Solid State Physics
Lecture 29
Thermal Properties of the Free Electron Gas

Hello, we have been discussing a Sommerfeld model, where electrons are treated not as the gas molecules of ideal gas. Rather they are treated as indistinguishable particles, that is identical particles and Pauli Exclusion Principle comes into effect. And, we have Fermi Dirac statistics that these particles that is electrons or any other fermions that obey. We have derived the Fermi distribution function the Fermi Dirac distribution function and now we are going to discuss the thermal properties of the free electron gas. (Refer Slide Time: 01:07)

So, as we know the energy of the free electron gas particles that is $\epsilon(\overrightarrow{k}) = \frac{\hbar^2 k^2}{2m}$, where k is the wave vector the crystal momentum and m is the mass. We first verify that the distribution function is consistent with the ground state properties, that we have derived earlier; ground state means the temperature equals 0. So, at the at absolute 0 temperature, the states that we have that are with energy less than or equal to the Fermi energy; Fermi energy is the maximum possible value of the energy for these electrons at absolute 0 temperature. Now, these the states with energy less than or equal to Fermi energy they are all occupied and higher energy states are completely empty. So, in this kind of a situation the probability of a state being occupied is $f_{\overrightarrow{k}s} = 1$ provided the $\epsilon(\overrightarrow{k}) < \epsilon_F$ And, this $f_{\overrightarrow{k}s} = 0$ provided $\epsilon(\overrightarrow{k}) > \epsilon_F$, this is valid at absolute 0 temperature. Now, on the other hand if we consider the limit that $T \to 0$, the for if we consider the Fermi Dirac distribution function here, that is $\lim_{T\to 0} f_{\overrightarrow{k}s} = 1$, provided $\epsilon(\overrightarrow{k}) < \mu$ that is denoted as μ. And, this quantity $\lim_{T\to 0} f_{\overrightarrow{k}s} = 0$ provided epsilon that is the function of the momentum $\epsilon(\overrightarrow{k}) > \mu$, that you can find from the expression of the Fermi function, that we have derived earlier. Now, if that, if we have to satisfy this and this together both of these can be simultaneously satisfied only if we have $\lim_{T\to 0} \mu = \epsilon_F$. Only then it is possible to satisfy all these both these conditions. So, this is necessary. So, we know that at $T \to 0 \mu = \epsilon_F$. And, we I can tell you that for metals the chemical potential and the Fermi energy, they remain almost same even at higher temperatures. So, the most important application of this Fermi Dirac statistics is the calculation of the electronic contribution to the constant volume specific heat of a metal. (Refer Slide Time: 06:06)

Specific heat at a constant volume C_v, so, how do we define C_v? C_v is statistically defined as $C_v = \frac{T}{V}(\frac{\partial S}{\partial T})_V$, this comes from statistical mechanics $= (\frac{\partial u}{\partial T})_V$. What is small u? Small u is the internal energy per unit volume (U/V). Now, if we perform independent electron approximation, we can write the internal energy as $U = \Sigma_k \epsilon(\overrightarrow{k}) f(\epsilon(\overrightarrow{k}))$. So, this gives us the Fermi function gives us the probability of a particular energy level being occupied by electron, and this is the corresponding energy summed over this is the internal energy with a factor of 2 that comes from the spin degeneracy. So, we have introduced the Fermi function to emphasize that, the probability depends on k through the electronic energy e. And, in this form we can write the Fermi function $f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/K_B T}+1}$, just what we have derived earlier. Now, if we divide both sides of this equation by the volume. Then, what do we get? We get u small u equals integration, we are converting the sum into an $\int \frac{d^3k}{4\pi^3}\epsilon(\overrightarrow{k}) f(\epsilon(\overrightarrow{k}))$, this is what we find. (Refer Slide Time: 09:37)

So, if we want to evaluate the total number of electrons, that can be given as capital $N = \Sigma_i f_i = \Sigma_i \frac{1}{e^{(\epsilon_i-\mu)/K_B T}+1}$. And, small n that is the density of electrons, the number of electrons per unit volume is given as converting the sum into integral form $\int \frac{d^3k}{4\pi^2} f(\epsilon(\overrightarrow{k}))$, f that is the function of energy and momentum through energy. We need to evaluate this integral which is so, it is of the form $\int \frac{d^3k}{4\pi^3} F(\epsilon(\overrightarrow{k}))$, any function F arbitrary function, not necessarily the Fermi function. So, we are now talking about this form of the integral and once we have learned we learn how to solve this form of integral, we will apply that for Fermi function to evaluate this quantity here ok. So, epsilon here as we

know is $\epsilon = \frac{\hbar^2 k^2}{2m}$. So, the k dependence is spherically symmetric. And, provided the k dependence is spherically symmetric, we can write $\int \frac{d^3k}{4\pi^3} F(\epsilon(\overrightarrow{k})) = \int_0^\infty k^2 \frac{dk}{\pi^2} F(\epsilon(\overrightarrow{k}))$. This can be written as $\int_{-\infty}^\infty dE g(\epsilon) F(\epsilon)$. So, we are converting the range of the integral from 0 to infinity, to minus infinity to infinity. How and we have introduced something new here g that is a function of epsilon. So, what is $g(\epsilon)$? Here, if we see how this quantity is introduced, how this is replaced this way. And, the differential of energy it has been brought considering that comparing these 2 equations, we can write $g(\epsilon) = \frac{m}{\hbar^2 \pi^2} \sqrt{\frac{2mE}{\hbar^2}}$ provided $\epsilon > 0$. And, this quantity $g = 0$, if $\epsilon < 0$. This is how we define this quantity $g(\epsilon)$? (Refer Slide Time: 14:28)

Now, what is this quantity? If, we examine the form of the integral, we can say that $g(\epsilon)\ d\epsilon$, $d\epsilon$ that is the differential. This gives us $\frac{1}{V} \times$ (the number of single electron levels in the energy range $\epsilon \to (\epsilon + d\epsilon)$. This is what it means. And, if that is the case, then we can give a concrete name a handy name to this quantity $g(\epsilon)$, the density of levels per unit volume, often called as the density of states. Now, we can also write this quantity the density of levels as $g(\epsilon) = \frac{3}{2} \frac{n}{\epsilon_F} (\frac{\epsilon}{\epsilon_F})^{1/2}$, if $\epsilon > 0$. And, this quantity $g(\epsilon) = 0$, if $\epsilon < 0$. We have already defined ϵ_F and k_F those are defined at absolute 0 temperature. Now, a quantity of particular numerical importance would be the density of levels at the Fermi energy. So, if we put Fermi energy here, we will get Fermi energy here. So, that will give us density of levels at the Fermi energy, this can be expressed as $g(\epsilon_F) = \frac{mk_F}{\hbar^2 \pi^2} = \frac{3}{2} \frac{n}{\epsilon_F}$. This is what we will get. So, here we have seen that the density of states for 3 dimension goes for independent electron model metals as the energy power half for positive energies. A homework for you would be to find out the density of states in 1 dimensional metal and 2 dimensional metal, how it depends on energy? Ok. (Refer Slide Time: 18:30)

After finding out the meaning of the dense $g(\epsilon)$, we can now rewrite the internal energy per unit volume as $u = \int_{-\infty}^\infty d\epsilon\ g(\epsilon)\ \epsilon\ f(\epsilon)$. Because the negative energies are not going to contribute anything our $g(\epsilon)$ is 0 for negative energies. So, we can extend the integration limit to minus infinity and anyway the upper limit was plus infinity. This is going to give us the internal energy per unit volume and the number of electrons per unit volume, that can be expressed as $n = \int_{-\infty}^\infty d\epsilon\ g(\epsilon)\ f(\epsilon)$. Now, let us plot the Fermi function. How do we plot the Fermi function? Let us consider Fermi function at different temperatures; at this axis we plot the energy ϵ. So, we are considering different temperatures. Here we are plotting the Fermi function at temperature equals 0. And, if we have say this as the chemical potential, then at 0 temperature the Fermi function say is 1 here will look like this, this, this at absolute 0 temperature. But, if we have the $T > 0$, then it would look somewhat different, if this point is 1, then it would go somewhat like this at finite temperature. And, this width is $\Delta\epsilon$. So, $\Delta\epsilon \approx K_B T$. Now, let us consider a generic function $H(\epsilon)$ a generic function and we consider it is Taylor expansion about $\epsilon = \mu$. So, $H(\epsilon) = \Sigma_{n=0}^\infty$, n is the index, this is not the number density of the electrons, $H(\epsilon) = \Sigma_{n=0}^\infty \frac{d^n}{d\epsilon^n} H(\epsilon)|_{\epsilon=\mu} \frac{(\epsilon-\mu)^n}{n!}$. this is the Taylor expansion. So, if we now integrate over H that is a function of epsilon, multiplied by the Fermi function, we would get $\int_{-\infty}^\infty H(\epsilon)\ f(\epsilon)\ d\epsilon = \int_{-\infty}^\mu H(\epsilon)\ d\epsilon + \Sigma_{n=1}^\infty (K_B T)^{2n} a_n \frac{d^{2n-1}}{d\epsilon^{2n-1}} H(\epsilon)|_{\epsilon=\mu}$. (Refer Slide Time: 25:16)

If, we now simplify this further we can write this quantity $= \int_{-\infty}^\mu H(\epsilon)\ d\epsilon + \frac{\pi^2}{6}(k_B T)^2 H'(\mu) + \frac{7\pi^4}{360}(k_B T)^4 H'''(\mu) + O(\frac{K_B T}{\mu})^6$. Now, if we want to evaluate the specific heat of a metal at a given temperature. The temperature is small compared to the Fermi temperature, what is Fermi temperature? $T_F = \frac{\epsilon}{K_B}$. Now our temperature is T which is less than or a lot less than the T_F, our temperature is much smaller compared to the Fermi temperature, under that kind of a situation, we can use this Taylor expansion to write the internal energy per unit volume as $u = \int_0^\mu \epsilon\ g(\epsilon)\ d\epsilon + \frac{\pi^2}{6}(k_B T)^2 [\mu\ g'(\mu) + g(\mu)] + O(T^4)$. And, the number density as $n = \int_0^\mu g(\epsilon)\ d\epsilon + \frac{\pi^2}{6}(k_B T)^2\ g'(\mu) + O(T^4)$. So, if we want to be correct up to temperature square terms T square terms. (Refer Slide Time: 28:51)

We can write $\int_0^\mu H(\epsilon)\ d\epsilon = \int_0^{\epsilon_F} H(\epsilon)\ d\epsilon + (\mu - \epsilon_F)\ H(\epsilon_F)$, this is correct. So, this is correct up

to the second order, second power of the temperature. Now, if we apply this for the internal energy per unit volume, we can write small $u = \int_0^{\epsilon_F} \epsilon\, g(\epsilon)\, d\epsilon + \epsilon_F[(\mu - \epsilon_F)g(\epsilon_F) + \frac{\pi^2}{6}(k_B T)^2 g'(\epsilon_F)] + \frac{\pi^2}{6}(k_B T)^2 g(\epsilon_F) + O(T^4)$. Similarly, the number density can be expressed as $n = \int_0^{\epsilon_F} g(\epsilon)\, d\epsilon + [(\mu - \epsilon_F)g(\epsilon_F) + \frac{\pi^2}{6}(k_B T)^2 g'(\epsilon_F)]$. Since, we are calculating the specific heat at constant density. So, we have n is independent of temperature, but here in this term we can see that there is a temperature dependence of this density. Now, if we have by definition of C_v that is the specific heat for a constant density, the temperature is the number density is independent of temperature, then the temperature independent first terms of u and g they give us the ground state. So, ground state means at 0 temperature, at absolute 0 temperature u is just $\int_0^{\epsilon_F} \epsilon\, g(\epsilon)\, d\epsilon$ and n is just $\int_0^{\epsilon_F} g(\epsilon)\, d\epsilon$. When we increase the temperature n has to still be just this, because n for calculation of C_v cannot be temperature dependent, but u can still be temperature dependent. If, n cannot be temperature dependent, then the remaining of the terms that is these terms here this must go to 0. In other words $0 = [(\mu - \epsilon_F)g(\epsilon_F) + \frac{\pi^2}{6}(k_B T)^2 g'(\epsilon_F)]$, this quantity must be 0. And, if this quantity happens to be 0, then that gives us the value of $\mu = \epsilon_F - \frac{\pi^2}{6}(k_B T)^2 \frac{g'(\epsilon_F)}{g(\epsilon_F)}$. So, this is the expression for the chemical potential as a function of temperature. We have obtained by requiring that n remains unchanged even at higher temperature, because we are calculating C_v. So, if this is the expression for mu the chemical potential, then and we know that for free electron the density of levels, this quantity $g(\epsilon) \sim \sqrt{E}$. (Refer Slide Time: 35:17)

Then, we can write $\mu = \epsilon_F[1 - \frac{1}{3}(\frac{\pi K_B T}{e \epsilon_F})^2]$. And, we can see that μ changes very little, if we increase the temperature from absolute 0 to room temperature, at room temperature the change is about 0.01 percent just this little. And, now if we want to calculate the internal energy per unit volume that can be given as u_0, which is the energy density at ground state. The internal energy per unit volume at absolute 0 temperature is given as u naught, the first term in the expression of $u = u_0 + \frac{\pi^2}{6}(k_B T)^2 g(\epsilon_F)$,the density of levels at the Fermi energy. Now, the specific heat can be calculated as $C_v = (\frac{\partial u}{\partial T})_n$. That is given as $\frac{\pi^2}{3}k_B{}^2 T g(\epsilon_F)$. And, so, for free electrons, we can write $C_v = \frac{\pi^2}{2}(\frac{k_B T}{\epsilon_F})n k_B$, by putting the expression for g F at sorry putting the expression for $g(\epsilon_F)$ in this expression for C_v. So, we have the we know the expression for the density of levels for free electron system and putting that we obtain this that is the electronic contribution to the specific heat. And, if we consider the classical ideal gas for that $C_v = \frac{3 n k_B}{2}$, which is a lot different from this one. There is no concept of Fermi energy for classical ideal gas and entire thing is very different, we can see that considering indistinguishable particles, Pauli Exclusion Principle, and Fermi Dirac distribution function, how much it differs the electronic contribution to the specific heat differs from the classical ideal gas.