Free Electrons in Metal

- Since the potential energy U = 0, the Schrödinger equation for a free electron has the following form:
- m is the mass of an electron.

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r})$$

Solution of Schrödinger equation

- Wave functions satisfying Schrödinger equation are plane waves
- The condition of normalization of the ψ - function is performed by integration over the volume L^3 of specimen

$$\psi(\mathbf{r}) = Ce^{i\mathbf{k}\cdot\mathbf{r}}$$

$$\psi = \frac{1}{L^{3/2}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

The boundary condition

- the wave vector components satisfy boundary conditions which are

  ψ = 0 at x = 0 and x = L

- the components of the wave vector are quantum numbers of this problem

$$\left.\begin{aligned} k_x &= (2\pi n_x / L) \\ k_y &= (2\pi n_y / L) \\ k_z &= (2\pi n_z / L) \end{aligned}\right\}$$

$$\psi = \frac{1}{L^{3/2}} \exp\left[i \frac{2\pi}{L} \left(n_x x + n_y y + n_z z \right) \right]$$

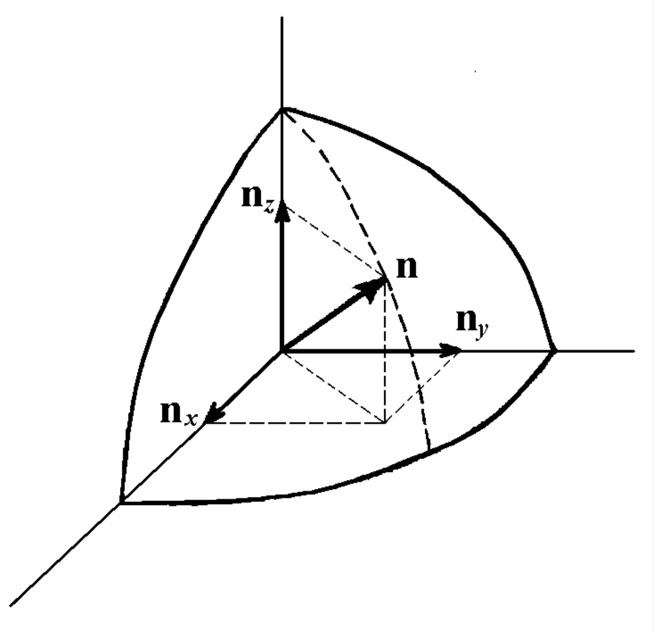
The energy level E_n

- the energy levels are quantized, and each is characterized by a set of three quantum numbers (one for each degree of freedom) and the spin quantum number m_s.

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

quantum number space

- The energy level E_n called "*energy state*" and represented by a point in quantum number space corresponds to each set of quantum numbers
- surface of equal energy has the shape of a sphere with radius *n*



$$n^2 = n_x^2 + n_y^2 + n_z^2$$

quantum state

- The number of quantum states η with energy equal to or smaller than E_n is determined by the double volume of the sphere

$$\eta = 2\times\frac{4}{3}\pi n^3 = \frac{8}{3}\pi\left(n_x^2+n_y^2+n_z^2\right)^{3/2} =$$

$$= \frac{8}{3}\pi V\frac{(2m)^{3/2}}{(2\pi\hbar)^3}E^{3/2}$$

The density of states

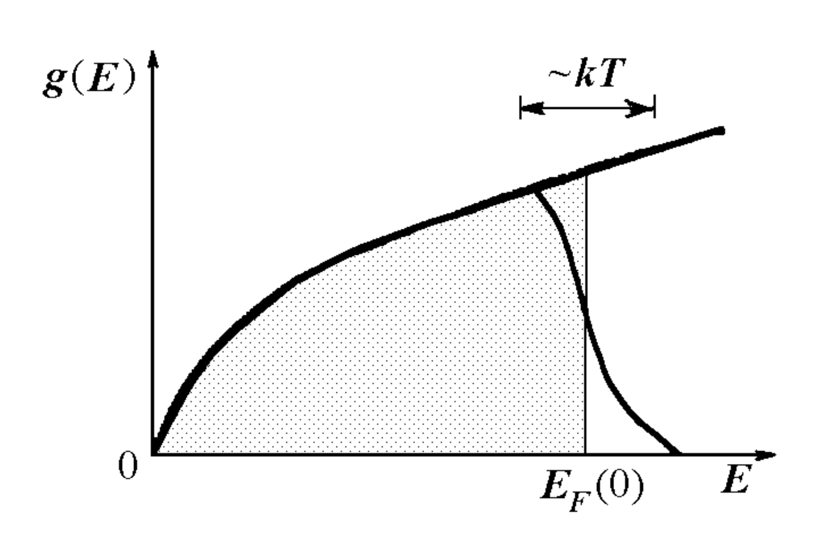
- differentiation of η with respect to the energy *E* provides the number of energy states per unit energy in the energy interval *dE*, i.e. the density of state, *g* (*E*)

$$\frac{d\eta}{dE} = g(E) = 4\pi V \frac{(2m)^{3/2}}{(2\pi\hbar)^3} =$$

$$= \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

Density of state g(E) versus energy E

- The density of states plotted versus the energy is a parabola.
- The hatched area within the curve is the number of states filled with electrons at absolute zero
- $E_F(0)$ is the Fermi level
- T_F is the Fermi temperature



$$T_F = \frac{E_F(0)}{k}$$

the Fermi surface

- An isoenergetic surface in k – space ($\mathbf{k} = \mathbf{p}/\hbar$) corresponding to the energy Fermi E_F is called the Fermi surface. For free electrons this surface has the form of sphere.
- The Fermi surface separates the states filled with electrons from the unfilled states.

$$E_F = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$$

What is Metal?

- A metal is a system with a very large number of energy levels.
- Electrons fill these levels in accordance with the Pauli Exclusion Principle, beginning with $E = 0$ and ending with E_F.
- At $T = 0$ K, the levels below the Fermi energy are filled up and those above the Fermi energy are empty.

Discrete structure?

- The levels are discrete but so close together that the electrons have an almost continuous distribution of energy.
- At 300 K, a very small fraction of valence electrons are excited above the Fermi energy.