivity parallel to the sheets to be excellent. So, there are examples real life examples, which we can very easily axis, which can which we can very easily locate and make measurements of graphite is very easily located in any you can easily get a piece of graphite of various quality from various different vendors and this is easily noticed. So, the point we need to, I want to draw a attention to is that real life materials, which we can very easily get our hands on, off and display significant anisotropic, not just marginal anisotropic, but significant anisotropic, why this of significant to as, it is of significant to us.

Because, if we look at even our new model, our improve Drude Sommerfeld model, where we have replace the Maxwell Boltzmann statistics by the Fermi Dirac statistics. If we look at our improved model, we still do not have anything in this model to suggest there be anisotropic as of now as of now, where we have come where we have simply replace the Maxwell Boltzmann statistics by the Drude Sommerfeld I am sorry by the Fermi Dirac statistics, I just this stage nothing has been incorporated in this model, which suggest any anisotropic. So, yes you may get a better value for the specific heat at constant volume or the electronic contribution to specific heat at constant volume, but it still does not explain to you, why conductivity should be better in one direction and should be worst in another direction right.

It does not explain does not even give you a hint, does not give you any possibility any anisotropic. So, this is an issue that we are we are now faced with, so as we just the way we we looked at drawbacks of our first model and we improved it. We now, recognize that in our improved model at in our first step at the improved model, where we just change the statistical distribution, by we have made some progress that alone is not apparently sufficient that alone is not apparently sufficient, there are additional features of material properties, which are not being captured by our Drude model right. So, that is the first thing that we wish to recognize make note of and therefore, act upon, so this is where we are...

So now, what can we do, so what can we do that will enable us to now start introducing some of the, I mean introducing in to our model features, that enable as to captured this anisotropic right. So this is something we have to recognize. Now, where does this anisotropic come from, I mean to some degree, we have to recognize the fact that, the way the ions are arranged through that solid, result in some periodic structure periodic structure which results in planar spacing of a certain kind in different direction and so on. In our model, we have not accounted for this in any way; we have completely ignored it, so in fact we have completely ignore the ionic course.

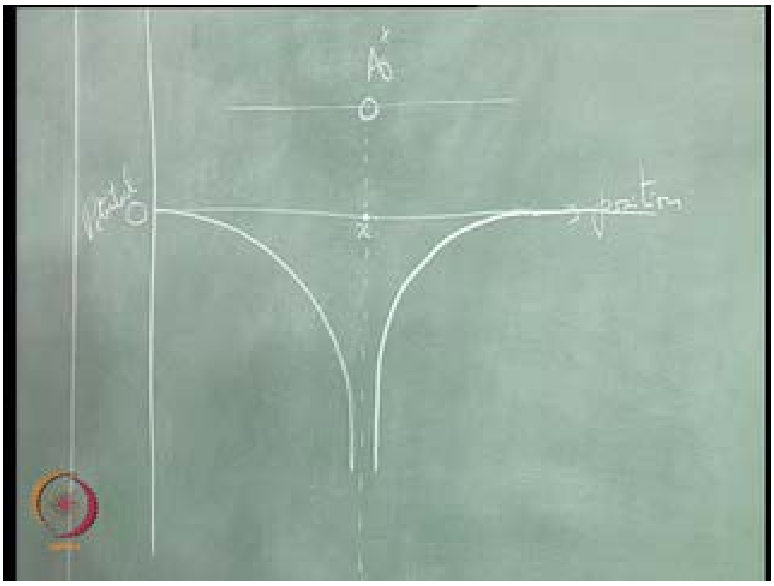
So, and we have in fact said everything is averaged, so that is where in fact we have sort of knowingly or unknowingly enforced isotropic. We have enforced isotropy into our model by saying that it is a free electron model, it is a free electron cloud everything sort of uniform, and therefore the electrons do not experience anything different from location to location. So, without specifically aiming to do so without specifically aiming to do so, without deliberate aiming to do so, we have somehow ended up creating a situation, where fundamentally the environment of the that the electron experience is isotropic, because everything has been average (( )) therefore it is behaviour is isotropic, therefore the material property that we measure is isotropic.

So, fundamentally down in a in a very first step we assumed isotropic, and therefore it is it is not surprising that our result is also isotropic fine, so that is the thing you have to recognize, we have assumed isotropic that is why our result is isotropic. If if we recognize that in fact at the sub I mean at the atomic level or at the crystal structure level things are not isotropic. Then perhaps in our final results that will begin to reflect in the property, and the ability of the property to also remain isotropic or anisotropic right.

So therefore, what we the specific point that we now narrow down to is that, we have to have a better picture for what is the potential that an electronic experiences through the extend of the solid. It is not enough for us to make the approximation that everything is averaged and it is ok to stay averaged. So, we have to recognize that it is not an average potential, there is a from location to location, possibly the electron experience is different potentials. So, we would like to incorporate in to our model, we dependence of potential as a function of position in a crystal. So, potential as experience by an electron, so an electron passing through the crystal.

Now, we have to incorporate in to our model the fact that as an electron passes through the crystal or moves from the one end of crystal to another end of crystal. In it is path, each location is not necessarily exactly the same as other location, every location has some differences in terms of what it is trying to do what is the interaction that the electron is force to have with it is immediate surrounding. So, this detail we have to incorporate in to our model and then see if by in what way, we can incorporate this detail to what degree of detail, we can in corporate this phenomenon. And therefore, what is the impact on the property of the material, so this is what will attempt to do.

(Refer Slide Time: 32:54)



So, now let us take a look at the at a single, let us look at a particular ion, so let us say that this is the this is the location of an ion, physical location of an ion. So, this is I will just say this is Ag plus. Now, independently I will say this is the axis of position, and this is potential, and I am only taking making use of this position of this atom is here fine, are this ions is is there fine, so that is where it is. And so this diagram has not got anything to do the axis, here only interested in this position, so I have this mark that position out here. Now, if you take, so this is 0 potential - 0 potential energy fine. So, this is the positively charged ion and it is located at this position, some position x here.

And we we would like to get a feel for what happens, what is an electron experiencing, as it comes from infinity close to this position. It is starts of at infinity and it moves towards is position, when you do that what is the electron experiencing. Now, when an electron is at infinity on an let us say that we have got enough distance here that we are heared towards infinity this side, when it is at an infinity with respect to at at infinite distance with respect to the position of this ion. It does not experience any force of interaction with this ion that is the definition of this of it being at infinite. So, at as you tend towards infinity, the potential of that electron tends to 0, it is free, it is truly free.

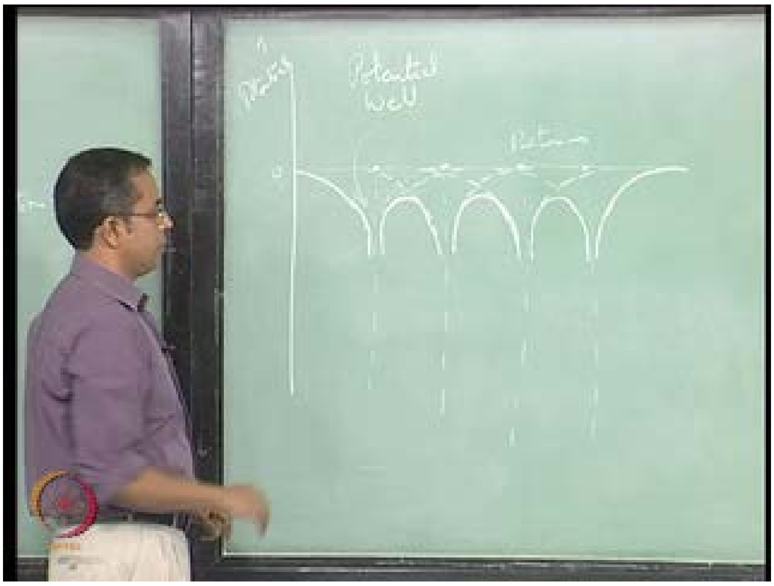
It has when it is free the potential around it 0, it can do whatever it wants it go up, go down any which direction, there is no preference nothing is fully it any direction and it is free to wherever it uses. So, we just use this as guideline for the position, now as it comes closer and closer to this ion, because this is positively charged, and that is negatively charged. The potential energy becomes more and more favourable for them to get closer and closer. So the attraction, forces of attraction are there, and so the potential energy keeps going down fine. So, it becomes more and more attract.

So, in general you see a tendency to, of the behaviour to look like this (No audio from 35:27 to35:35) this this is the potential as a function of position for the electron coming from say minus infinity towards this location x fine. So, this is what is occurring here. Now, if the same thing could hold true from coming from other side, so you started positive infinity and you move towards this ion, then this same thing would occur. You will start of at 0 somewhere at positive infinity, if it stay at 0 and as you get closer and closer to this ion, in a way symmetric manner, it will do this. So, this is the potential as a function of position, that the electron experiences as you come from either minus infinity or plus infinity towards the position of the ionic core.

And this is I am taking a one dimensional case, in principle you can do this three dimensions, I am just taking a one dimensional case because it illustrate our point, that which is all we are interested. So, this is the with respect to a single ionic core, this is what is happening. So when it gets very close to the ionic core it will start experiencing the electronic cloud of that ionic core also, but that something that we will not really worry about at this stage. It is just that there coming, it is coming for of this is potential that experiencing, so this is with respect to a single ionic core.

Now, we will take we will extend this we will make a one dimensional lattice, a one dimensional lattice where ever so periodically you have an ionic core. So, we will do that to see, what is realistic, what is more realistic in terms of what is it that the electronic experiences as it moves from one end of crystal to other end of crystal. So were taking of a path which is which involves series of ionic course, so it is a single line of ionic course and along that line we are moving that electron, we would like to see what is the what is the electron experiencing.

(Refer Slide Time: 37:27)



So, we will see here what it is a experiencing, so I just say we have for simplicity sake I just taken four ionic course let say say that we have four, we start from this is potential, and this represent the position of those ionic course. So, the position of those ionic course so this is potential position right. So, we come from we will just put the guidelines down there,(No audio from 38:06 to 38:12) as we can expect whatever we described for a single ionic core will be true for each of those ionic cores. We will say that, it is a one dimensional lattice that we are interested in and so that our discussion is focussed on a one dimensional lattice.

And for simplicity sake, it has to start somewhere, it it is a finite lattice, so there is only a certain finite number of atoms there; it is not an infinite lattice. So, it is a finite lattice and for our simplicity sake, we have to step to four four ionic cores, so that we can at least see what we, what it is that we are trying to illustrate here. So, around this ionic so around each of those ionic cores, if it take each of this ionic cores independently independently and look at them, then what I just describe will hold true for each of those ionic cores right. So, there is nothing that distinguishes one ionic cores from the other, nothing that distinguishes one electron from other, in terms of behaviour therefore there interaction is going to be exactly the same.

So, for each of this ionic cores, in principle we can draw this same kind of diagram that we have just draw right, except that these ionic cores are within the our our actually inside the material, whereas this is the one that is the outer most limit, and that is the one that is the outer most limit. Therefore, when we actually sum up the contribution, we have there be some changes. So, first we will draw as though they are independent, then we will see what is happening because they are not they are not independently existing, but they are existing next to each other in a crystal. So, if they are independent then we see this behaviour, I will just put it as dotted line initially (No audio from 39:36 to 39:47) and this occurs as we go towards plus infinity, so it is I I mean we need not I do not want mislead you here, so we just say that that goes that way.

Similarly, for this ion you will see behaviour that would like this (No audio from 40:05 to 40:12) for the next ion to see a behaviour that would like that (No audio from 40:17 to 40:36) So we now, see that for each ionic core, we can think of it as a potential well, which is called a potential well. So, it goes at as the electron is at for away from this first ionic core, there is no, it is not experiencing any potential, so it is free, so the potential is 0. So potential is 0 here, as it gets closer and closer to this ionic core, it experiences of potential well, where it is potential energy decreases very sharply as you gets closer and closer to this ionic core.

So, independently again as you move away you see the behaviour following this curve, for this ionic core these are the two curves of relevance, for the third ionic core these are the two curves are relevance, and for the last ionic core these are two curves of relevance, but behaviour essentially exactly the same. So, for independently for this four ionic cores we have seen, what are the, what is the behaviour that the electron, what is the potential that the electron will experience. Now, we recognize the fact we additionally have to incorporate the fact, that these are not independent ionic cores, but they are sitting at fixed position with respect to each other.

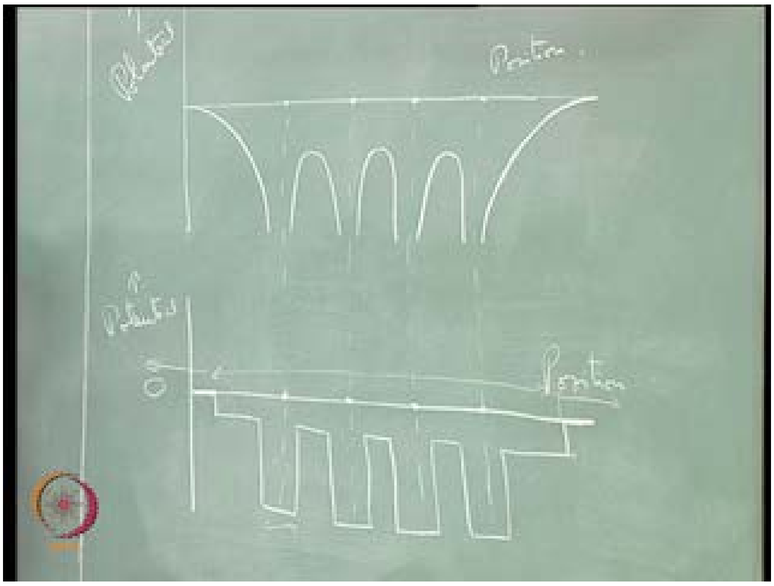
And and they are in a in a crystal together right. So therefore, an electron that comes here will experience is potential well coming from infinity, because there this is the first ionic core that it is experiencing right. Now, as it starts moving away from this ionic core up to this point it is potential energy keeps increasing, but beyond this point. It is actually beginning to see the potential well of the next ionic core right. So, therefore it is will now instead of just going of plus infinity it will actually have to sorry instead of going off to 0 as it move as you move away from this ionic core. We have to account for the fact that as you move away for this ionic core, you are actually getting closer to this ionic core right.

So therefore, the potential of this ionic core will take over, then you will come out of the potential well of this ionic core, and you will enter the potential well of the third ionic core, the electron will enter the potential well of third ionic core. Again it will come out of the potential well of third ionic core, enter the potential well of the fourth ionic core, and then after the fourth ionic core as you move away there is no no further ionic cores this side, potential can go back to 0 fine. As you move further and further away towards infinity, so it can go back to 0. So therefore, the resultant behaviour that you see is what I will draw with this, with the with now the complete line (No audio from 42:51 to 43:03) with solid line (No audio from 43:04 to 43:18)

So an electron now traversing through this one dimensional crystalline solid, which has ionic cores at these specific location, actually experiences potential verses function that look something like this. It is 0 when you are for away at infinity with respect to this entire one dimensional crystal, then you it experiences the first potential well, when it when you come close to the this structure is called a potential well. Because, it is a well because it is deed, and it is it is it is a well of potential energy that is what it is, so that is why it is called a potential well.

So, potential well (No audio from 43:49 to 43:55) exist in this region, so that is the potential well so that is the potential each of them is a potential well. So, potential goes towards I mean sharply drops as you come close to the ionic core, again goes up as you move away then falls into the second ionic core, comes out goes in to the third ionic core falls in to the third fifth potential well I am sorry fourth potential well, and then comes out. So, this is potential verses position.

(Refer Slide Time: 44:24)



We will we will just redraw it for sake of clarity, (No audio from 44:24 to 44:36) potential or energy it is, so it is basically the same potential or energy and this is position. So, we have if you only plot the solid line and not worry about the (( )) this suggest for guideline for our plot. So, we have behaviour that looks like this, (No audio from 44:55 to 45:10) So this is the potential verses function I am sorry potential verses position for the system that we are looking at fine. So, now therefore for our analysis to become more complete for our analysis to become more complete, for our model to become more complete.

We have to accommodate for the fact that the as the electron moves through the solid, it is not actually seeing an averaged response from the entire crystal all the time. The other it there are there is there is a specific feature to the whole potential energy verses position that it is experiencing therefore, it is as it moves through the through the crystal. It is force to interact with this phenomenon, with this background, the extend of interaction may vary. So, but it this this background is a reality this background is a reality, that it cannot completely ignore depending on where it is, it may be more significantly affected by this background or less significantly affected by the background. So, that is the extend of it is impact on the electron can change and the, we will look at that, but we what we are recognizing at this stage is that into the model.

We have to build enough sophistication in to the model, enough detail in to the model, that this information is getting incorporated in to the model, so that is the think we have to do. Now, having said that the feature that we see here, if we wish to put it all down in equation and so on, it can get a little bit complicated in terms of this exact level of all the features even though I have drawn this ionic cores independently, the second, the third, the fourth will also ionic cores will also impact the exact form in which this this curve changes. This curve moves or the shape of this curve is not going to be impacted only by the outer most ionic cores, it will have some contributing factor from all the other ionic cores and so on, plus the fact that this is a surface.

So, the exact shape of each of this lines is something that needs a lot of calculations, before you can actually say that this is the exact shape of that curve. So, it terms out that our purposes in fact that level of detail is not immediately necessary, so in our in moving forward for with this models by we will incorporate the basic idea that this figure is conveying to us. It it it is not immediately necessary for us to incorporated in exactly the form that we are seeing on the board, so we will approximate this form, we will make an approximation of this form such that, that approximation something that we can work with, that we can make calculations with and we...

So that, this form is actually being incorporated, and therefore, the model is definitely getting more realistic, because it is now looking more and more like the real material. At the same time, it is not so complicated that it makes the calculations impossible, it makes the calculations reasonable, it makes the calculations possible is the kind of approximation that we need to make. So, what we will do is, instead of a having all these curves lines that that we see here, we will convert them to some some sort of straight lines, which still captures the basic idea of this picture of this picture. So, I will just draw that picture then we will explain it, so we will will look at the explanation of it.

So, same think we will look at, I will assume the same crystal I mean sorry lattice position here. So, in terms of lattice position I am not going to change anything, I am going to leaving it, as it is. So, that senses the reality of the actual material is captured, nothing else I am changing there, this is 0 in potential energy and this is position, so all of that is still the same, what we will say is that at infinity it is the potential experience by the electron is 0. So, I will just stick to this x axis here, then I will I will say that there is a slight potential well here. (No audio from 49:08 to 49:40)

So, this picture here, is now being approximated by this picture here, where we are saying, where what are the features that we are capturing. We will just look at what are the features of this picture that we are capturing here and what is the approximation that we are actually making. The features that we are capturing here are that as the electron is for away from this set of ionic cores, so the ionic cores are here, as the electron is for away from the set of ionic cores, the potential it experiences 0, and therefore that is 0 here. At some point as it approaches this ionic cores the... it the potential that it is experience from experiencing from those ionic cores starts becoming significant.

So, at that point there is a drop in potential of this electron, potential energy associated with electron as it comes towards towards the material. Then as it gets closer and closer to an ionic cores thus a very significant drop corresponding to this drop here, which represents the potential well, that is very close to the ionic core. Then again in between the ionic cores there is raise in potential energy and then again drop in to next potential well, raise in potential energy drop in to third potential well, raise in potential energy drop in to the fourth potential well. And then as you move away since there are only four ionic cores in our example, as you move away from the last ionic core, eventually reach a state where we impact of this ionic cores on the on that electron that way looking at becomes negligible, and can effectively be treated as 0. So, we have taken the electron away from this material, for away for away enough that it no longer interact with this ionic the system of this collection of ionic cores. In terms, so in that sense we are capturing all the detail of this picture here, this is the more real picture from this real picture.

We have made this approximation; much of the interaction that is present that is shown in this picture has been captured in this approximation. The neither the only real difference that we have done is, these are all curved (( )) as a curved lines so to speak, so curves that have here. We have approximated them by straight lines, so so so so these are sort these are also referred to since a straight lines and a parallel lines we call them square potential well, so to speak more squarely shaped potential well, there is not exactly more rectangular I just, but the the fact is that these are potential wells that are based on straight lines that are parallel. So, the width of this potential wells is fixed whereas, the width of this potential well is actually getting is changing with position marginally.

So this, we just have a narrow deep potential well of of a certain fixed width and that is what we do in in all of this potential well. So, so there is in terms of the exact form of the potential well we have made an approximation, but we have captured the idea that there is a potential well, that it is centred along around this ionic cores and then and then there is a feature to this whole process that you come from infinity, you there is a drop in potential as you get close to the material, and there is a definite potential wells around each on every single ionic core. So, very important pieces of details corresponding to this real picture have been captured in the approximate picture, and we have made some simplifications in terms of the exact shape of the well, that simplification will enable as to make the calculations much more effectively, so that is why we have made those simplifications, and of course it is left for us to judge later based on our results, whether or not that simplifications was acceptable.

At the moment, we are made this simplifications, if the results indicate that our simplifications was reasonable great that means this is a very good way of approximating the solid. If for some reason, it shows that I know our approximation gives very wild answers, then we will have to re examine, I mean I might as just tell you affront this is the pretty reasonable approximation, this is considered pretty reasonable approximation. So therefore, we can use this, also in the contacts of this picture I also want to point out that you know, when you say, when the potential is 0 that is the same as saying that the electron has escape the material, so it has escape the material, so when you do, you know, say when you see photoelectric effect, when you when you say an electron has been ejected from the material.

Then you have actually got potential being equal to 0, that that electron has truly escape the material. So, being in this region or being in this region means that the electron has escape from the material, so that is a truly free electron. So, when we mentioned when so for we have use that term free electron and free electron cloud strictly speaking, you cannot call them free electrons because they still within that solid. So therefore, they are they are not strictly truly free electrons, a truly free electrons is one that as escape from this solid, which which which means the potential it experiences would be 0, then there are electrons which fall within this potential, this slightly shallow potential well above this level.

They are electrons, which are track within the solid, but or not held by any particular ionic core, in fact what we were referring to as a free electron gas previously or in fact these electron which are trap within this material, because obviously they are not running out of the material, the trap within that material, but they are not struck to any one ionic core, they are free to run across the extend of the solid. So therefore, these are electrons that we would actually call as nearly free electrons, they are not truly free because they are not escape from the solid, but they are relatively free because they can run through the solid. So, those are nearly free electrons right.

And finally, there are electrons which are struck to the ionic core, those are the electrons which belong to part of that ionic core. So, those are referred to as bound electron, they are the electrons that that are part of the ionic core, they are all the other electrons which are struck to that Ag plus ion, so to speak. So, those are the bound electrons, so electrons that are in this regime or bound electrons, electrons which are here or nearly free electrons and electrons which are pass this point at truly free electrons. So, so this is the picture, in the next class we will start once again from this picture and we will look at some of the neurons of this picture and we will relate whatever else we have discussed so for with and see what it means with respect to this picture.

And then see how we can utilize this picture, we will see what does say Fermi energy mean with respect to this picture, what does work function mean with respect to this picture and so on. And then utilize that and that way relate whatever else we would discussed so for with this picture, and from there on we will take it forward, and utilize the features of this picture to modify and improve our models of the materials, and therefore our understanding of the material and how it behave. So, with that we will halt for today, we will take it up in the next class thank you.