Lecture 16

- **Housekeeping: schedule for rest of quarter**
- **Review: 3D free electron gas**
- **Heat capacity of free electron gas**
- **Semi classical treatment of electric conductivity**

Review: 3D fee electron gas

This model ignores the lattice and only treats the electrons in a metal. It assumes that electrons do not interact with each other except for pauli exclusion.

- Wavelike-electrons defined by their **momentum** eigenstate k: $\psi_{\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$
- Treat electrons like quantum particle in a box: confined to a 3D box of dimensions L in every direction
- Periodic boundary conditions on wavefunction: $\psi(x+L,y,z) = \psi(x,y,z)$

$$\psi(x,y+L,z) = \psi(x,y,z)$$

$$\psi(x,y,z+L) = \psi(x,y,z)$$

➔ Permissible values of k of the form:

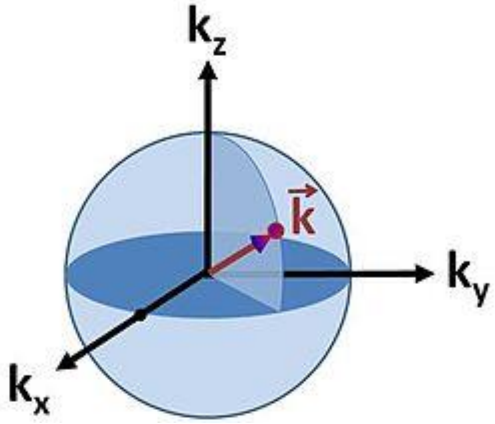
$$k_x = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \dots$$

- Free electron schrodinger's eqn in 3D + boundary conditions gives energy eigenvalues:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi_k(r) = \epsilon_k\psi_k(r)$$

$$\frac{\hbar^2}{2m}\left(k_x^2+k_y^2+k_z^2\right) = \epsilon_k = \frac{\hbar^2k^2}{2m}$$

- There are N electrons and we put them into available eigenstates following these rules:
    - Every state is defined by a unique quantized value of (k_x, k_y, k_z)
    - Every state can hold one spin up and one spin down electron
    - Assume that single-electron solution above applies to collection of electrons (i.e. electrons do not interact and change the eigenstates)
    - Fill low energy states first. In 3D, this corresponds to filling up a sphere in k space, one 'shell' at a time. Each shell is defined by a radius k, where $k^2 = k_x^2 + k_y^2 + k_z^2$, and every state in the shell has the same energy, although different combinations of k_x, k_y, k_z

- 

Important concepts:

- **Fermi energy**
- **Fermi temperature**
- **Fermi velocity**
- **Density of states**
- **Fermi surface**

Fermi energy:

When we have used up all our electrons, we are left with a filled sphere in k space with radius k_F (called the Fermi momentum) such that

$$\epsilon_F = \frac{\hbar^2}{2m} k_F^2$$

The boundary of this sphere is called the **fermi surface** and it demarcates the separation between occupied and unoccupied states.

This sphere in k-space has a volume $\frac{4}{3}\pi k_F^3$ and it is divided into voxels of volume $\left(\frac{2\pi}{L}\right)^3$

If we divide the total volume of the sphere by the volume of each 'box' and account for the fact that each box holds 2 electrons, we get back how many electrons we put in:

$$2 * \frac{\frac{4}{3}\pi k_F^3}{\left(\frac{2\pi}{L}\right)^3} = N = V k_F^3 / 3\pi^2$$

Here, $V = L^3$ is the volume of the solid. We can use this relationship to solve for k_F and show that it depends on electron density (N/V)

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

Plugging this back into the expression for ϵ_F we get:

$$\epsilon_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

Fermi temperature is the temperature equivalent of the Fermi energy: $T_F = \epsilon_F / k_B T$. Physically, the fermi temperature represents the temperature when a free electron gas starts to act like a classical gas instead of a quantum gas. As we calculated in the last lecture, a typical Fermi temperature is >30,000K, well above the melting point of any metal.

Fermi velocity describes the typical velocity of electrons at the Fermi energy, and it is given by $v_F = \hbar k_F / m$. Typical values are ~10^6 m/s.

The **density of states** describes the number of eigenstates at a given energy.

$$D(\epsilon) \equiv \frac{dN}{d\epsilon}$$

We can find it by expressing N in terms of ϵ and taking a derivative. We begin by considering a sphere in k-space with an arbitrary radius k and asking how many electrons that will hold

$$N(k) = Vk^3/3\pi^2$$

The relationship between energy and momentum in a free electron gas is pretty straightforward too (unlike with phonons):

$$\epsilon = \frac{\hbar^2 k^2}{2m}$$

Solving for k, and plugging in above we get

$$N(\epsilon) = \frac{V}{3\pi^2}\left(\frac{2m\epsilon}{\hbar^2}\right)^{3/2}$$

Now we can just take the derivative with respect to energy and get:

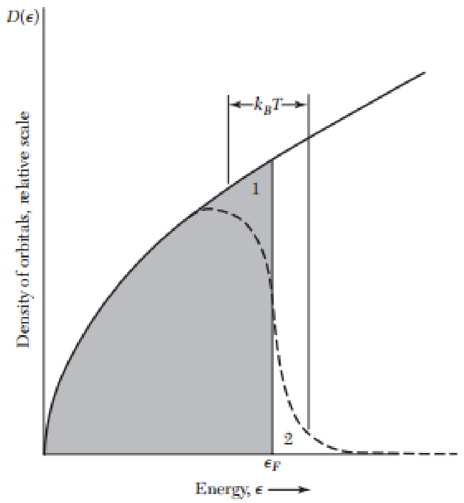
$$D(\epsilon) \equiv \frac{dN}{d\epsilon} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \epsilon^{1/2}$$

Effect of temperature

Temperature introduces a 'cutoff' by the Fermi-dirac function

$$f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1}$$

Such that some states with $\epsilon > \epsilon_F \sim \mu$ can be occupied and some states with $\epsilon < \epsilon_F \sim \mu$. Temperature only affects states roughly within $k_B T$ of the Fermi energy. Another way to think of the effect of temperature is the fuzzing out of the boundary of the Fermi surface.



Heat Capacity of free electron gas

In chapter 5, we learned about lattice heat capacity—how inputting energy into a solid raises the temperature by exciting more vibrational modes. However, in metals, particularly at low temperature, this is not the whole story, because electrons can absorb heat as well.

Qualitative derivation

In a free electron gas, only electrons with energy within $\sim k_BT$ of the Fermi level do anything. This represents a small fraction of the total electrons N, given by NT/T_F where T_F is the Fermi temperature which is usually $\sim 10^4 K$, well above the melting point of metals.

Thus, the total electronic thermal kinetic energy when electrons are heated from 0 to temperature T is

$$U_{el} \approx \left(\frac{NT}{T_F}\right) k_BT$$

The heat capacity is found from the temperature derivative:

$$C_{el} = \frac{\partial U}{\partial T} \approx Nk_BT/T_F$$

This sketch of a derivation is intended only to achieve the proper temperature dependence: $C_{el} \propto T$, which we will show more rigorously in the next section

Quantitative derivation

This derivation of electron heat capacity is applicable to the regime when a Fermi gas **does not** behave like a classical gas—when $k_BT \ll \epsilon_F$

The change in internal energy when electrons are heated up to temperature T from 0K is given by:

$$\Delta U = U(T) - U(0) = \int_0^\infty d\epsilon\ \epsilon D(\epsilon) f(\epsilon) - \int_0^{\epsilon_F} d\epsilon\ \epsilon D(\epsilon)$$

Where $f(\epsilon)$ is the Fermi function, $f(\epsilon)=\frac{1}{e^{(\epsilon-\mu)/k_BT}+1}$, which describes the occupation probability of a given energy level. It is equal to 1 for $\epsilon \ll \mu$ and 0 for $\epsilon \gg \mu$ and something in between 0 and 1 for $|\epsilon-\mu| \sim k_BT$. The parameter μ is called the "chemical potential", and it's value is temperature dependent and close to ϵ_F for most temperatures one might realistically encounter.

And $D(\epsilon)$ is the density of states, where for a 3D free electron gas, $D(\epsilon)=\frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\epsilon^{1/2}$

The integral terms above take each energy slice, multiply it by how many electrons have that energy (via the density of states multiplied by the Fermi function), and sum up over all the energies available to an electron. The second integral truncates at $\epsilon=\epsilon_F$ at its upper bound because at T=0, $\mu=\epsilon_F$, and the Fermi function is a step function which is equal to zero for $\epsilon > \epsilon_F$.

The Fermi energy is determined by the number of electrons and there are two ways to express this similarly to the integrals above:

$$N=\int_0^\infty d\epsilon\ D(\epsilon)f(\epsilon)=\int_0^{\epsilon_F} d\epsilon\ D(\epsilon)$$

The right-most integral is the total number of electrons at zero temperature, and the other integral is the total number of electrons at finite temperature. They must be equal since electrons (unlike phonons) cannot be spontaneously created.

We now multiply both integrals by ϵ_F, which is a constant. This is just a mathematical trick.

$$\int_0^\infty d\epsilon\ \epsilon_F D(\epsilon)f(\epsilon)=\int_0^{\epsilon_F} d\epsilon\ \epsilon_F D(\epsilon)$$

And split up the first integral:

$$\int_0^{\epsilon_F} d\epsilon\ \epsilon_F D(\epsilon)f(\epsilon)+\int_{\epsilon_F}^\infty d\epsilon\ \epsilon_F D(\epsilon)f(\epsilon)=\int_0^{\epsilon_F} d\epsilon\ \epsilon_F D(\epsilon)$$

$$\int_0^{\epsilon_F} d\epsilon\ \epsilon_F D(\epsilon)\ (f(\epsilon)-1)+\int_{\epsilon_F}^\infty d\epsilon\ \epsilon_F D(\epsilon)f(\epsilon)=0$$

Use this to rewrite the expression for ΔU

$$\Delta U=\int_0^\infty d\epsilon\ \epsilon D(\epsilon)f(\epsilon)-\int_0^{\epsilon_F} d\epsilon\ \epsilon D(\epsilon)$$

$$\Delta U=\int_{\epsilon_F}^\infty d\epsilon\ \epsilon D(\epsilon)f(\epsilon)+\int_0^{\epsilon_F} d\epsilon\ \epsilon D(\epsilon)f(\epsilon)-\int_0^{\epsilon_F} d\epsilon\ \epsilon D(\epsilon)+\int_0^{\epsilon_F} d\epsilon\ \epsilon_F D(\epsilon)\ (f(\epsilon)-1)$$
$$+\int_{\epsilon_F}^\infty d\epsilon\ \epsilon_F D(\epsilon)f(\epsilon)$$

$$\Delta U=\int_{\epsilon_F}^\infty d\epsilon\ (\epsilon-\epsilon_F)D(\epsilon)f(\epsilon)-\int_0^{\epsilon_F} d\epsilon\ (\epsilon_F-\epsilon)D(\epsilon)[1-f(\epsilon)]$$

The first integral describes the energy needed to take electrons from the Fermi level to higher energy levels, and the second integral describes the energy needed to excite electrons from lower energy levels up to the Fermi level.

The heat capacity is found by differentiating ΔU with respect to temperature, and the only terms in the integrals which have temperature dependence are $f(\epsilon)$

$$C_{el} = \frac{\partial \Delta U}{\partial T} = \int_0^\infty d\epsilon\ (\epsilon - \epsilon_F) D(\epsilon) \frac{\partial f(\epsilon, T)}{\partial T}$$

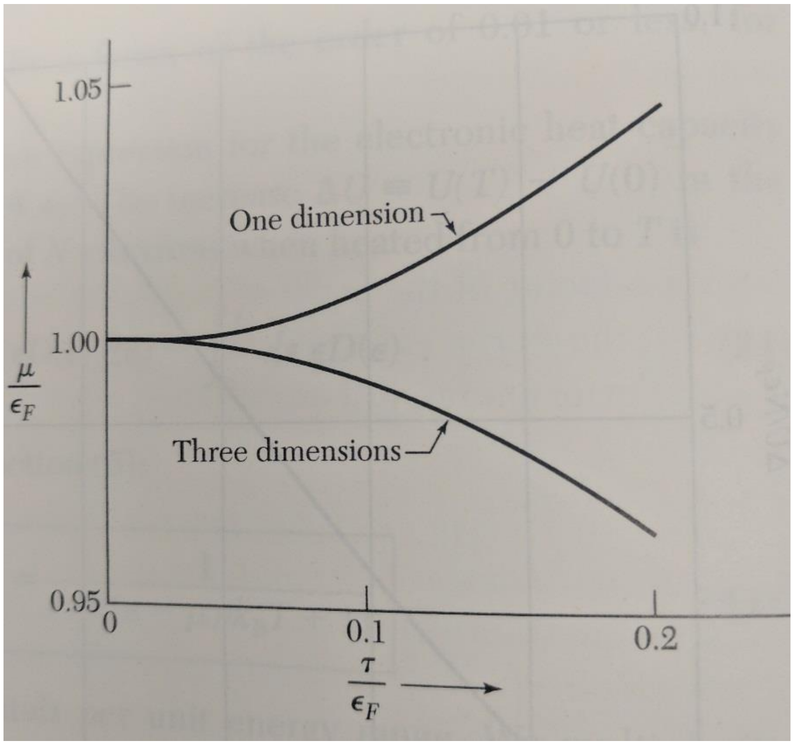
Where we have spliced the integrals back together after the temperature derivative produced the same integrand

At low temperature, $\mu \sim \epsilon_F$

And the temperature derivative of $f(\epsilon, T)$ is peaked close to ϵ_F, so the density of states can come out of the integral (this is another way of saying that only electrons very close to the Fermi level matter)

$$C_{el} \approx D(\epsilon_F) \int_0^\infty d\epsilon\ (\epsilon - \epsilon_F) \frac{\partial f(\epsilon, T)}{\partial T}$$

To solve this integral, first set $\mu = \epsilon_F$. This is a decent approximation for most ordinary metals at temperatures we might realistically encounter (remember that $\frac{k_B T}{\epsilon_F} = \frac{\tau}{\epsilon_F} \sim 0.01$ at room temperature)



$$\frac{\partial f}{\partial T} = \frac{\left(\frac{\epsilon - \epsilon_F}{k_B T^2}\right) e^{\frac{\epsilon - \epsilon_F}{k_B T}}}{\left(e^{\frac{\epsilon - \epsilon_F}{k_B T}} + 1\right)^2}$$

Define a new variable x and plug back into integral

$$x \equiv \frac{\epsilon - \epsilon_F}{k_B T}$$

$$C_{el} \approx D(\epsilon_F) k_B^2 T \int_{-\epsilon_F/k_B T}^{\infty} dx \, \frac{x^2 e^x}{(e^x + 1)^2}$$

Since we are working at low temperature, we can replace the lower bound of the integral by $-\infty$ because $k_B T \ll \epsilon_F$ (our starting assumption)

$$C_{el} \approx D(\epsilon_F) k_B^2 T \int_{-\infty}^{\infty} dx \, \frac{x^2 e^x}{(e^x + 1)^2} = D(\epsilon_F) k_B^2 T \frac{\pi^2}{3}$$

We can further express the Density of states at the Fermi energy in another way:

$$D(\epsilon_F) = \frac{3N}{2\epsilon_F} = 3N/2k_B T_F$$

This gives $C_{el} = \frac{1}{2}\pi^2 N k_B T/T_F$

This is very similar to our 'qualitative derivation' from earlier, except the prefactors are exact. Again, the key thing to remember is that for a 3D free electron gas, the heat capacity of electrons increases linearly with temperature.

Putting it together: heat capacity from electrons and phonons

In a metal, both electrons and phonons contribute to the heat capacity, and their respective contributions can simply be added together to get the total. At low temperature ($T \ll \theta, T \ll T_F$) we can write an exact expression for the total heat capacity

$$C = C_{phonon} + C_{el} = \frac{12\pi^4}{5} N_{primitive\ cells} k_B \left(\frac{T}{\theta}\right)^3 + \frac{1}{2}\pi^2 N_{electrons} k_B T/T_F$$

This can be rewritten in terms of new constants, A and γ

$$C = AT^3 + \gamma T$$

At very low temperature, the electronic contribution (T-linear) will dominate and when the temperature increases a little, the phonon contribution to specific heat (T^3) will dominate. At room temperature, the phonon specific heat typically dominates over the electron contribution, even if we are outside the regime where the approximation $T \ll \theta$ holds.

$$\frac{C}{T} = \gamma + AT^2$$

If C/T is plotted as a function of T^2, A will give the slope, and γ will give the y-intercept. This is actually observed in many/most metals.

Q: what is γ in an insulator?

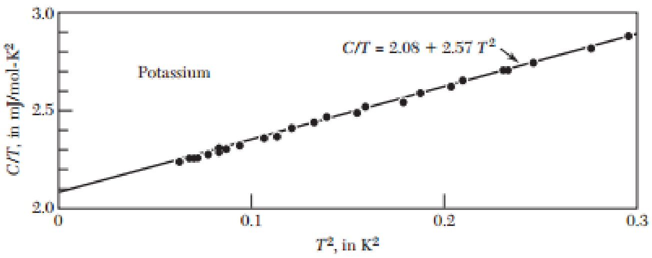


Figure 9 Experimental heat capacity values for potassium, plotted as C/T versus T^2. (After W. H. Lien and N. E. Phillips.)

The experimental value of γ is very important because it is a customary way of extracting the effective electron mass. In real metals, the electrons do not always behave as if they have $m = m_e$. Sometimes they behave as if they have a heavier mass, and this is called the "effective mass" m*. In some compounds called 'heavy fermion' compounds, electrons can behave as if they have effective masses up to 1000x the free electron mass! An enhanced effective mass can be caused by interactions between electrons and other electrons or electrons and the periodic lattice potential. When heat capacity is used to extract an effective mass, this is called the "thermal mass", m_{th}.

$$\frac{m_{th}}{m_e} = \frac{\gamma_{observed}}{\gamma_{free}}$$

γ is related to an electron mass because it is inversely proportional to the Fermi temperature