Statistical Mechanics

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Lecture - 32
Free Electrons (Fermi Gas) in a Metal

So, good morning students, today we will talk about the Free Electron Fermi gas and the discussion here is basically to complete the topic of heat capacity of a solid at low temperature.

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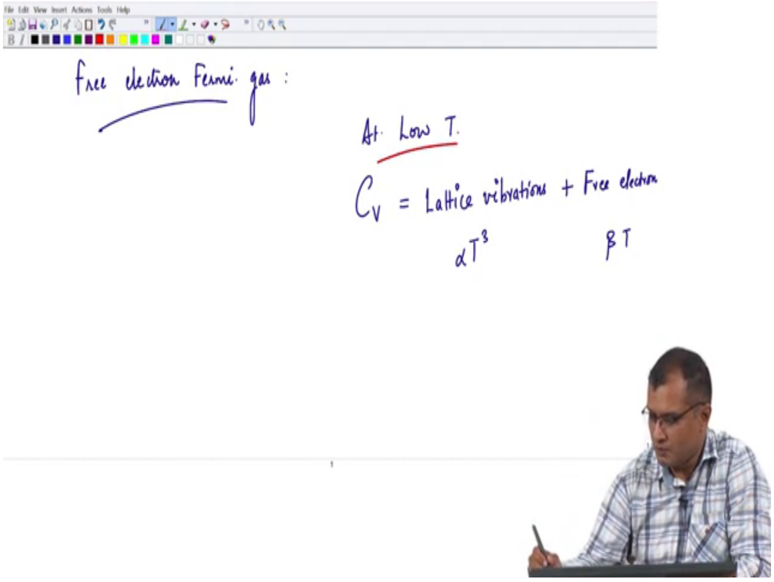

Free electron Fermi gas :

At Low T.

$$C_V = \text{Lattice vibrations} + \text{Free electron}$$

$$\alpha T^3 \qquad \beta T$$

So, the motivations are to get an ultimate expression of heat capacity at low temperature and what I mean by my statement is that. So, we know that the heat capacity of a solid is due to lattice vibrations which is due to vibration of ions about their mean position. So, these vibrations are quantized in terms of phonons. So, we had used the boson theory of solids and we had derived an expression due to d by which said that at low temperatures the behaviour is T cube.

So, let us say that the proportionality constant is alpha. Today we will discuss another contribution to the overall heat capacity of solids at low temperature, and that comes from the free electrons in a metal. So, naturally our discussion is contextually valid only for metals, which have three electrons to contribute to the overall heat capacity. So, here at the end of our discussion, we will see that this is proportional to temperature at very low values of temperature. So, both the lattice vibrations and free electron contributions saturate to 3 by 2 or saturate to 3 kT in terms of energy at high temperatures.

So, the heat capacity at very high temperatures when neither the lattice vibrations contribute nor the electrons contribute, we see that the heat capacity becomes 3 n k which is the Dulong Petits law. The exciting stuff only happens at low temperature where both lattice vibrations and electrons pitch in contribute to the overall heat capacity ok. So, we need to keep this in mind that we have only completed in the first 2 lectures.

The first half of the heat capacity which is due to lattice vibrations; today we will extend the discussion and include the free electrons that are there in any metal copper for example, iron for example, we shall see how the heat capacity is affected in due to free electrons as well. So, that being the introduction, I can start from the statistics of electrons which are fermions.

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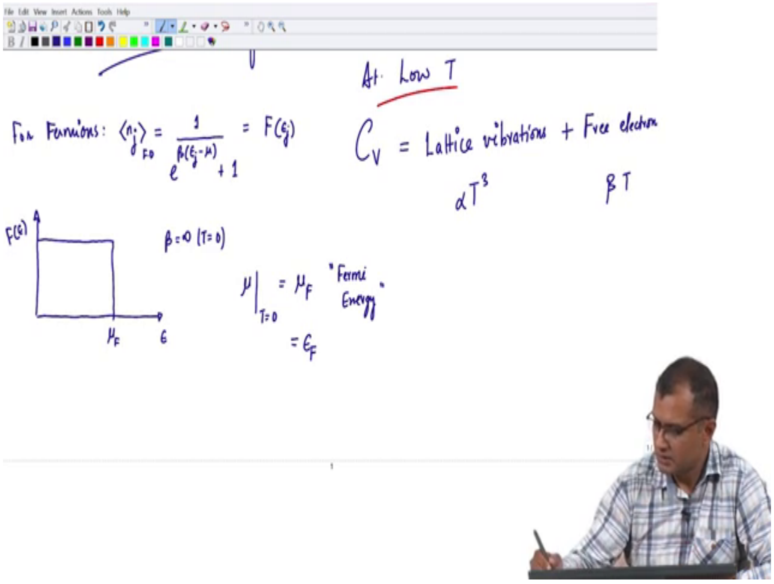

At. Low T

For Fermions: $\langle n_j \rangle_{FD} = \frac{1}{e^{\beta(\epsilon_j - \mu)} + 1} = F(\epsilon_j)$

C_V = Lattice vibrations + Free electron

αT^3

βT

$\beta = \infty \; (T = 0)$

$\mu \big|_{T=0} = \mu_F$ "Fermi Energy"

$= \epsilon_F$

So, for fermions I have already discussed that is statistics is due to the Fermi Dirac statistics. And we can write down these statistics in terms of the occupation number average occupation number of any j th level as 1 over e to the power beta E j minus mu plus 1 and just to keep in mind that this is a Fermi Dirac statistics, I am going to call this as a function of just the energy and you can construct the Fermi function especially at 0 temperature, which is basically the limit of infinite beta.

As if you look at the Fermi function for all energy values which are less than this chemical potential mu as beta goes to infinity, the exponential turns to 0 because its e raise to minus infinity. So, for all energy values below the chemical potential which is called as the Fermi energy at T equal to 0, we have the occupation exactly 1 and it is 0 for all energy values above the Fermi level.

So, I am going to call this as the Fermi function or the average occupation number. At T equal to 0 or infinite beta, all energy levels are fully occupied. So, there is no sense of an average occupation whether it is exactly 1 because anyway you have taken an extreme case of T equal to 0. So, what is also indicated in this figure is that I have conveniently taken the chemical potential at T equal to 0 as the Fermi energy ok. We can also call this as E F if you can call it as E F Fermi F they are the same.

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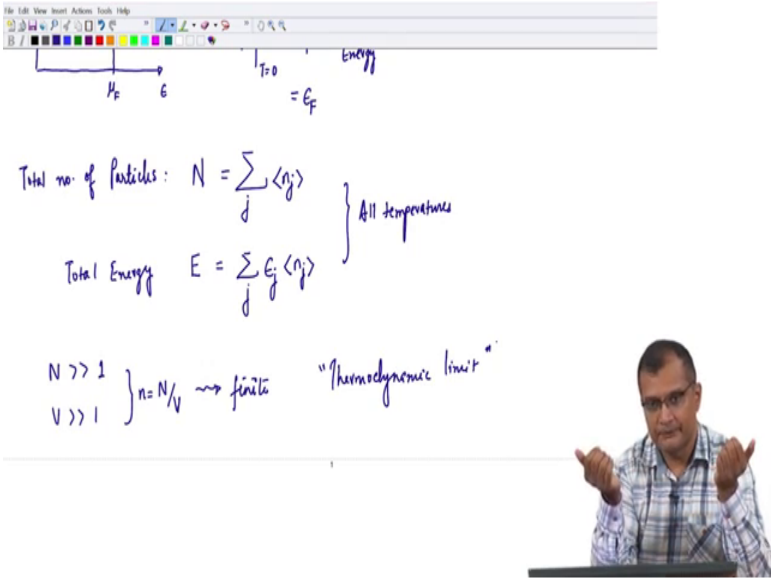

Total no. of Particles: $N = \sum_j \langle n_j \rangle$

Total Energy $E = \sum_j \epsilon_j \langle n_j \rangle$

} All temperatures

$N >> 1$
$V >> 1$
$\Big\} n = N/V \rightsquigarrow$ finite "Thermodynamic limit"

So, just to continue the discussion I can write down the total number of particles in our system as a simply sum over all the average occupation numbers in our Fermi system. So, that will sum up to the total number of particles in the system, I can also compute the total energy by simply sampling the energy of each level.

Let us say E j and sampling in the distribution which is the Fermi Dirac distribution ok. So, naturally at T equal to 0 this would simply be sum over all the energies from 0 to Fermi level and the excitation of each level is just 1 it would be nothing, but number of fermions that are there in the system times their energies. So, these definitions that I have written is precisely you know validate all T. So, which means they are it applicable at all temperatures not just at T equal to 0 because if you take temperature T equal to 0 then n j is strictly becomes 1 and it comes outside the summation you simply sum over all E j’s to get the total energy of the system ok. As you can see from this figure; that our Fermi Dirac statistics is exactly 1 for a T equal to 0 for all energy values below the Fermi surface.

Now we are looking in general systems where the number of particles usually is a very large number. For example, we are dealing with you know metal objects in our laboratory experiments or we are dealing with solids where N is of the order of 10 to the power 23 it is a very large number. And of course, the volumes are very large the volumes are millimeter cube or centimeter cube compared to the volume occupied by an atom or a molecule this is a very large volume.

So, the numbers themselves are very large and, but we have a finite density. So, this limit of the extensive variables N and V being very large such there is the intensive variable density becomes finite is called as a thermodynamic limit. So, we are working in thermodynamic limit where these two extensive quantities N and V are so, large that the energy levels become almost a continuum and the spacing betweens and that is because you are stacking too many modes in the energy spectrum, that the separation between modes essentially goes to 0 as number of particles in volume go to infinity.

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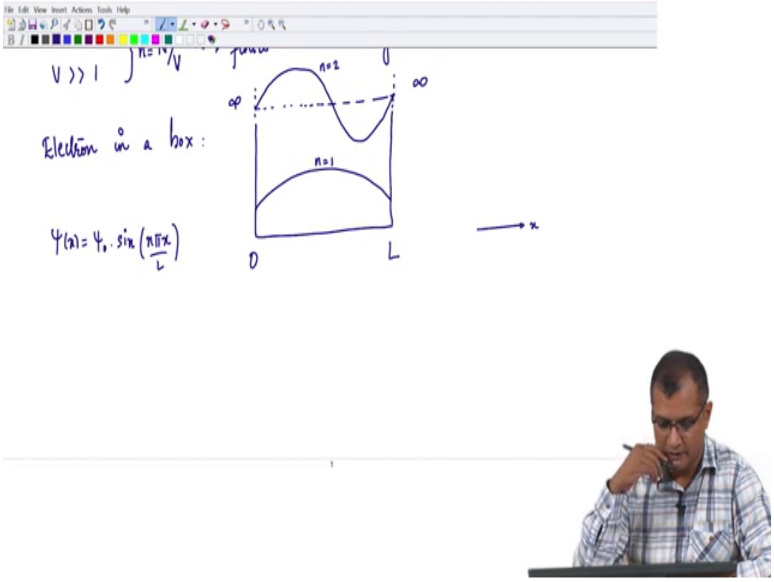

Electron in a box :

$\psi(x) = \psi_0 . \sin\left(\frac{n\pi x}{L}\right)$

For example if you look at a typical electron in a box, we are having many electrons in the box. So, let us look at just one electron in a box, the meaning of thermodynamic limit becomes very clear here. So, this is a standard electron in a box problem that you have seen in your quantum mechanics introductions, if you have not, but then I am going to assume that you already know a little bit about particle in a box. So, I have taken a box of length L. So, I am going to take it as the box lengths to be the walls at 0 and L.

And this is going to be my x axis and this is basically infinite well in the sense that my potential energy outside the box is infinite and it is 0 inside 0 or any constant value after all it is the gradient or the change in potential energy that translates into a force, the ref the reference values of the potentials into themselves do not really you know it is just an additive constant in the overall energy of the system.

So, the infinity potential here only implies that the particle is never allowed to escape from the box. It is like a if you take imagine a conductor of length L, I would never respect the electrons and they conducted to leave the conductor most of the conductors length here is the L here ok. Now you can think of the electron as a as a wave that is in some sense solution of a Schrodinger equation. So, you can think of the wave like solutions as psi of x as some normalization constant into sin of n pi x by L. You will do it you will do it for many electrons right now I am showing it for just one electron.

And so, on naturally this would be the case for n equals to 1 you can consider higher ends for n equal to 2 you can consider another case such as right.

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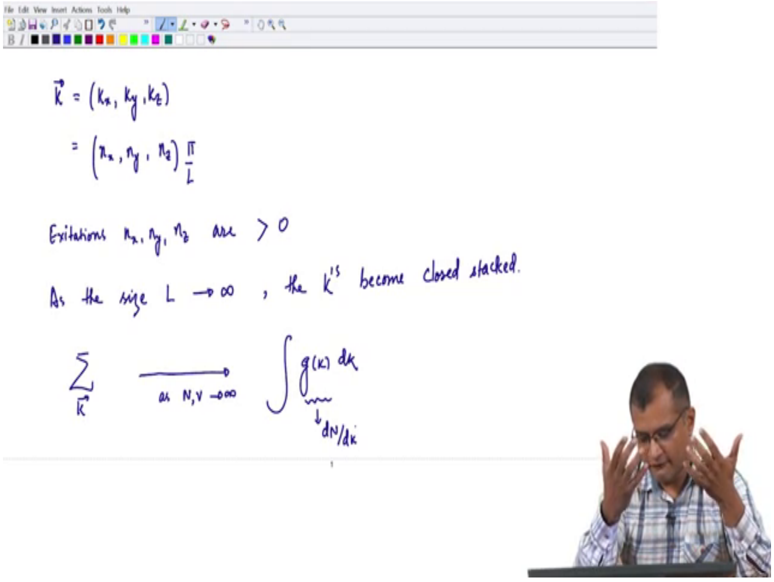

$\vec{k} = (k_x, k_y, k_z)$

$= (n_x, n_y, n_z)\frac{\pi}{L}$

Excitations n_x, n_y, n_z are > 0

As the size $L \to \infty$, the k's become closed stacked.

$$\sum_{\vec{k}} \xrightarrow[\text{as } N,V \to \infty]{} \int \underbrace{g(k)}_{\downarrow\, dN/dk} dk$$

So, now if I write down the wave function like this, it is immediately clear that the allowed wave vectors that I can I have assumed are basically well this was a 1D case. So, in three dimension it would be a product of three sin functions and I can write down my wave vector as a triplet of kx ky and kz which essentially means that I can write down this as a triplet of the excitation numbers nx ny and nz times pi by L. So, that would be my k in three dimensions.

Now, these values of k kx ky and kz which are due to the excitations nx ny and nz they actually are always positive. The simple reason being that if I take negative values of these excitations, it does nothing to my wave function except for an except that it incurs an overall negative sign in my wave function, which does not pose any problem because at the end of the day I will be looking only at the expectation value which is required the for which the probability density is required and that is mod psi star and so, the negative values of the wave functions oppose no bearing on the expectation value of observables in quantum mechanics.

So, I am going to take only positive values of these excitations, negative values affect the system in no way except that the overall a wave function becomes negative and we are not interested in negative eigen negative excitations precisely for that matter. Now so, I can now write down if you can see now as the system size which is L goes to infinity that is my volume goes to infinity, these become very closely stacked right because as L goes to infinity the spacing between them which goes as you know 1 upon L in some sense becomes very very small and so, the energy spectrum becomes almost a continuous spectrum.

Which means that my summation over all the modes have to now be replaced as N and volume both go to infinity by an integral over modes. And naturally when I replace the summation by an integral, I need to account for a certain density of states which I am which in some sense is a number of states per unit mode number because dimensionally gk has to have dimensions of 1 upon k so, that the integral becomes dimensionless.

So, that is the effect of increasing a system size to infinity that you naturally get the concept of a density of states.

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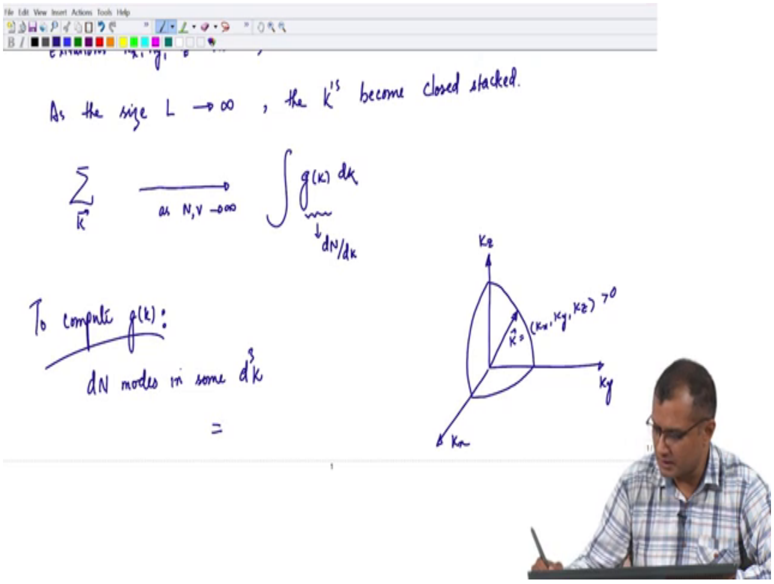

As the size $L \to \infty$, the k's become closed stacked.

$$\sum_{\vec{k}} \xrightarrow[\text{as } N, V \to \infty]{} \int \underbrace{g(k)}_{\downarrow\, dN/dk} dk$$

To compute g(k):

dN modes in some d^3k

=

Now, to compute density of states, you can imagine your k space as basically an octant where kx ky and kz are positive for the reason that we have just mentioned that we are interested only in positive values of the excitations the negative values have no bearing on the overall observables. So, I can think of you know one octant in my in my k space, this so, called the octant where all values of my components of the wave vector k are positive.

So, I can take one on this surface I can take some value of my k which is given as the set of three components, all greater than 0 and now I can just compute the number of states inside this octant ok. So, if I was going to compute the number of states in an entire sphere of radius k, I would get precisely 8 times the number of modes that I need for my calculation ok, but I do not want that. Which means when I write down for the number of modes, let us say dN in some arbitrary volume element this would be nothing but the volume of this volume element that is d cube k over the minimum volume one can imagine inside this k space.

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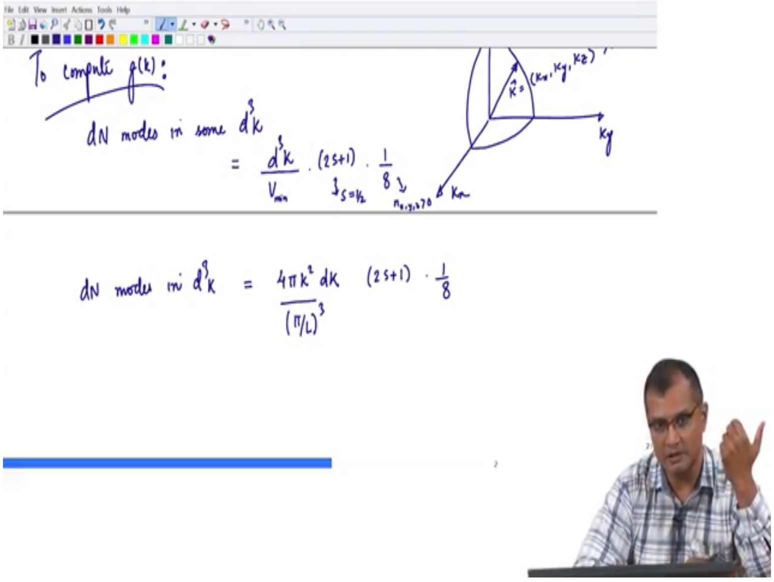

To compute $\rho(k)$:

dN modes in some d^3k

$$= \frac{d^3k}{V_{min}} \cdot \underbrace{(2s+1)}_{s=1/2} \cdot \underbrace{\frac{1}{8}}_{n_{x,y,z}>0}$$

dN modes in d^3k $= \frac{4\pi k^2 dk}{(\pi/L)^3} (2s+1) \cdot \frac{1}{8}$

The minimum volume is due to the minimum k values and naturally this has to be multiplied to the degeneracy of the fermions because each fermion has a spin half and that gives it in some sense 2 polarizations for any value of k. So, it can means you know in 2 states s being half. So, 2 s plus 1 is the degeneracy. So, it can be a plus 1 or minus 1 states and you have to also account for the fact that we are only interested in the octant where kx ky and kz are positive. If you do not take into consideration: that you would be over counting the number of states by a factor of 8.

So, precisely to account for that positiveness of the excitations in xn yn z, I have taken the factor of 1 by 8. So, this is basically to remind us that we are taking only nx y n nz as positive ok. So, now, we can write down dN modes in volume element d cube k as I can write down the volume element as 4 pi k square into dk, 4 pi k square here being the surface area of this sphere at radius k and dk is a small you know shell at the radius k.

So, the volume of the spherical shell is 4 pi k square d k multiplied by of course, our degeneracy factor into the fact that I am going to be interested only in the positive values of the excitations. So, hence only one eighth of the total volume is going to be constructed is going to be used and I am going to divide it by the minimum volume and that is constructed by simply taking the minimum k. Now the minimum k here is if you take nx ny and nz as 1 the minimum k comes out to be just pi by L ok.

So, along the x direction the minimum k is pi by L along the y direction its pi by L and along the z direction is pi by L corresponding to nx ny and nz taken as 1. So, I am going to take pi by L and raise it to power 3.

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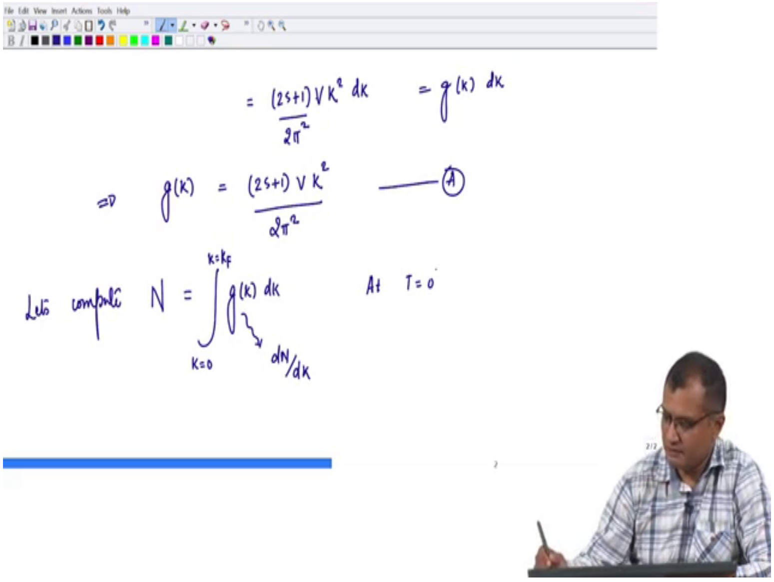

$$= \frac{(2s+1) V k^2 \, dk}{2\pi^2} \quad = g(k)\, dk$$

$$\Rightarrow \quad g(k) = \frac{(2s+1) V k^2}{2\pi^2} \quad \text{——} Ⓐ$$

Lets compute $N = \int_{k=0}^{k=k_F} \underbrace{g(k)}_{dN/dk} \, dk$ At $T=0$

So, then this will give me if I take all the pre factors in one place, I would be getting 2 s plus 1 into k square into volume dk over 2 pi square 4 times 2 is 8 and we have a pi cube in the denominator and a pi in the numerator.

I think I have taken care of all the factors. So, now this is my g of k into d k. So, this is basically giving us the density of states in the k space. So, my g of k is now 2 s plus 1 into volume into k square over 2 pi square. So, then I can compute a few important quantities. So, lets compute first N the total number of particles. So, N is nothing, but integral density of states into k. So, basically this quantity if you recall is nothing, but number of particles per unit k space.

So, if you integrate this density over the entire k space, then you should recover the total number of particles as long as you take the limits on the integral from 0 to the Fermi wave number because we are integrating it at T equal to 0. I expect all my electrons to be within the Fermi sphere. So, the upper limit of my integral is Fermi wave vector and this will give me the total number of particles to be as n.

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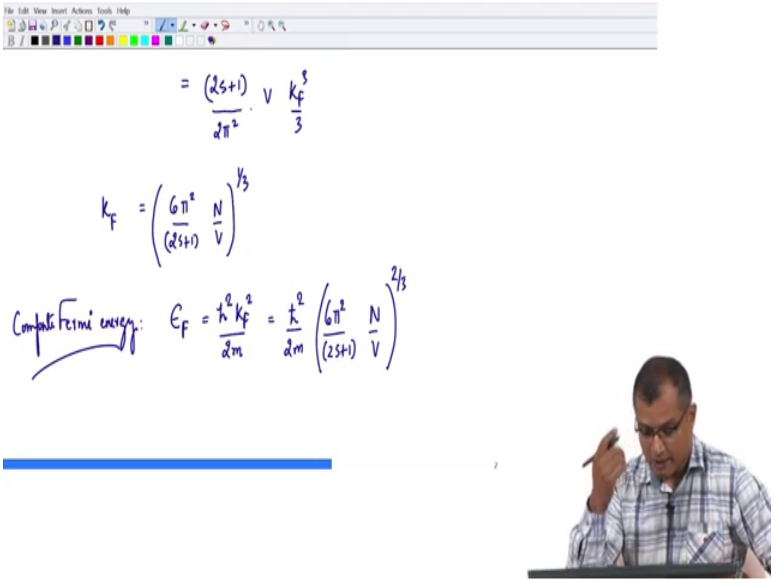

$$= \frac{(2s+1)}{2\pi^2} \cdot V \frac{k_F^3}{3}$$

$$k_F = \left(\frac{6\pi^2}{(2s+1)} \frac{N}{V} \right)^{1/3}$$

Compute Fermi energy: $\epsilon_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{6\pi^2}{(2s+1)} \frac{N}{V} \right)^{2/3}$

So, at T equal to 0 if I do this integration, I will recover the number of particles and that would give me the definition of the Fermi wave vector. Let us do that integral we will simply substitute gk from up above and that would become 2 s plus 1 over 2 pi square into V and integration on k square will simply become kF cube by 3. So, you can recast this equation in terms of the Fermi wave vector as simply 6 pi square over 2 s plus 1 into N by V the whole thing raised to power one third ok. So, this is my Fermi wave vector I can also compute now because I have the Fermi wave vector with me I can compute my Fermi energy.

So, computing Fermi energy, I can use this expression of the energy h cut square kF square over 2 m and this will give me the Fermi energy as nothing, but I just have to multiply h cut square by 2 m to the above obtained expression for Fermi energy the Fermi wave vector. So, this would be just 6 pi square over 2 s plus 1 into N by V raise to the power two third and let us compute one more quantity which is Fermi temperature.

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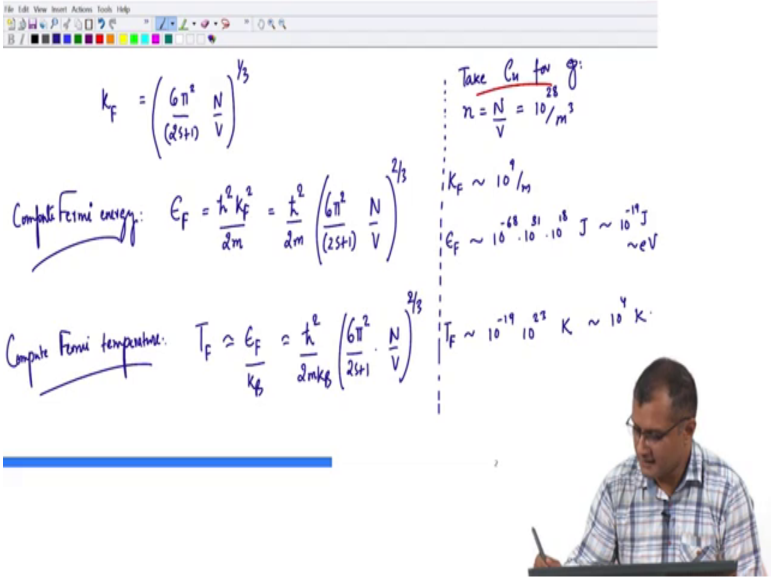

$$k_F = \left(\frac{6\pi^2}{(2s+1)} \frac{N}{V}\right)^{1/3}$$

Compute Fermi energy: $\epsilon_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{6\pi^2}{(2s+1)} \frac{N}{V}\right)^{2/3}$

Compute Fermi temperature: $T_F \simeq \frac{\epsilon_F}{k_B} \simeq \frac{\hbar^2}{2mk_B}\left(\frac{6\pi^2}{2s+1} \cdot \frac{N}{V}\right)^{2/3}$

Take Cu for eg:

$n = \frac{N}{V} = 10^{28}/m^3$

$k_F \sim 10^{9}/m$

$\epsilon_F \sim 10^{-68} \cdot 10^{31} \cdot 10^{18}\ J \sim 10^{-19} J$
$\sim eV$

$T_F \sim 10^{-19}\ 10^{23}\ K \sim 10^{4} K.$

Now, since we have an energy scale I can always compute a temperature commensurate with it energy scale. So, the Fermi temperature I can compute by simply saying that this is of the order of the Fermi energy over the Boltzmann constant ok. So, this would be nothing, but h cut square over twice m the Boltzmann constant into 6 pi square over 2 s plus 1 into N over V raise to two-third now let us get a feeling of these numbers. So, you can just to get a feel of these numbers which is important because say they are the consequence of our system being treated quantum mechanically.

So, the consequence of treating electrons as a system of fermions which obey Pauli’s exclusion principle, and the fact that we are squeezing so, many of them in a small volume in a volume which is you know pushing your densities to 10 to the power 28 per meter cube. For typical metals like copper has natural consequences on these values and you should see the strength of these numbers to sort of have an appreciation of the quantum mechanics that goes into the calculation ok. So, take for example, copper and which is an extremely good conductor.

So, the number density of copper is roughly number density of electrons is usually 10 to the power 28 per meter cube and just to get a feel of these numbers for typical metal numbers will not very much. So, it will give you an order of magnitude estimate. So, let us compute for example, the Fermi wave vectors magnitude, this would be of the order of the density to the power one third and that is nothing, but roughly if I take 10 to the 28 and raise one third of its roughly 10 to the power 9 per meter ok.

And so, the wavelength will typically a nanometer because k is inverse of the wavelength. And if you want to get a feel for the Fermi energy, this would be if you look at the expression of a Fermi energy on the left I have a Planck constant to the power 2. So, that is giving me a 10 to the minus 68, I have an electron mass in the denominator that is giving me 10 to the power minus 31 which when taken upstairs becomes 10 to the power 31 and I have the density to the power two third.

Density is about one third is already 10 to the power 9 if I raise it to the power 2, it becomes 80 and this would be in Joules. So, if you sum up all the terms this becomes roughly 10 to the power minus 19 Joules which is like an electron volt. So, the Fermi energy comes out to be of the order of an electron volt, I just to give an exam just to give you a feel in electron volt is a very high energy scale because if you compute the temperature corresponding to an electron volt it will come out to be a very large number ok.

So, the Fermi temperature which corresponds to an energy of the order of an electron volt, comes out to be you know I will take electron volt which is a 10 to the power minus 19 Joules and divided by the Boltzmann constant which is roughly I am going to just take the Boltzmann constant upstairs. So, this would just give me in 10 to the power 23 and so, that is in Kelvin and we will come out to be around 10 to the power 4 Kelvin. So, about 10000 Kelvin is the temperature of the Fermi surface you know whose energy is around electron volt.

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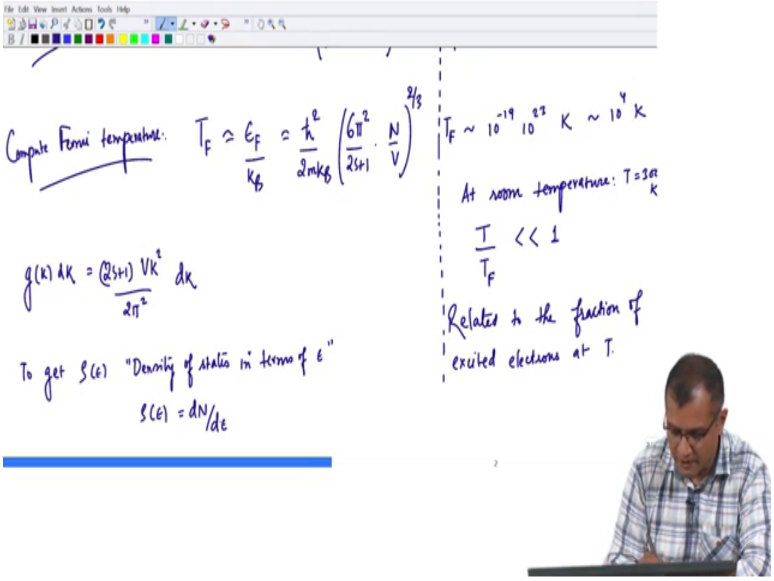

Compute Fermi temperature: $T_F \simeq \frac{\epsilon_F}{k_B} = \frac{\hbar^2}{2mk_B}\left(\frac{6\pi^2}{2s+1}\cdot\frac{N}{V}\right)^{2/3}$

$T_F \sim 10^{-19}\,10^{23}\ K \sim 10^4\ K$

At room temperature: $T = 300\ K$

$\frac{T}{T_F} << 1$

Related to the fraction of excited electrons at T.

$g(k)\,dk = \frac{(2s+1)\,Vk^2}{2\pi^2}\,dk$

To get $\rho(\epsilon)$ "Density of states in terms of ϵ"

$\rho(\epsilon) = dN/d\epsilon$

So, this immediately tells me something that at room temperature. The ratio of you know; if I take the room temperature with 300 Kelvin which is not a which is an decent approximation the ratio of T over T F is going to be a very small number, and it tells me that for most purposes room temperature is considered to be a classical regime because the corrections that are going to be you know done over and above the Dulong Petits law out of the order of T by T F. So, they are become very very small as temperatures are equal or above the room temperature, where you know you where you always see the heat capacity becoming an independent of temperature become just 3 kB.

3 times n kB; so, this ratio of n T over T F will be will be shown that it is related to the fraction of you know the fermions excited at room temperature fraction of excited electrons at any temperature which is taken to be the room temperature in this case. So, roughly T over T F fraction of the total number of electrons will contribute to the heat capacity. Now this is a very small number so, it is enough to have a very small fraction of the electrons of that the total 10 10 to the power 28 in your form if you take a meter cube sample.

Then out of these 10 to the power 28 only about T over T F which is a number that is very small that is just 1 upon 100 if at if you are taking temperature to be room temperature contributing to your overall heat capacity. So, let us now compute the density of states in terms of energy. So, what we have computed so, far is the g of k and this was computed to be 2 s plus 1 VK square upon 2 pi square into d of k and if you to get the density of states in terms of energy ok.

So, I am going to call this as let me use a different symbol for density of states a in terms of energy. So, let me call density of states for energy as rho in terms of energy; that means, I am looking for density of states which will give me a number of states per unit energy interval ok.

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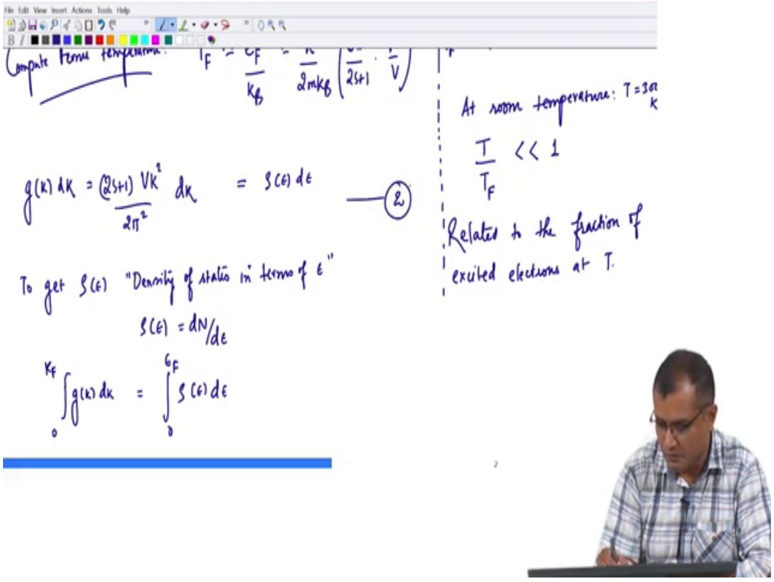

Compute Fermi temperature:

$$g(k)\,dk = \frac{(2s+1)\,Vk^2}{2\pi^2}\,dk = \rho(\epsilon)\,d\epsilon \quad \text{—} ②$$

To get $\rho(\epsilon)$ "Density of states in terms of ϵ"

$$\rho(\epsilon) = dN/d\epsilon$$

$$\int_0^{k_F} g(k)\,dk = \int_0^{\epsilon_F} \rho(\epsilon)\,d\epsilon$$

At room temperature: T = 300 K

$$\frac{T}{T_F} << 1$$

Related to the fraction of excited electrons at T.

So, I can compute this by equating it to rho E dE because after all whether I compute the density in k space or energy space, the conservation of the number of particles says that I must get the same number of particles whether I integrate the density in k space or density in energy space ok. I am going to use symbol rho E ok. So, then if I look at the expression here, I am going to call is at equation 2 call this as equation 1.

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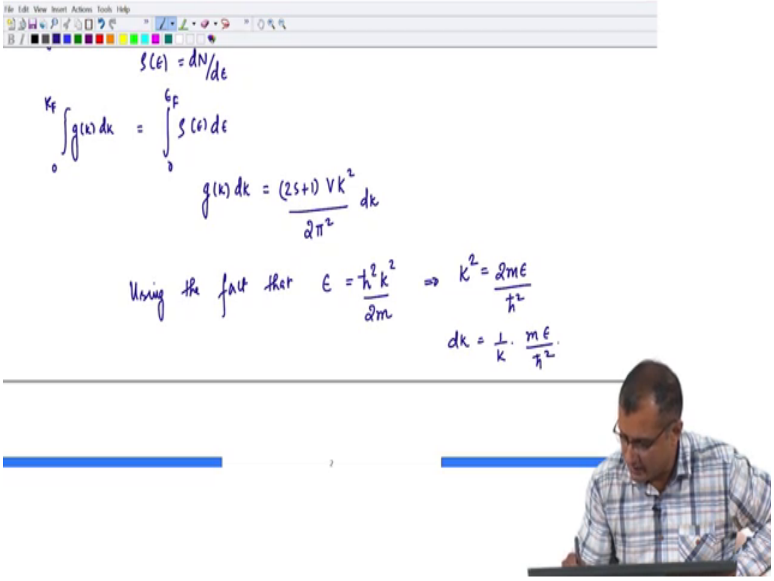

$$\rho(\epsilon) = dN/d\epsilon$$

$$\int_0^{k_F} g(k)\,dk = \int_0^{\epsilon_F} \rho(\epsilon)\,d\epsilon$$

$$g(k)\,dk = \frac{(2s+1)\,Vk^2}{2\pi^2}\,dk$$

Using the fact that $\epsilon = \frac{\hbar^2 k^2}{2m} \Rightarrow k^2 = \frac{2m\epsilon}{\hbar^2}$

$$dk = \frac{1}{k}\cdot\frac{m\epsilon}{\hbar^2}.$$

So, I can use equation 2 and write down for my g of k which is basically g of k d k as simply 2 s plus 1 into VK square over 2 pi square d k and simply using the fact that the energy is related to the wave vector as h cut square k square by 2 m. So, this gives me K square as nothing, but twice m E over h cut square and it can give me dk as 1 upon k m E over h cut square ok.

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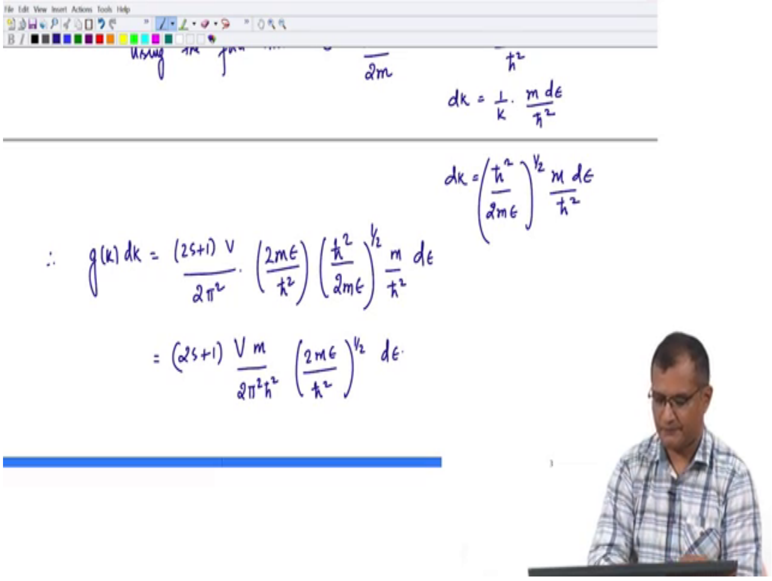

$$dk = \frac{1}{k}\cdot\frac{m\,d\epsilon}{\hbar^2}$$

$$dk = \left(\frac{\hbar^2}{2m\epsilon}\right)^{1/2}\frac{m\,d\epsilon}{\hbar^2}$$

$$\therefore\quad g(k)\,dk = \frac{(2s+1)\,V}{2\pi^2}\cdot\left(\frac{2m\epsilon}{\hbar^2}\right)\left(\frac{\hbar^2}{2m\epsilon}\right)^{1/2}\frac{m}{\hbar^2}\,d\epsilon$$

$$= (2s+1)\frac{Vm}{2\pi^2\hbar^2}\left(\frac{2m\epsilon}{\hbar^2}\right)^{1/2} d\epsilon.$$

So, I can write for dk as h cut square over 2 m E to the power half into m E by h cut square fine. Of course, there has to be this will be m times dE fine because if I take a derivative with respect to k, I get 2 k dk equals to 2 m dE by h cot square the factor of 2 cancels from both sides and now I can write this as.

So, therefore, I can write down my density of states as g of k dk as 2 s plus 1 into V times k square which is a twice m E over h cut square and dk has already been written as h cut square over twice m E raised to half into m by h cut square dE fine. So, then I can write down the density of states as 2 s plus 1 into V into V m over 2 pi square h cut square into twice m E over h cut square to the power half d E.

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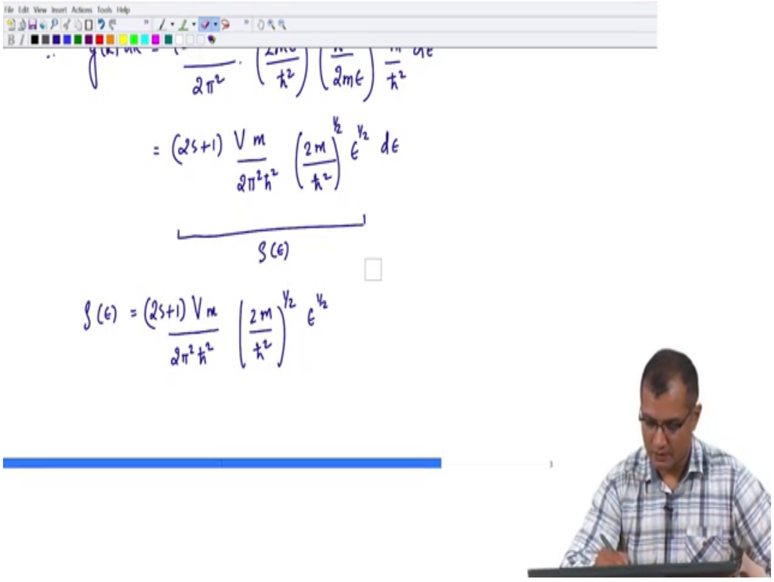

$$= \underbrace{\frac{(2s+1)\,V m}{2\pi^2\hbar^2}\left(\frac{2m}{\hbar^2}\right)^{1/2}\epsilon^{1/2}}_{g(\epsilon)}\, d\epsilon$$

$$g(\epsilon) = \frac{(2s+1)\,V m}{2\pi^2\hbar^2}\left(\frac{2m}{\hbar^2}\right)^{1/2}\epsilon^{1/2}$$

You can take the e raise to half outside to show that the density of states and this is nothing, but your density of states in terms of energy ok. So, our density of states now in terms of energy is 2 s plus 1 into V m by 2 pi square h cut square into 2 m by h cut square raise to half into E raise to half de yeah. So, then let us check if everything is fine. So, our E was defined as h cut square k square by 2 m and now you have defined it like this. So, I have substitute for k square and so, I see me by h cut square and substitute for dk as 1 upon k.

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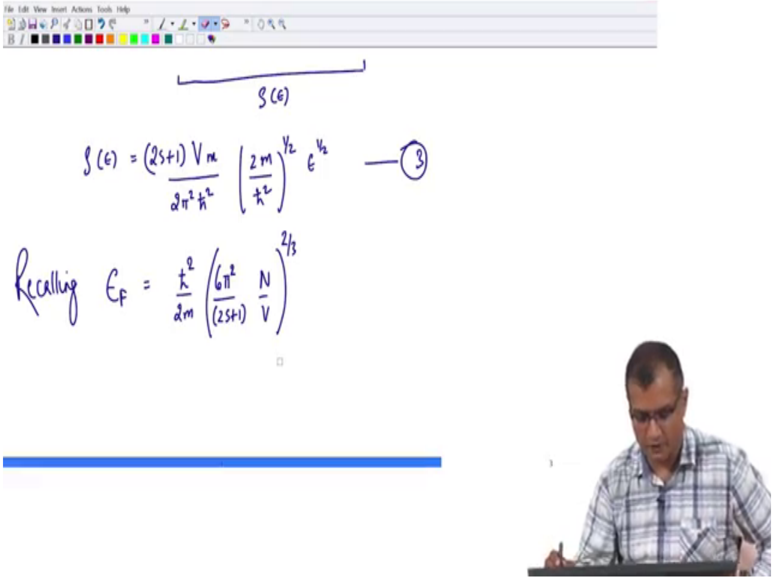

$$\underbrace{\qquad\qquad\qquad}_{g(\epsilon)}$$

$$g(\epsilon) = \frac{(2s+1)\,Vm}{2\pi^2\hbar^2}\left(\frac{2m}{\hbar^2}\right)^{1/2}\epsilon^{1/2} \quad — ③$$

$$\text{Recalling} \quad \epsilon_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2}{(2s+1)}\,\frac{N}{V}\right)^{2/3}$$

I can also simplify this expression let us call this as the equation 3. So, if you use this expression of the Fermi energy, we can actually write down a simpler expression. So, we can use this expression of Fermi energy. So, you recall that your Fermi energy was given by this expression. So, I can compute for.