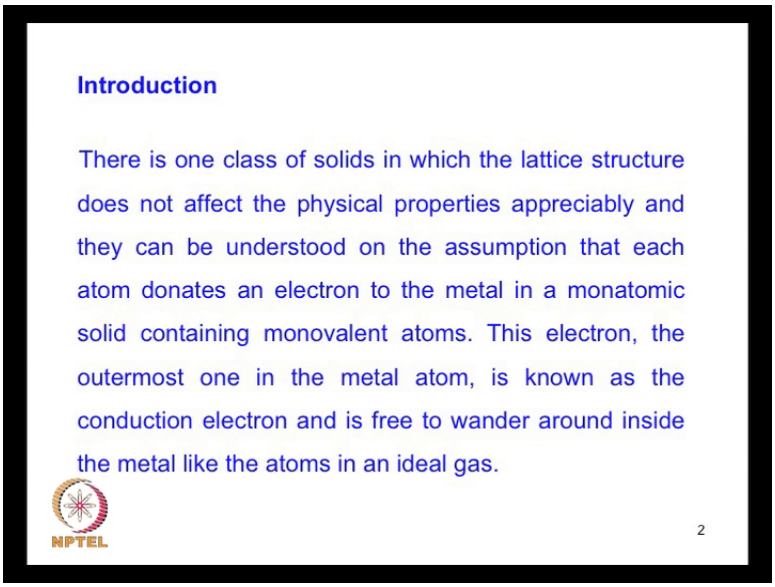
Condensed Matter Physics
Prof .G. Rangarajan
Department of physics
Indian Institute of Technology, Madras

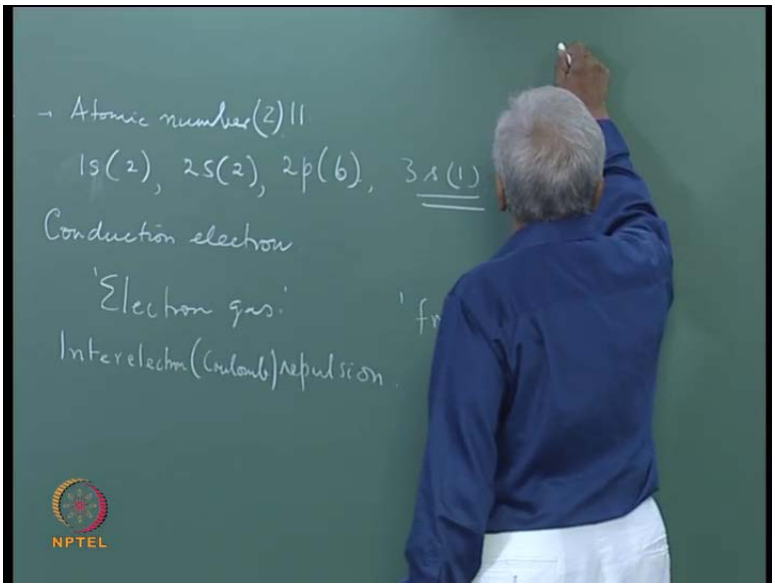
Lecture - 9
The Free Electron Theory of Metals

(Refer Slide Time: 00:32)



We saw in the last session how the physical properties of solids depend rather strongly on this symmetric properties; however there is 1 class of solids in which the details in the lattice structure does not play a very big role on the physical properties, these are metals such as gold silver copper and so on. This metals their behavior can be understood on the assumption that each atom donates in the case of mono valid metal one-electron to the metal, and this electron is usually the outermost 1 in the metal atom.

(Refer Slide Time: 01:37)



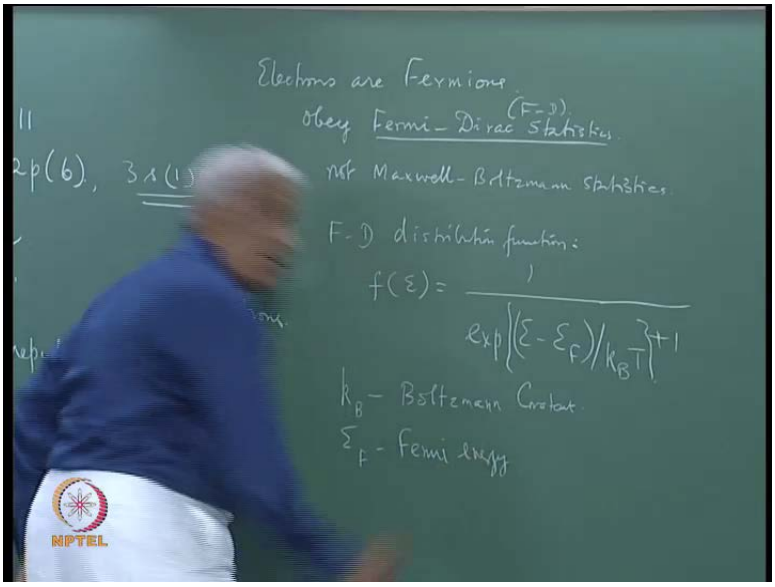
For example, in the case of sodium which has an atomic number atomic number is the number of electrons of leaven z is the usual symbol. There are leaven electrons in the sodium atom of which 10 of them go into this so-called 1 s 2 electrons go into 1 s shell and then 2 electrons go into the 2 s shell and then six electrons go into the 2 p sell. So, this is the so-called close shell structure out of these leaven.

Electrons ten of them go into the close shells leaving only one-electron in the outermost three s shell. So, this the electron which is the outermost in the metal atom this is just an example similarly 1 can look at any metal atom and then analysis the outermost electron is available for conduction, because it is rather weekly bound to the parent atom and therefore, can be ionized rather readily. And this becomes this outermost electron is known as the conduction electron because this gets ionized and this electron becomes available and is free to wander around inside the metal. So, it is the very much like the atoms and molecules in an ideal guess.

So, one speaks of an electron gas in this case. So, this means that even though the metal is the conduction this system a condensed matter a solid, but the electrons inside are behaving very much like the atoms. And molecules in an ideal gas be one made ask what happens to the coulomb repulsion between the 2 electrons pars of electronics this intel electron repulsion is rather week in comparison to the attraction between the electrons and the positive ions which are left behind after the ionization. So, 1 has 1 neglects the

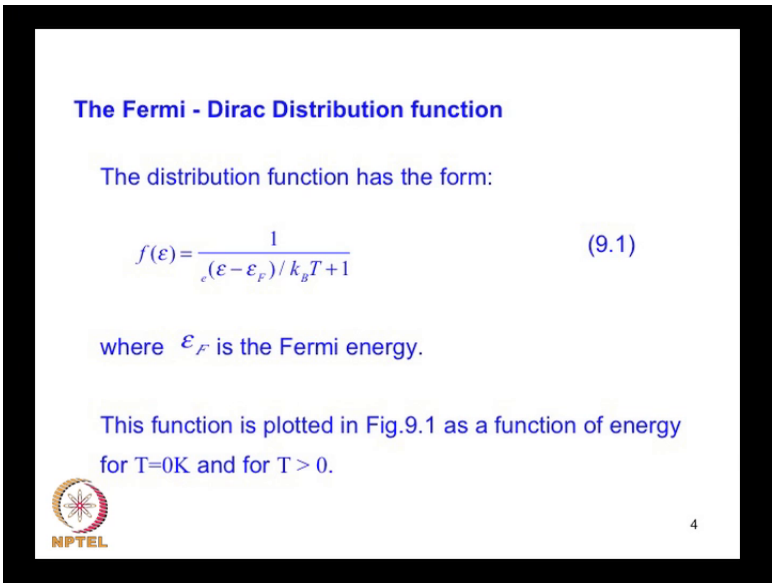
first approximation inter electron are coulomb repulsion. If overlooked ignore to start with. So, that one can think of free electrons which are not strongly interacting free electron for free in the sense that the free-for conduction to carry electricity insight, that is why metals are such good conductors of electricity only thing is these electrons the ideal gas molecules are atoms are classical particles.

(Refer Slide Time: 05:32)



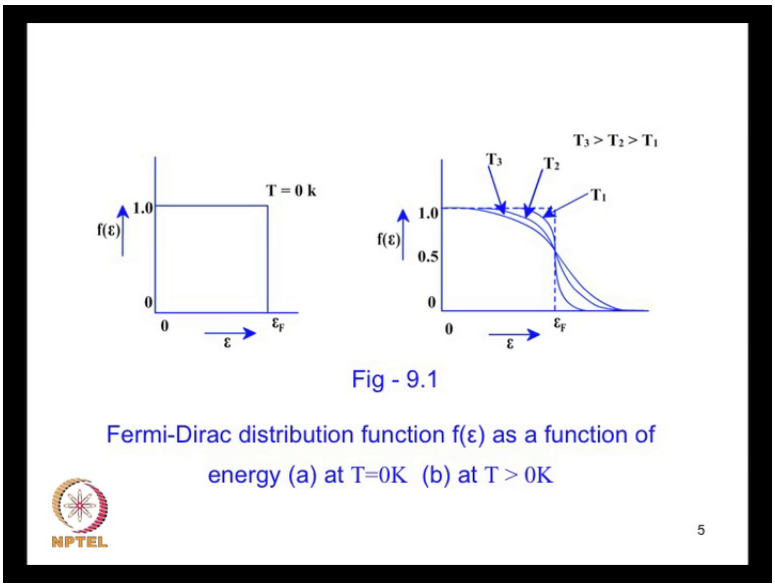
Whereas electrons are quantum particles which obey electrons are known as fermions fermions means they obey so-called for me the dirac statistics rather than not Maxwell Boltzmann statistics. So, there collective behavior is not describe by classical Maxwell Boltzmann the statistics which are which is obey it by ideal gas molecules and atoms, but in then we discuss the properties of this electron gas we have to take count of the fact that they obey fermi dirac statistics. So, we have to use fermi dirac statistics in order to describe.

(Refer Slide Time: 06:39)



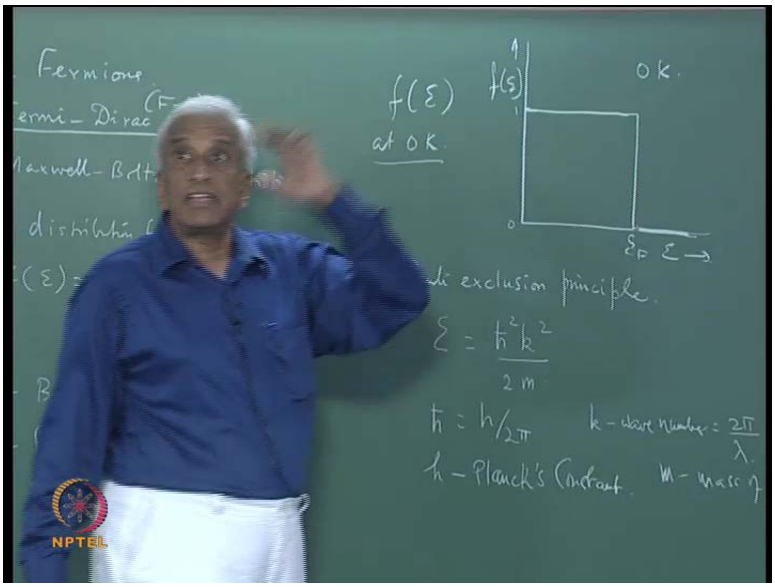
They are collective behavior this is are other important factor up the fermi direct distribution function I will write it as a f t for short the fermi direct distribution function as the following firm f of e that is the distribution function which describes how the electrons are distributed into the various energy states. So, this system of electrons has different energy levels the electron energies are different. And therefore, the electrons occupy these energies and the way we are distributed energy is given by this function 1 by a exponential e by the e f by kb t plus 1, where kb is the Boltzmann constant and the e f is known as the fermi energy k b is the universal constant as you know. And the fermi energy is a characteristic of the metal now everything will depend the collective behavior will depend on the statistical distribution how the electrons are distributed an energy.

(Refer Slide Time: 08:55)



Therefore let us look at how this function looks, this function is plotted in this figure.

(Refer Slide Time: 09:11)

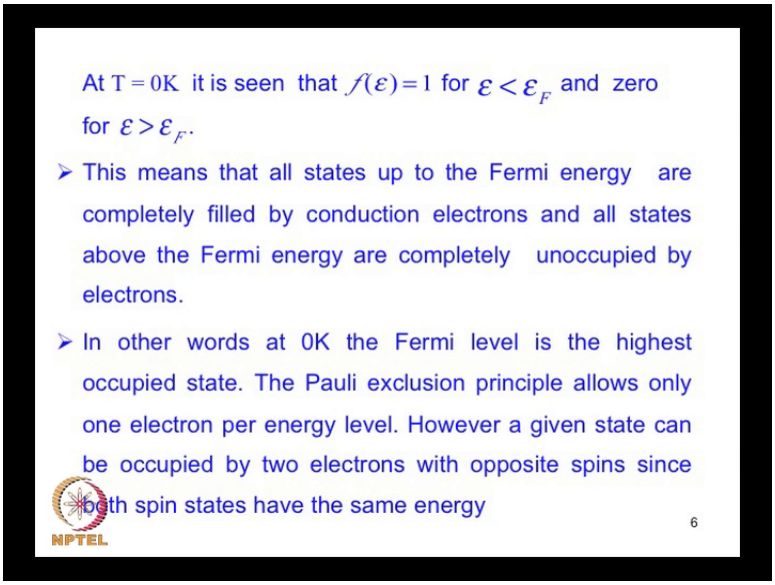


Let us look at the figure on the left side, which gives the value this function plotted at absolute 0 lets discussed the behavior of the metal at absolute 0 and then we can go to finite temperatures this simpler. So, you can see that this function looks like this. So, if I as the fermi energy here than this is 0 this is one. So, that is the behavior of this function at absolute 0. So, this is at 0 k what is this there the physical meaning of this picture is that if you look at all state's all energies which are less than the fermi energy. If you look

to the left that this ef in the graph on the energy access all this states are occupy with a probability of unity. In the sense that this mean that they are fully occupied the states are all completely occupied by the electrons none of the state's is empty all the states below e f are all occupy by electrons this. Whereas all the state above ef the fermi energy are completely empty they have 0 probability the f of e is 0.

So, the probability of occupation of the state about the fermi energy at absolute 0 is 0 that mean that they are completely an occupy. This is because the electron obey what is known as Pauli is crucial principle that is way they are fermions this means that it if 1 state are 1 energy level is occupied by an electron then another electron cannot be found in the same state it is excluded from occupying the same state. So, each state is occupied by an electron, and you have all the states below e f occupy well this picture is slightly modified at finite temperature, but we will come to that a little latter the it is this is enough for as…

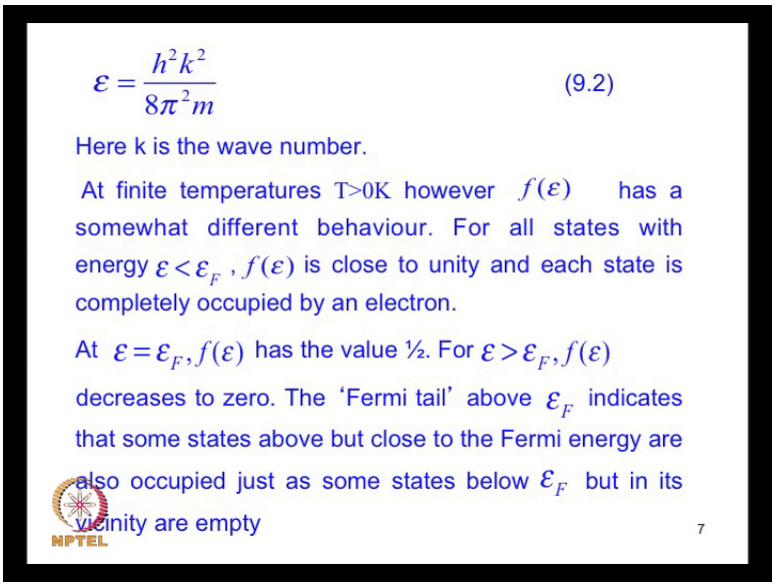
(Refer Slide Time: 12:06)



Now, So, if this is. So, at 0 kelvin the fermi level e f is the highest occupied state now of course, then I say that each state is occupied by one-electron according to the Pauli principle what I mean is that we do not consider this spin of electron if you consider the spin of the electron. Then we know that electron can have has a spin of half and. So, can occupied 2 states with parlor or anti parallel spin beer given direction in space therefore, these 2 electrons with opposite spins both have the same energy. And so each of the

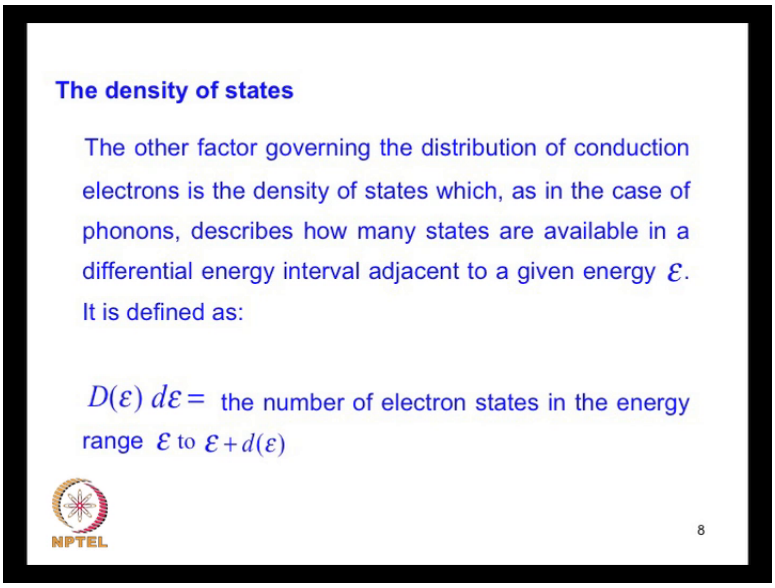
states can be occupied by through electrons with opposite spins without violating only principle.

(Refer Slide Time: 13:10)



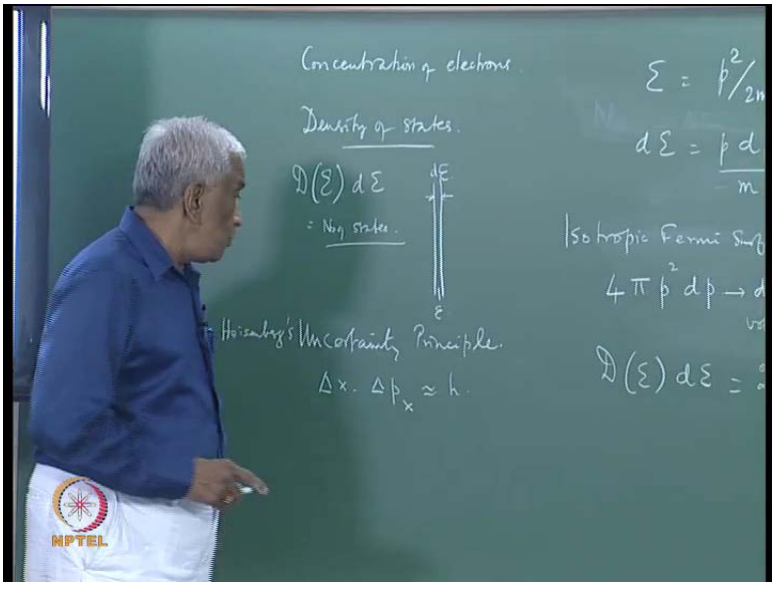
You will remember this, but this spatial energy of these electron is simply given by the kinetic energy, which is h cross square k square by 2 m there h cross is h by 2 pi h is the planck's k is the wave number which is equal to 2 pi by lambda we already talked about lambda broglie wavelength. And m is the mass the electron. So, the energies of the electron in the state is given by the wave vector k, and this is just the kinetic energy h cross square k square by 2 m.

(Refer Slide Time: 14:29)



Now, if we why do we need this we need this information united calculatefor example, the number of electrons conduction electrons inside a metal the metal is now somewhat like a box with in which this electron gases free to wonder around, but the electron is not a allow to escape out of the better. So, that is a the only constraint on the electrons. So, within the metal they are free to wander around very much like the atoms and molecules of a gas.

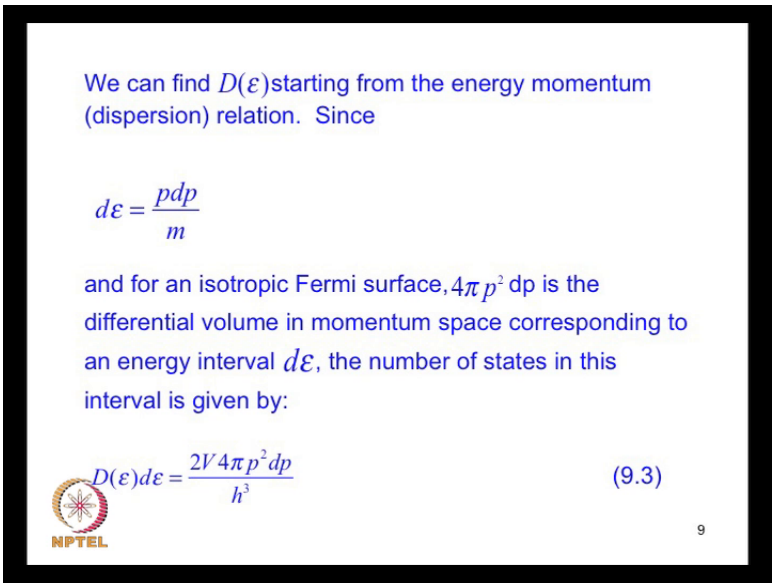
(Refer Slide Time: 15:18)



So, next we should to calculate the concentration of electrons which is the number of electrons for unit volume can I say electron I only mean the conduction electrons in order to find this t we have to also consider in addition to the distribution function. We have to consider what is known as the density of states this is because the distribution function tells us how the electrons are distributed in the energy, but as you can see from this equalization connecting the energy and the wave vector are the wave number it is the wave number which decides that the electrons state.

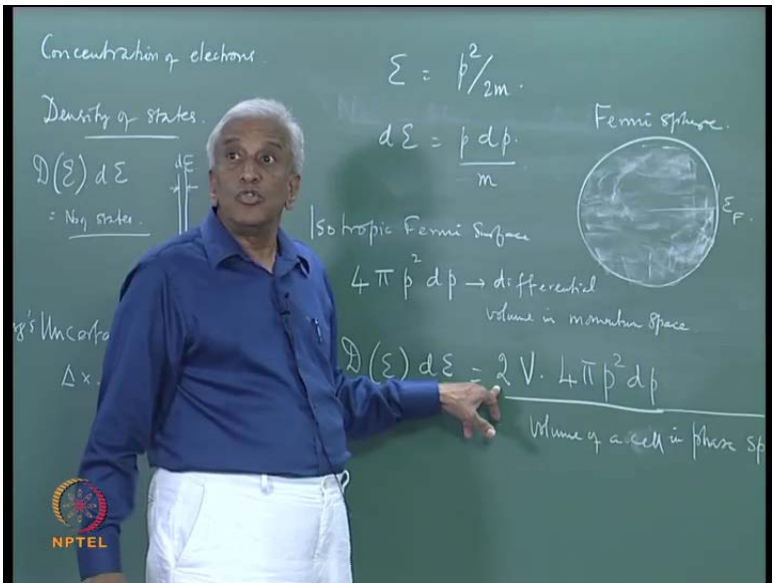
So, we want to also know how the hold me a conduction electrons are distributed indifferent states corresponding to a given energy. So, this is given by what is known as the density of states. So, it tells us how many states are available in a differentia energy interval agents to a given energy. So, if I look at a particular energy. So, I would loot look at an infinite this month d e around a given energy. So, if I take this infinity dismal energy interval we d f e is the density of a state function which described the d f e d e gives the the number of steps in this energy interval.

(Refer Slide Time: 17:18)



So, we wish to find out this density of states together the distribution function ff e and the density of the state function d f e d e together will determine the average this statistical properties are this electron gas how do you find this density of states function we will just discuss this next.

(Refer Slide Time: 17:43)



So, we have we know that the energy is just p-square by 2 m because the electron have only kinetic energy. So, d e is p d p by m now if I look at the momentum space and if I regard the fermi energy as corresponding to a value which corresponds to an isotropic fermi surface which means it is fermi surface. So, it is the spear with radios e f in energy space. So, that is the fermi spear and all the inside state inside this or occupy by electron gas. So, we know that radios the volume of this will differential volume is four pi p square d p.

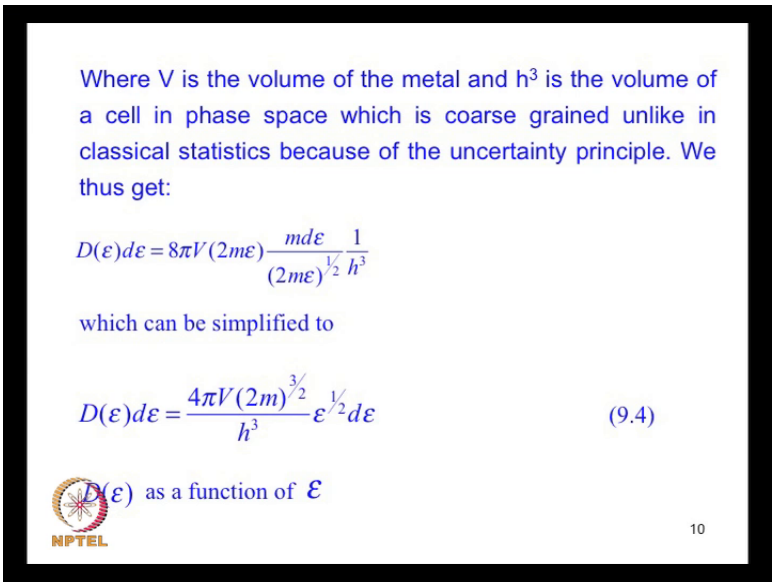
This is the differential volume in momentum space position and momentum together define a state in statically physics. So, this is the differential volume in momentum space if we take the number. Now, we count the number or state in this interval by writing d f e d e e equals v the actual volume in real physical space the position space multiplied by the differential volume in momentum space times 2 the factor 2. In order to take it account this spin and divide this by the volume of f s cell in phase space sell means state each cell each of the cell correspond to 1 state of the electron as we discussed already according to the pauli principle.

Now, this volume of a cell in phase space is given by the so-called uncertainty principle in quantum mechanics as I already told you the electrons are quantum particles. So, we have discussed as statistical behavior according to the quantum statistics and fermi dirac statistics is a quantum statistics. Now the main feature of quantum behavior comes from

the so-called uncertainty principle due to Haisonbag this principle states that the product in uncertainties of position. And momentum is of the order of the planks constant and therefore, this is in 1 by mention therefore, we can write the volume of a cell in phase space as the product of the uncertainty you cannot look it a particle beyond this accuracy in quantum mechanics. So, this is the minimum uncertainties.

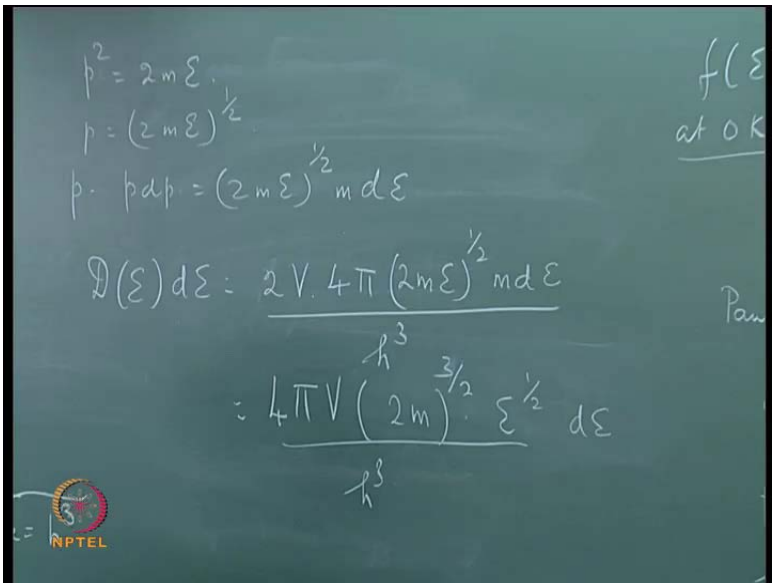
So, this is the spatial and momentum, extent the extension in space and a real space and momentum is given is order of the planks constant. So, if we use the same argument for all the three dimensions and in real space and all the three components of linear momentum then they get this volume is h cube this is h for each dimensions. So, there are three dimensional. So, each time it is multiplied. So, get h cube and that is the uncertainty to which you can locate a given state in phase space in quantum mechanics therefore, that corresponds. So, this space the phase space is quantum mechanics is course grain and this is the volume occupied by a a state in phase space. So, you derive the total volume available physical volume v times the differential volume in momentum space times the factor 2 due to spins state and divide the whole thing by h cube.

(Refer Slide Time: 23:10)



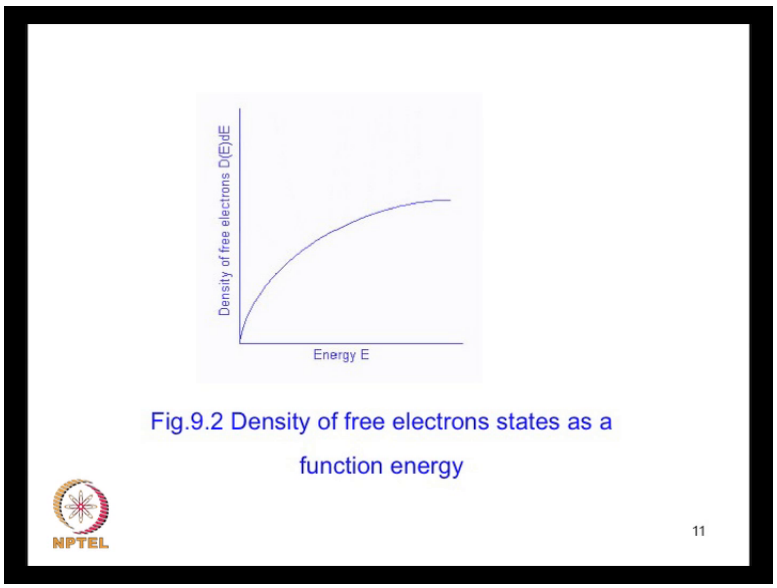
That will give the number are state which is intern to the given by d f e d e. So, this gives as the way to calculate density of state function therefore, we just substitute p square is just 2 m e.

(Refer Slide Time: 23:27)



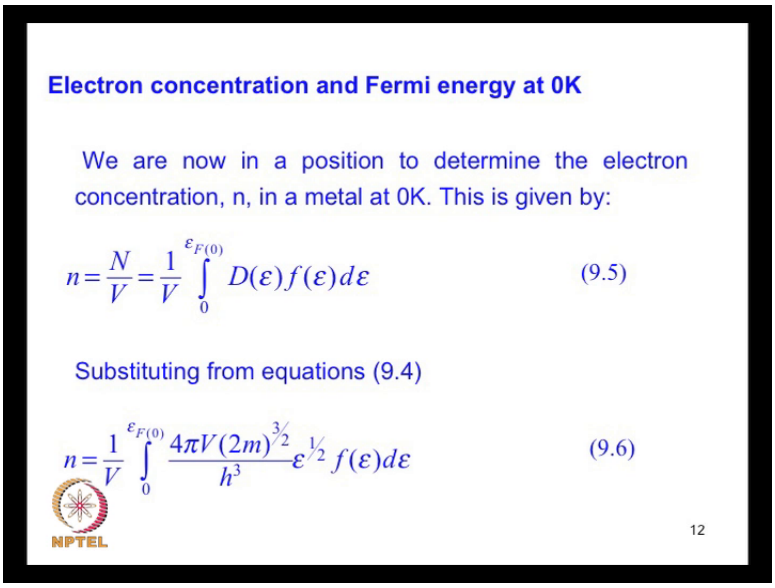
So, 4 pi. So, p is 2 m e to the power half. So, here I have p square d p which I can write as p times p d p p d p already I have as m d e. So, 2 m e to the power half times m p e therefore, substituting here d f e d e 2 v into four pi into p square d p which is here to m e to the power half into m d e pi h cube. So, this some simplification gives you the density of space function as four pi v.

(Refer Slide Time: 24:36)



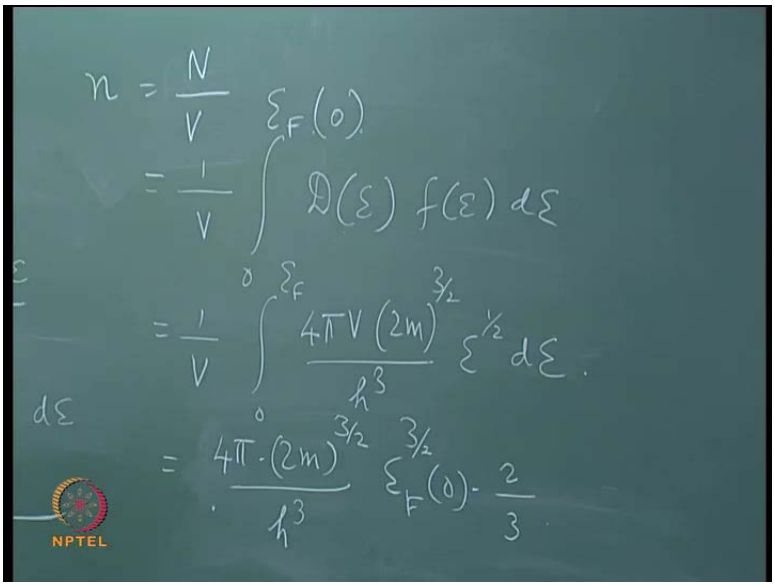
So, you can see that this is the density of state function which is plotted these together. So, you can see the density of state goes as e power half.

(Refer Slide Time: 24:48)



Now, we have a all the we have developed all the things that we need 2 evaluate the electron concentration at 0-kelvin let us do this now.

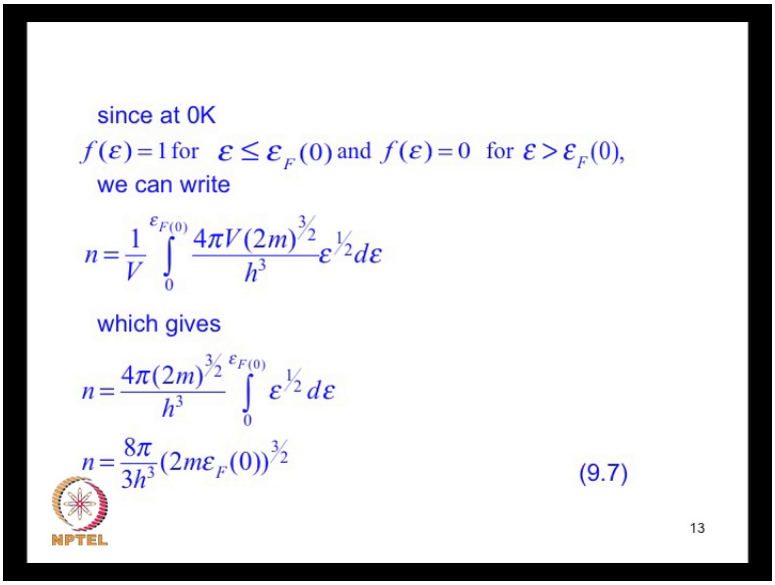
(Refer Slide Time: 25:10)



So, the number of electrons in unit volume is the total number divided by volume and that will be the total is what is given by this. So, I have 1 by integral of e f of e d e comes 0 to e f this is because of ff e gives you how the electrons are distributed in energy. And d f e gives you use you how the energies are distributed at in states and therefore, the product of these 2 integrated over an energy interval from 0 to fermi energy up to the all

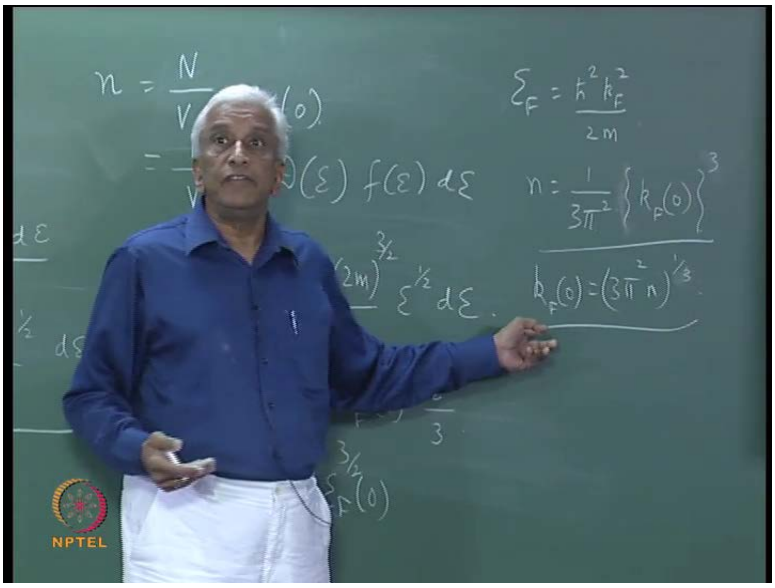
states are completely occupied rest of them are completely empty. So, it is enough if I integrated over all the energies from 0 to e f let me write e f at 0 in order to remind ourselves of the fact, that we have calculating it at 0 kelvin. So, if I substituted the this 1 by b 0 to e f, then I have this four pi v into 2 m to the power three by 2 by h cube e power half d e and I have removed f of e because this is going to be 1 for all the states. So, it is going to have a value 1 at absolute 0.

(Refer Slide Time: 26:45)



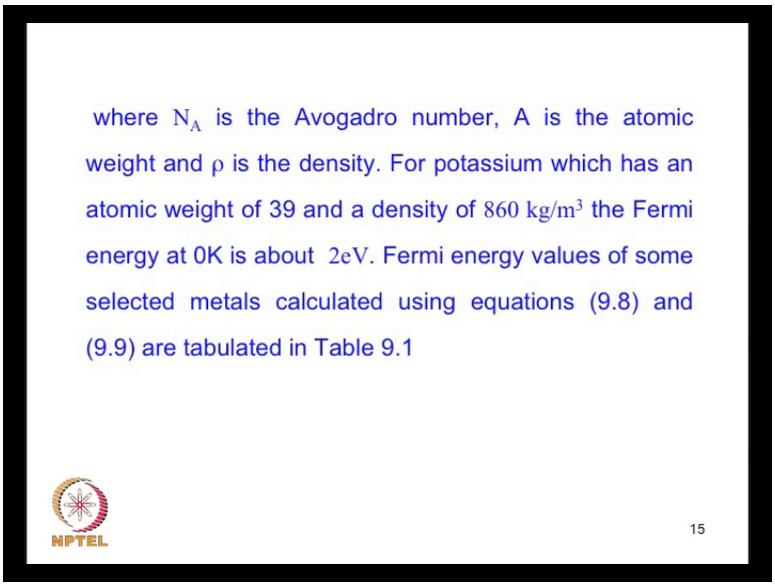
So, we can write all these constants can be back out v cancels for 4 pi 2 m to the power 3 by 2 by h cube e f 0 to the power 3 by 2 into 2 by 3 as a result of integration.

(Refer Slide Time: 27:30)



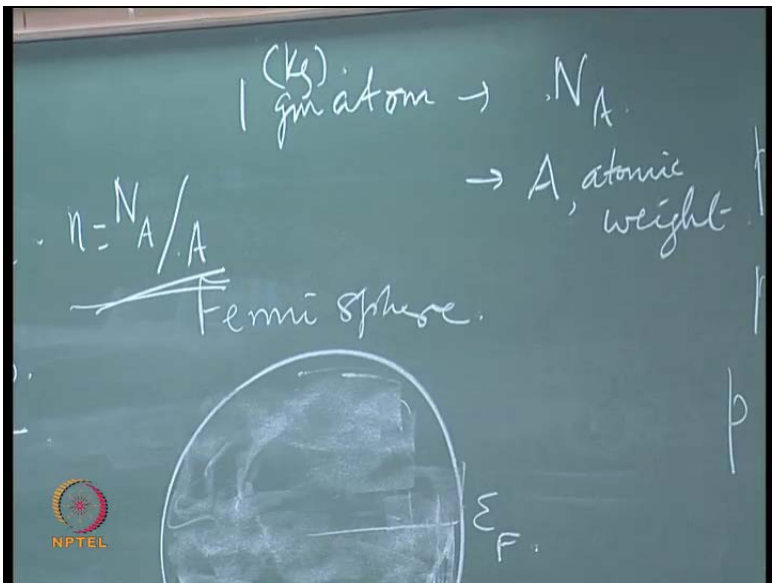
So, that gives me final result as using this and using ef as we already saw e f is nothing, but the kinetic energy up to the wave vector at fermi energy h cross square k f square by 2 m therefore, we get n s. So, that gives you rather compact relationship between the fermi wave vector at absolute 0 and the electron concentration n now me assume that because for example, in a metal like sodium each atom donates 1 electron to the conduction band. So, if we have a moral a gram atom of this solid then this will contain as is well known and number of atoms. So, that correspond to the number of electrons donate at a conduction electron and do not donated.

(Refer Slide Time: 28:37)



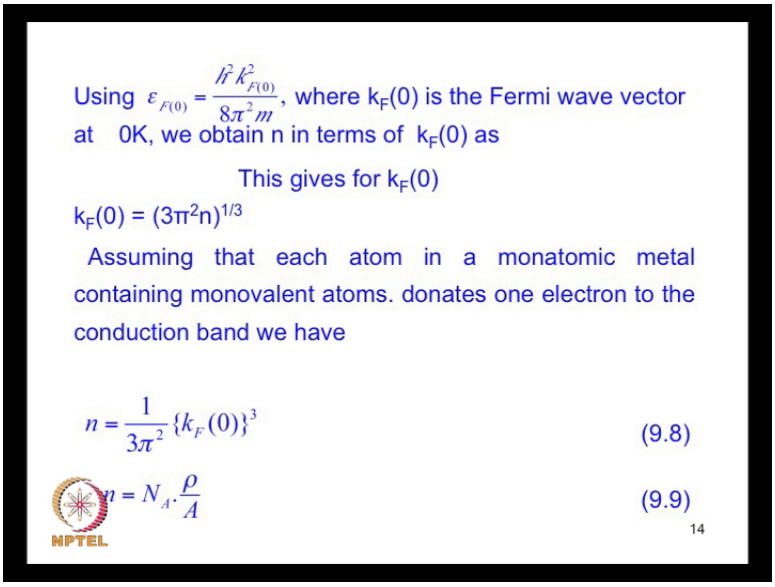
So, if you take number and divide by the atomic wait.

(Refer Slide Time: 28:51)



So, that gives me in 1 gram atom are kilogram atom correspond to n a number of atoms and I have each atom gives you 1 electron in a monatomic solid. So, this is the number of electrons. So, this correspond to your weight of a where this is atomic weight therefore, the number of electron is just in 1 mole is n a by a times.

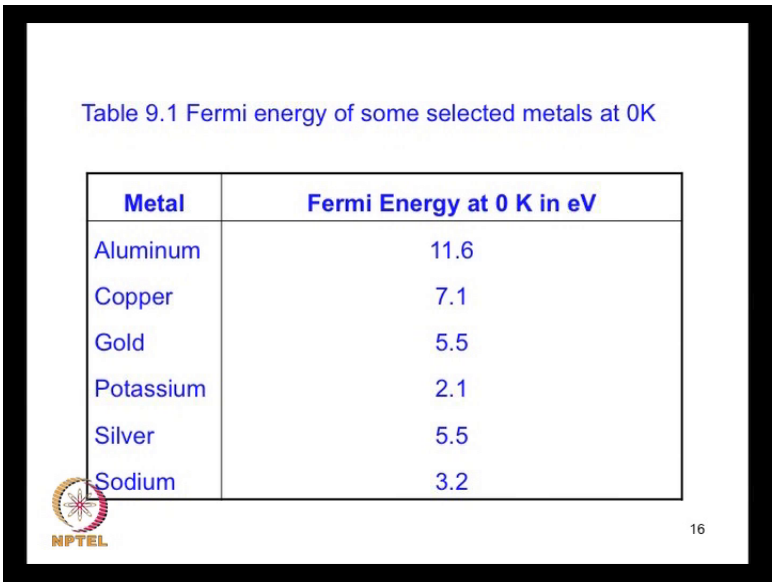
(Refer Slide Time: 29:35)



They have to we are forgetting the fact that we have also row because it this gives you the number half electrons per unit mass, and then we have to multiply this by the density.

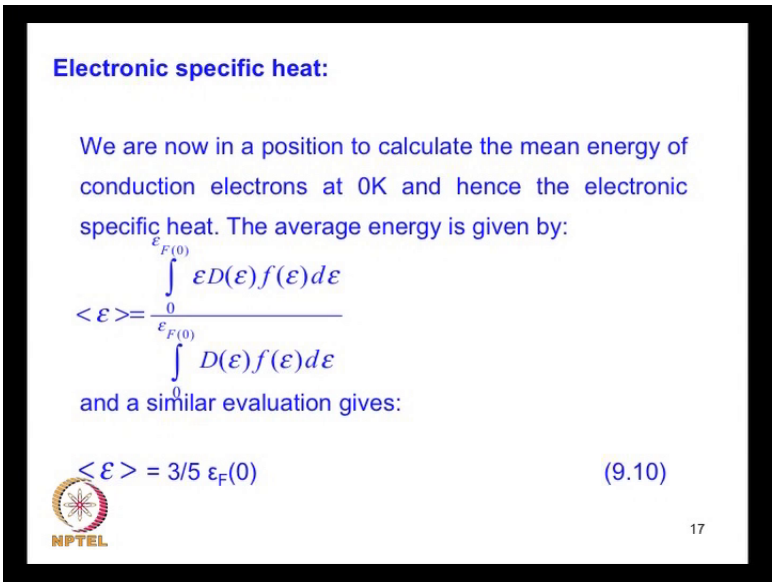
So, we can calculate n and therefore, calculate the fermi wave vector and inurn the fermi energy. So, we have way of calculating the fermi energy from this formula.

(Refer Slide Time: 30:09)



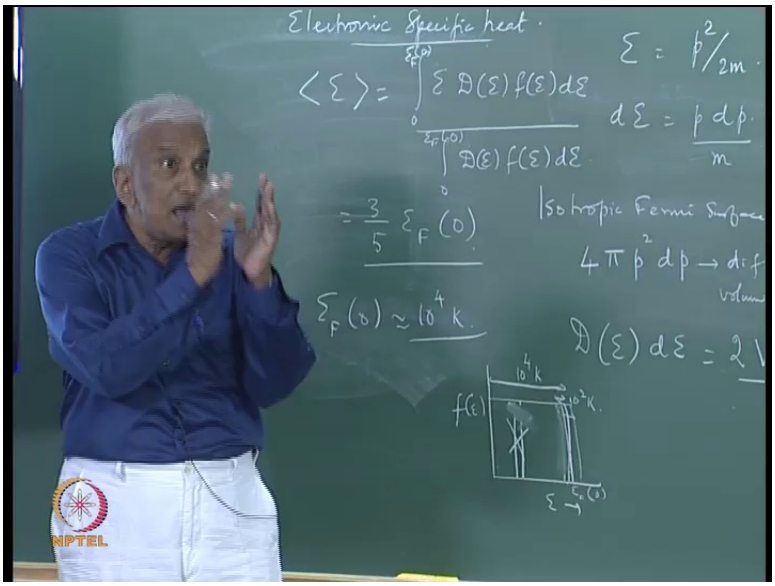
So, the fermi energy values calculated in this way are also shown in the table. So, the fermi energy at 0 kelvin the values are given in an electron volt which is a convenient unit in a the case of atomic physics. This gives you the energy of an electron when is accelerated through a potential of 1 volte, now the various metals aluminum copper gold potassium silver sodium.

(Refer Slide Time: 30:48)



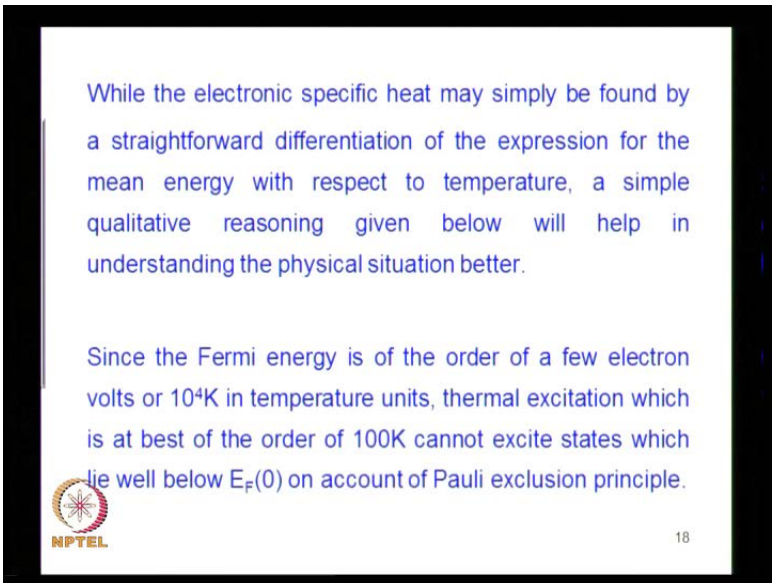
You can see the fermi energy the various from something like eleven points six electron volts to the three-point to electron volts in any case all of the order of electron volts. So, this is a very important idea because if you converted by using Boltzmann constant to equal intemperate this will be a the order of ten to the power of four kelvin. So, a very high temperature. So, the energies the fermi energy corresponds to be a very high temperature the corresponding temperature in temperature units. Now we will use these concepts to calculate an important thermal property namely be electronic specific heat this means that this electron gas, if you inject some heat and energy into it they electron absorbs this energy. And that temperature goes up though these this specific heat is defined as the rate of change of the mean internally energy of the conduction electron at 0 k with respect to temperature.

(Refer Slide Time: 32:02)



So, the electronic specificate can be calculated that by calculating the average energy of this electron gas which is simply done by again at absolute 0. This is done by integrating from 0 to e f 0 of e d f e f f e d e by 0 to e f 0 of e f e f of e d. So, this gives going by the same procedure they arrive at the result this is three fifth of e f 0.

(Refer Slide Time: 32:54)



The average energy is three fifth of fermi energy at absolute 0 now the electronics specific heat having got the average energy, we can simply differentiate this expression fermi energy with respect to temperature that gives you the electronic specific heat. Now we will first qualitatively see what kind results that we are going to get or this calculation the electronic specific heat, since we said that the e f 0 is the order of ten to the power four kelvin in temperature units.

So, if you thermal exited usually thermal excitation is at best of the order of hundred kelvin. So, it is a very small if you go back to the energy distribution this is e f 0 if you go back to this this is of the order of this in temperature e units is that the the order of ten thousand kelvin, but our energy excitations thermal energy excitation is only at the order of a hundred kelvin. So, it is small temperature window. So, the exhibition is going to shift states from this to this, but the state's are all remember that they are all completely occupied and are subject to the electron for subject pauli is crucial that mean if state is completely occupying already you can put another electron.

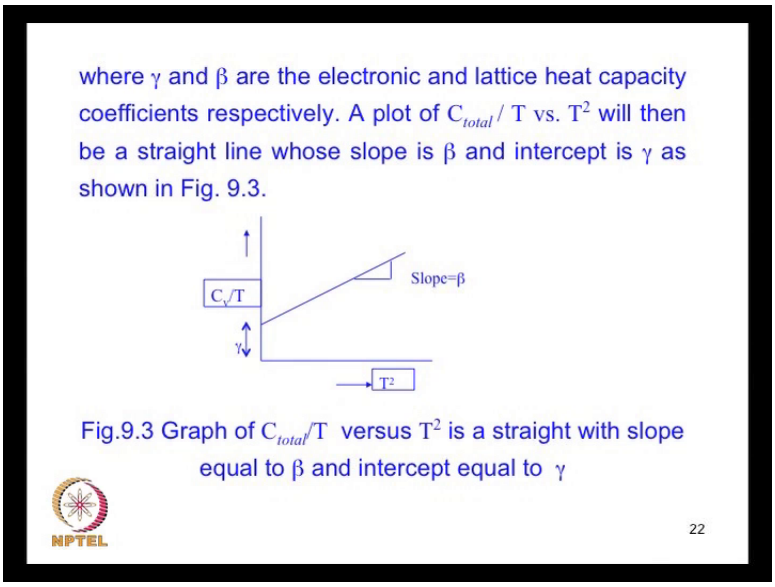
So, this exhibition from this one occupy state to another occupy state in this whole range is not going to be possible even though you give with excitation, the electrons cannot be exited fermi occupied state here into another occupied state which is not empty. So, this is only pass only at this edge this is not possible and the thermal exhibition is one only

possible here here. So, this is of the order of ten to the power four Kelvin, and this is order of ten square. So, this is only possible across this fermi energy if it bring it here.

So, it can excite across in to 1 of the empty state here. So, only the a fraction of the electron which occupy a stated within this ten hundred kelvin in the neighborhood of the fermi energy only they will be able to get excited. So, what is this fraction they are k b t by k b t r k b t f corresponds to all the states the electrons not the energy scale and response b t corresponds to the energy of the thermal excitation.

So, this is the fraction which is t by t f that is the fraction of electrons excited exited thermally and each of them has an exhibition of order of k b t therefore, the excitation energy is as the order of k b t square by t f, so d by d t I of this use this specific. So, these are the order of k b t. So, this tells me that the electronic specific is the order of k b t it is proportional to the temperature t. So, the electronic heat capacity r c e electronic specific heat is plus equal to the constant times the temperature. So, that is the basic results that we get for the electronic specific heat of the conduction electronic gas, so you get this is the value at absolute 0.

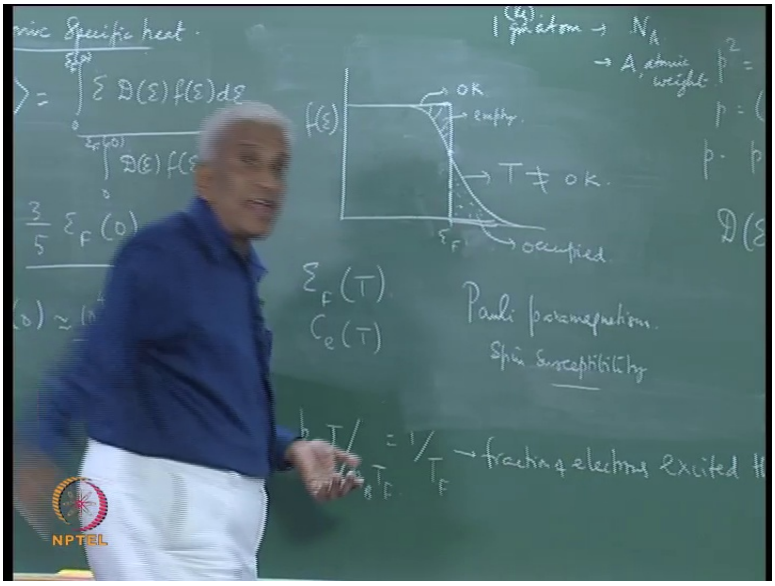
(Refer Slide Time: 37:44)



So, this is shown graphically. So, in figure of course, you will never be able to measure the electronic heat capacitance alone it will be also the specific with includes the contribution from the electron. And also from the lattice of ions are the atoms in the solid and that as we will see later is given by the may be theory specificate and that

temperature depend is a t q dependence. So, the overall behavior is given off by a relation of this time c total and therefore, if you brought c by t verses p-square that would be a straight line that is what is shown in figure. So, from the intercept of this we can get the heat capacity question gamma, we have discussed everything at absolute 0, but the question arises w what happens? Then you have an electron at a finite temperature the this the bit more difficult to calculate, we will not go through the details at this calculation here, but I will just roughly.

(Refer Slide Time: 39:19)



It what happens by looking at the distribution function. So, at a finite temperature the fermi dirac distribution function this at a finite temperature which is not 0. So, the distribution function, now deviate from the behavior at absolute 0, this is at 0 kelvin as we have already seen, and at finite temperature, this reduces to something like this. That is the behavior here at the not equal to 0 at any finite temperature it the f f e decreases from the value 1 to something like of fermi energy. And then it goes on beyond it is non-zero even beyond the ef this means that some of this state or empty even before even below the fermi energy, and some on the state or above the fermi energy are occupy and these the number occupied states goes on increasing.

So, this is the behavior and this will modify the fermi energy the fermi energy will be a function of temperature. Now and the heat capacity equation which is still found to be a linear function of temperature, but but the constant the linear heat capacity question is

slightly different. We will not calculate this this is the overall behavior now electron gas also processes many other interesting properties the electron have a magnetic moment because that that is been and this contributes to magnet. So, this is known as Pauli paramagnets or this is a spin susceptibility this is the magnetic susceptibility which arises from the fact that the electron Aspin's, and therefore a magnetic moment. So, this is another important characteristic of the conduction electron gas in metals in addition the metals most important characteristic is that metal is a very good contact to have electricity. Now we would like to have an expression far the electrical conductivity of a metal.

And how it depends on for example, temperature and not only the electrical conductivity the a metal is also a good conductor of heat. So, we would like to know how the thermal conductivity is determined by the behavior electron gas, we also know that there is such a thing called thermo electric power the phenomenon the thermo electricity in which metal junction used in order to produce the thermo electricity and e m f. So, we would also like to know how the thermoelectric power of a good conductor is determined by the behavior the electron gas these are things we will discuss in next lecture.