Chapter # 6:
The Free Electron Model

Lecture 2: The Free Electron Model: Quantum Description (Sommerfeld Model)

Fermi Gas, Energy Levels, and Density of States

As we discussed in the last lecture, the classical model failed because it did not describe how electrons are ***distributed in energy***. We now use quantum mechanics to describe this distribution correctly.

6-6 Fermi Gas of Free Electrons

The classical free electron model (Drude model, 1900) successfully explains some electrical and thermal properties of metals; however, it fails to account for several important experimental observations, particularly the electronic contribution to heat capacity and the correct distribution of electron energies.

To resolve these limitations, Arnold Sommerfeld developed a quantum version of the free electron model in 1928. **By incorporating quantum mechanics and the Pauli exclusion principle, this model provides a more accurate description of the behavior of electrons in metals.**

The Sommerfeld model is a quantum extension of the free electron model. In this model, conduction electrons are treated as free particles moving inside the metal, with negligible interaction with the ion cores.

As in the free electron model, electrons move freely within the material, while the positive ions form a uniform background. This gives rise to the picture of a "sea of free electrons" in which the ions are embedded.

The periodic potential of the lattice is approximated as constant, so that the total energy of the electrons is purely kinetic.

How is the electron described mathematically?

Using the **Schrödinger equation**:

$$H\psi = E\psi$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right)\psi_i = E_i\psi_i \qquad (1)$$

where:

- i: refers to different states
- ψ: electron wave function

- E: total energy
- V: crystal potential

Knowing ψ_i and E_i ⇒ knowing the electronic properties

Thus, Schrödinger's equation can be written as:

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i = E_i\psi_i$$

$$E = \frac{\hbar^2 k^2}{2m} \qquad (2)$$

We replaced the periodic lattice potential with a constant—this is the key approximation of the Sommerfeld model.

- **Boundary conditions:**

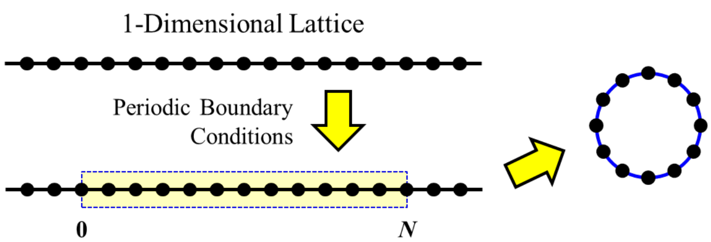
A solution to this equation can be written as:

$$\psi_i(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}.\vec{r}} \qquad (3)$$

Boundary Conditions (Born–von Karman):

$$\psi(x) = \psi(x + L_x)$$

$$\psi(y) = \psi(y + L_y) \qquad (4)$$
$$\psi(z) = \psi(z + L_z)$$



This implies:

$$e^{ik_x x} = e^{ik_x(x+L_x)}$$

This condition is satisfied when: $e^{ik_x L_x} = 1$ (5)

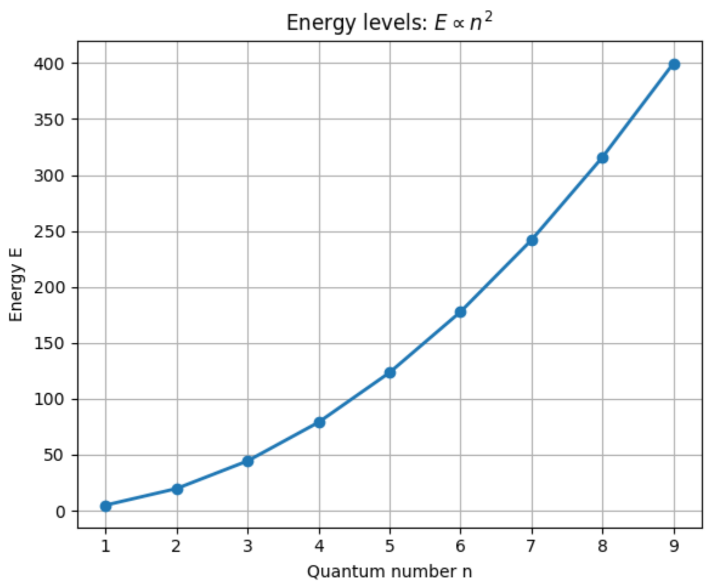
Thus, the allowed values are: $k_x L = 2\pi n_x$ (6)

Similarly: $k_y L = 2\pi n_y$ and $k_z L = 2\pi n_z$

Thus, the Energy Expression can be written as follows:

$$E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2) = \frac{2\hbar^2}{m}\left(\frac{\pi}{L}\right)^2 n^2$$

$$E_n = \frac{2\hbar^2}{m}\left(\frac{\pi}{L}\right)^2 n^2 \quad (7)$$



This relation shows that energy is **quantized** in the free-electron Fermi-gas model. We find that electrons occupy distinct and well-defined energy levels, consistent with the **Pauli exclusion principle**, which states that each energy level can accommodate at most two electrons, one with spin-up and the other with spin-down.

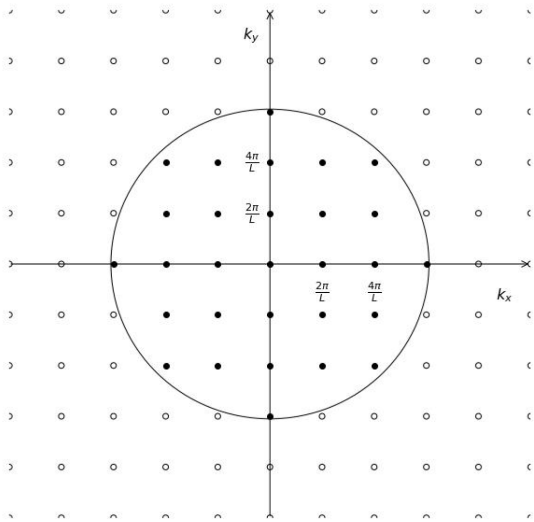
As a result of this distribution, electrons begin filling the lowest energy levels first, followed by higher levels, at absolute zero, until all electrons are accommodated. The highest occupied energy level is called the **Fermi level** or **Fermi energy**.

The Fermi energy is the most important energy scale in metals, as it determines which electrons participate in physical processes.

6-7 Density of States

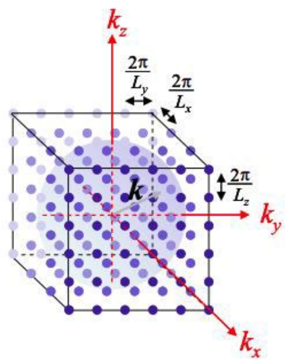
In this section, we discuss the number of states within the Fermi energy.

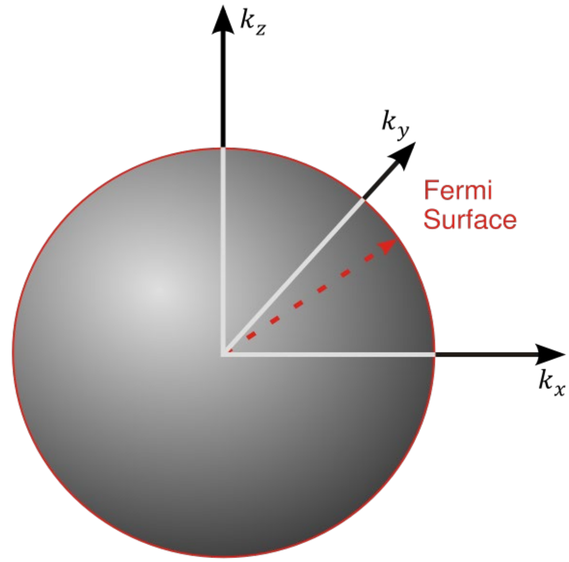
First, we represent the values of k in two dimensions, where each point represents an allowed k-value as defined in equation (6), as shown in Figure 1.



Each allowed value of k represents one quantum state, so counting states becomes equivalent to counting points in k-space.

Then, we extend this to **k-space**, where the allowed values form a regular lattice (Figure 2).





Now, consider a finite sample (a sphere of radius R) containing N electrons, with Fermi energy E_F. At absolute zero, all states below E_F are occupied:

$$R = \sqrt{\frac{2mE_F}{\hbar^2}} \qquad (8)$$

Where: $R^2 = k_x^2 + k_y^2 + k_z^2$

Thus, all values of k inside the sphere satisfy:

$$\frac{\hbar^2 k^2}{2m} < E_F \qquad (9)$$

Question:

How many k-points lie inside this sphere?

$$\frac{\hbar^2 k_F^2}{2m} \leq \frac{\hbar^2 R^2}{2m} \leq E_F \qquad (10)$$

We use the same method as for counting vibrational modes of phonons.

Each allowed k-state occupies a volume: $\left(\frac{2\pi}{L}\right)^3$

The volume of the sphere of radius R is: $\frac{4}{3}\pi R^3$

Number of States:

$$N = 2.\frac{\frac{4}{3}\pi\left(\frac{2mE_F}{\hbar^2}\right)^{3/2}}{\left(\frac{2\pi}{L}\right)^3} = \frac{V}{3\pi^2}\left(\frac{2mE_F}{\hbar^2}\right)^{3/2} \qquad (11)$$

where $V=L^3$.

The factor 2 is due to electron spin (two states per k).

Fermi Energy:

Thus, we can get the Fermi energy from eq. (11):

$$E_F = \left(\frac{3N\pi^2}{V}\right)^{2/3} . \frac{\hbar^2}{2m} \qquad (12)$$

This shows that the **Fermi energy depends only on electron density**: $\left(\frac{N}{V}\right)$

Density of States:

The density of states determines how many electrons can occupy a given energy range.

$$g(E) = \frac{dN}{dE}$$

$$g(E)dE = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}dE$$

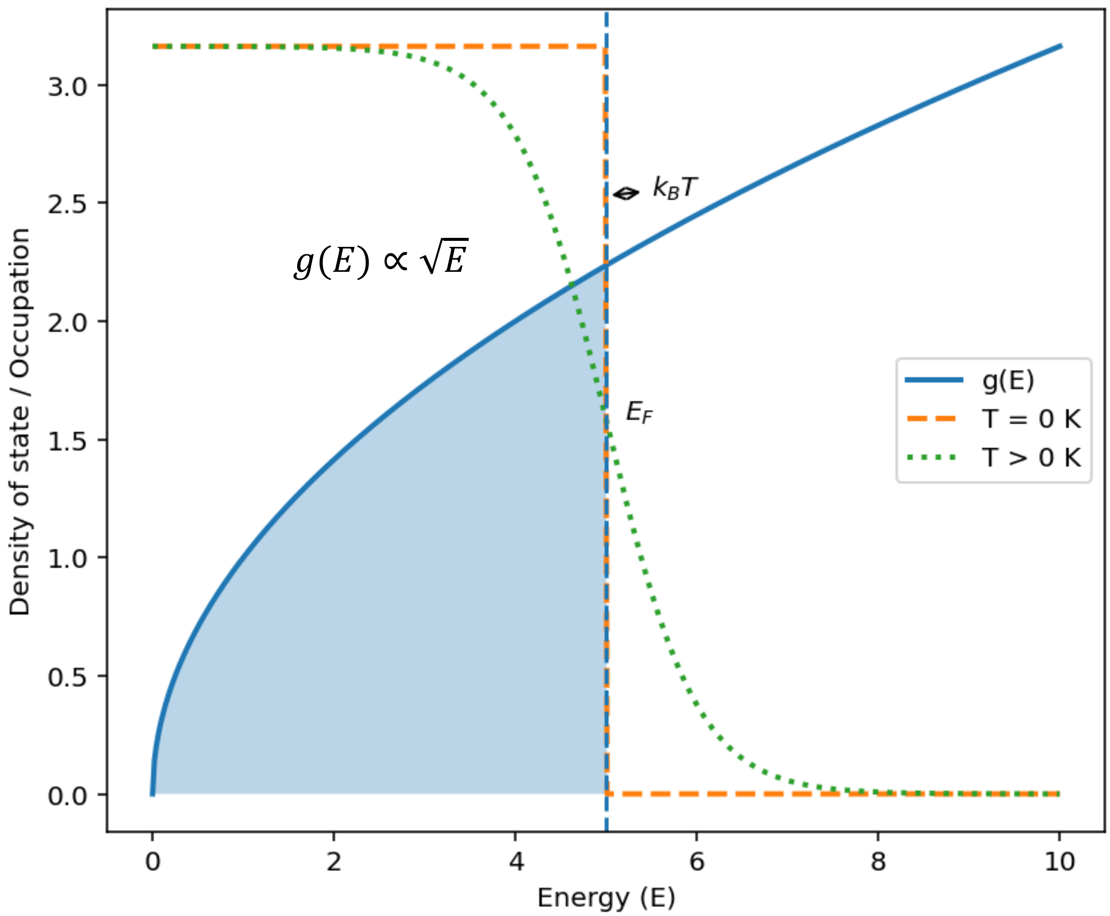
$$g(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E} \qquad (13)$$

Thus:

$$g(E) \propto \sqrt{E} \qquad (14)$$

This means that the curve g(E) is parabolic.

This means that the number of available states increases with energy, so higher energies contain more accessible states for electrons.



At T=0, all states below E_F are completely filled, while those above are empty. At finite temperature, the distribution becomes smooth, and only electrons near E_F are affected.

Density of States: Phonons vs Electrons

Aspect	Phonons (Debye Model)	Electrons (Free Electron Model)
Physical entity	Lattice vibrations (quanta of sound waves)	Particles (fermions)
Wavevector space	q-space	k-space
State counting	Each q → one vibrational mode	Each k → one quantum state
Dispersion relation	($\omega \propto k$) (linear, low (k))	($E \propto k^2$) (quadratic)
Energy variable	$\hbar\omega$	E
Density of states	$g(\omega) \propto \omega^2$	$g(E) \propto \sqrt{E}$
Origin of the DOS shape	Linear dispersion	Quadratic dispersion
Occupation statistics	Bose–Einstein	Fermi–Dirac

Occupancy limit	Unlimited per state	Max 2 electrons (spin up/down)
Physical consequence	Heat capacity (~ T^3) (low (T))	Heat capacity (~ T) (low (T))