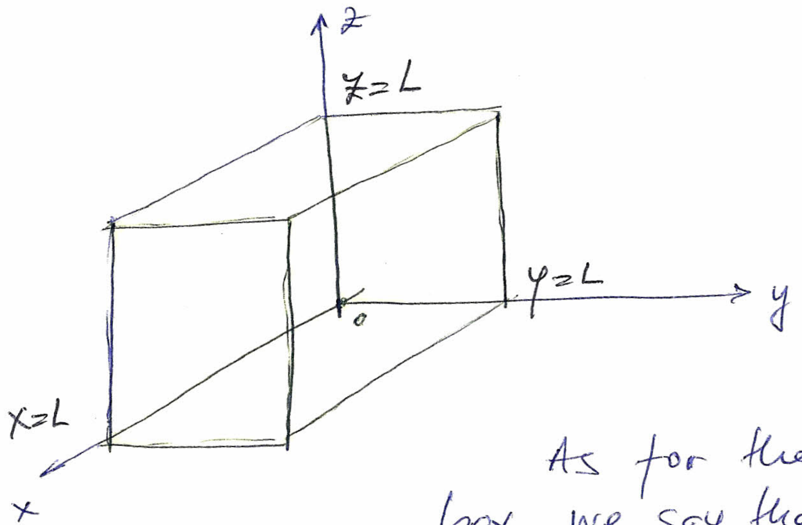
Particle in a 3D box

Consider a particle enclosed within a cubical box of side L. This could represent an electron that is free to move anywhere within the interior of a solid metal cube but cannot escape the cube. We choose the origin at one corner of the box



The particle is contained in the region:

$$\begin{cases} 0 \leq x \leq L \\ 0 \leq y \leq L \\ 0 \leq z \leq L \end{cases}$$

As for the particle in the 1D box, we say that the potential energy is zero in the box and infinite outside

The 3D Schrödinger equation is:

$$\boxed{-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi(x,y,z)}{\partial x^2}+\frac{\partial^2\psi(x,y,z)}{\partial y^2}+\frac{\partial^2\psi(x,y,z)}{\partial z^2}\right)+ U(x,y,z)\,\psi(x,y,z)=E\,\psi(x,y,z)}$$

because outside of the box $U(x,y,z)=\infty$, $\psi(x,y,z)$ has to be zero and hence the density of probability $|\psi(x,y,z)|^2$ is zero outside the box.

Inside the box: we will separate the variables so that:

$$\boxed{\psi(x,y,z)=X(x)\,Y(y)\,Z(z)}$$

and $U(x,y,z)=0$ $\Rightarrow$

which substituted in the Schrödinger eq. will give:

$$-\frac{\hbar^2}{2m}\left[Y(y)Z(z)\frac{d^2X(x)}{dx^2}+X(x)Z(z)\frac{d^2Y(y)}{dy^2}+X(x)Y(y)\frac{d^2Z(z)}{dz^2}\right]=$$

$$= E\,X(x)\,Y(y)\,Z(z) \qquad \Big|\ \frac{1}{X(x)Y(y)Z(z)}$$

$$\Rightarrow \left(-\frac{\hbar^2}{2m}\frac{1}{X(x)}\frac{d^2X(x)}{dx^2}\right)+\left(-\frac{\hbar^2}{2m}\frac{1}{Y(y)}\frac{d^2Y(y)}{dy^2}\right)+$$

$$+\left(-\frac{\hbar^2}{2m}\frac{1}{Z(z)}\frac{d^2Z(z)}{dz^2}\right)=E$$

Let: $\boxed{E = E_x + E_y + E_z}$ → tells us how much of the total energy is due to motion along x, y and z. (because U inside = 0 the energy is purelly kinetic)

$$\begin{cases} -\dfrac{\hbar^2}{2m}\dfrac{d^2X(x)}{dx^2} = E_x \\[2ex] -\dfrac{\hbar^2}{2m}\dfrac{d^2Y(y)}{dy^2} = E_y \\[2ex] -\dfrac{\hbar^2}{2m}\dfrac{d^2Z(z)}{dz^2} = E_z \end{cases}$$

To satisfy the boundary conditions:

$\psi(x,y,z) = X(x)\,Y(y)\,Z(z) = 0$ outside the box

we have:

$$\begin{cases} X(x)\big| = 0 & \text{at } x=0 \text{ and } x=L \\ Y(y) = 0 & \text{at } y=0 \text{ and } y=L \\ Z(z) = 0 & \text{at } z=0 \text{ and } z=L \end{cases}$$

⇒ from a complicated 2^{nd} differential eq with 3 variables we deduced a much simple set of 2^{nd} order differential equation, each one with one variable (independent equations).

The solutions:

$$X(x) = Ae^{ikx} + Be^{-ikx}$$

$$X(0) = X(L) = 0 \quad \Rightarrow \quad A + B = 0 \; ; \quad \underline{A = -B}$$

and $\quad e^{ikL} - e^{-ikL} = 0 \quad \Leftrightarrow$

$$2i \sin kL = 0 \quad \Rightarrow \quad kL = n_x \pi \quad \Rightarrow$$

$$K_x = \frac{n_x \pi}{L} \qquad n_x = 1, 2, 3, \ldots$$

$$\Rightarrow X(x) = A(e^{ik_x x} - e^{-ik_x x}) =$$

$$= 2iA \sin \frac{n_x \pi}{L} x = C \sin \frac{n_x \pi}{L} x$$

$$\Rightarrow \begin{cases} X_{n_x}(x) = C_x \sin \dfrac{n_x \pi x}{L} & n_x = 1, 2, 3, \ldots \\ Y_{n_y}(x) = C_y \sin \dfrac{n_y \pi y}{L} & n_y = 1, 2, 3 \ldots \\ Z_{n_z}(x) = C_z \sin \dfrac{n_z \pi z}{L} & n_z = 1, 2, 3, \ldots \end{cases}$$

The corresponding energy values are: $\quad E_i = \dfrac{\hbar^2 k_i^2}{2m}$, $i = x, y, z$

$$\begin{cases} E_x = \dfrac{n_x^2 \pi^2 \hbar^2}{2mL^2} & (n_x = 1, 2, 3, \ldots) \\ E_y = \dfrac{n_y^2 \pi^2 \hbar^2}{2mL^2} & (n_y = 1, 2, 3, \ldots) \\ E_z = \dfrac{n_z^2 \pi^2 \hbar^2}{2mL^2} & (n_z = 1, 2, 3, \ldots) \end{cases}$$

Obs: There is only 1 quantum number for the particle in the 1D box but THREE quantum numbers n_x, n_y, n_z for the 3D box.

$\Rightarrow \psi(x,y,z) = X(x)\, Y(y)\, Z(z)$ and note $C = C_x C_y C_z$

$$\Rightarrow \boxed{\psi(x,y,z) = C \sin\frac{n_x \pi x}{L} \sin\frac{n_y \pi y}{L} \sin\frac{n_z \pi z}{L} \qquad n_x = 1,2,3\ldots, \quad n_y = 1,2,3\ldots \quad n_z = 1,2,3\ldots}$$

The stationary-state wave functions for a particle in a 1D box were analogous to standing waves on a string. Similarly, in the 3D case (box) $\psi(x,y,z)$ is the analogous of a standing electromagnetic wave in a cubic cavity.

$$|\psi(x,y,z)|^2 = |C|^2 \sin^2\frac{n_x \pi x}{L} \sin^2\frac{n_y \pi y}{L} \sin^2\frac{n_z \pi z}{L}$$

represents the density probability to find the particle

$\Rightarrow$ there are zones where $|\psi(x,y,z)|^2 = 0$

Normation:

$$\int |\psi_{n_x,n_y,n_z}(x,y,z)|^2 dV = 1 \iff$$

(the particle is compulsory inside the box)

$$|C|^2 \int_0^L \int_0^L \int_0^L \sin^2\frac{n_x \pi x}{L} \sin^2\frac{n_y \pi y}{L} \sin^2\frac{n_z \pi z}{L}\, dx\,dy\,dz = 1$$

$$|C|^2\left(\int_0^L \sin^2\frac{n_x\pi x}{L}\,dx\right)\left(\int_0^L \sin^2\frac{n_y\pi y}{L}\,dy\right)\left(\int_0^L \sin^2\frac{n_z\pi z}{L}\,dz\right)=1$$

$$\sin^2\theta=\frac{1-\cos 2\theta}{2} \qquad \text{e.g. } \theta=\frac{n_x\pi x}{L}$$

$$\Rightarrow \int_0^{n_x\pi}\sin^2\theta\,d\theta=\frac{L}{2}$$

$$\Rightarrow |C|^2\frac{L^3}{8}=1 \quad\Rightarrow\quad \boxed{C=\left(\frac{2}{L}\right)^{3/2}}$$

$$\Rightarrow \boxed{\psi_{n_x,n_y,n_z}(x,y,z)=\left(\frac{2}{L}\right)^{3/2}\sin\frac{n_x\pi x}{L}\sin\frac{n_y\pi y}{L}\sin\frac{n_z\pi z}{L}}$$

Energy levels, degenerancy, symmetry

The allowed energy for a particle of mass m in the box are:

$$\boxed{E_{n_x,n_y,n_z}=\frac{(n_x^2+n_y^2+n_z^2)\pi^2\hbar^2}{2mL^2}} \qquad \begin{aligned} n_x&=1,2,3,\ldots\\ n_y&=1,2,3,\ldots\\ n_z&=1,2,3,\ldots\end{aligned}$$

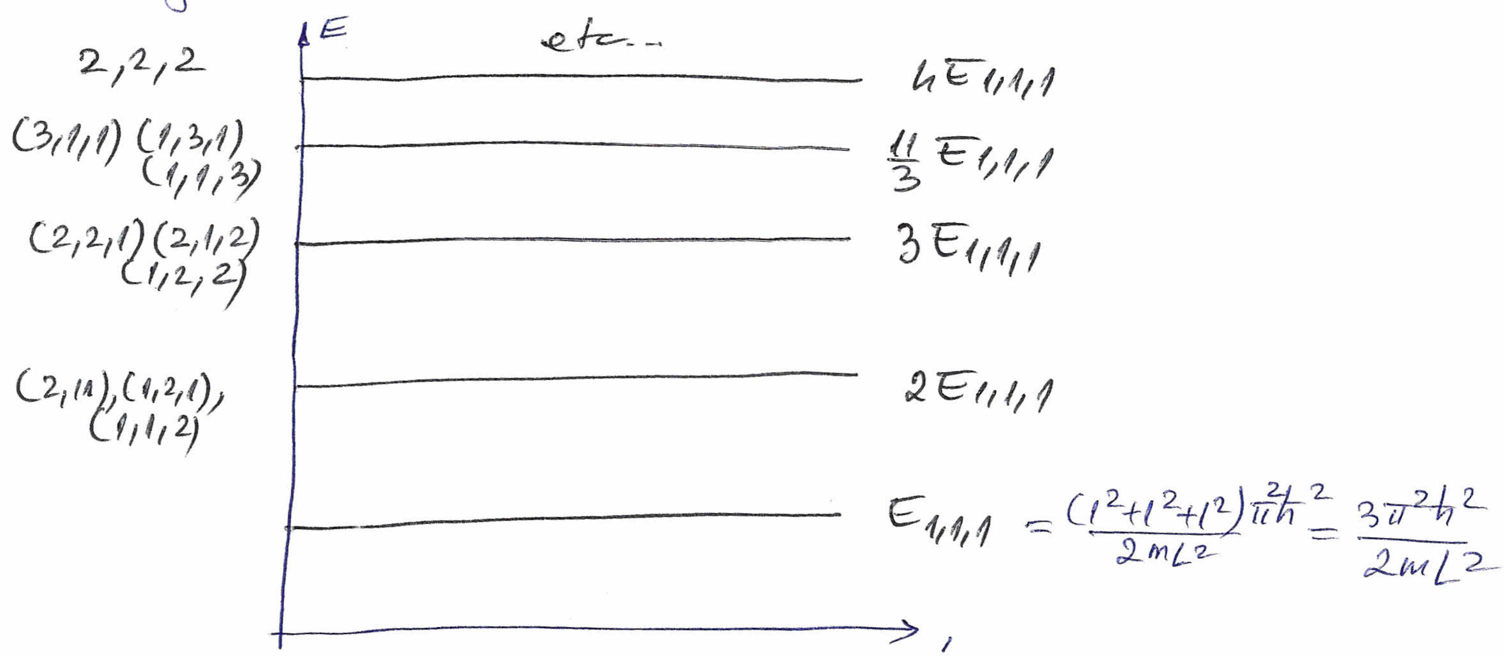
Most energy levels correspond to more the 1 set of quantum numbers:, so that $n_x^2+n_y^2+n_z^2$ is the same:

e.g: $(n_x,n_y,n_z)=(2,1,1),(1,2,1),(1,1,2)$ are degenerate

Having two or more distinct quantum states with the same energy is called <u>degenerancy</u>.

The reason of the degenerancy is the symmetry
For the cubic box all sides of the box have the same dimensions.

For example each of the states $(2,1,1)$, $(1,2,1)$, $(1,1,2)$ can be transformed from one to the other by a symmetry operation, which is a rotation by 90°. The rotation does not change the energy, so the three states are degenerated.



Since the degenerancy is a consequence of the symmetry, we can remove the degenerancy by breaking the symmetry (e.g. making the box asymmetric) $\Leftrightarrow$ impose different L_x, L_y, L_z

$$\Rightarrow \boxed{E_{n_x, n_y, n_z} = \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)\frac{\pi^2\hbar^2}{2m}} \quad \begin{cases} n_x = 1,2,3\ldots \\ n_y = 1,2,3,\ldots \\ n_z = 1,2,3,\ldots \end{cases}$$

Free-Electron Model of Metals

This model assumes that the electrons are completely free inside the metal and they do not interact with ions and with each other, but there are INFINITE potential energy barriers at the surfaces. The idea is that an electron moves so rapidly inside the metal that it "sees" the effect of the ions and other electrons as a uniform potential energy function whose value one can fix to zero.

$\Rightarrow$ the electron in a metal $\Leftrightarrow$ electron in a 3D box.

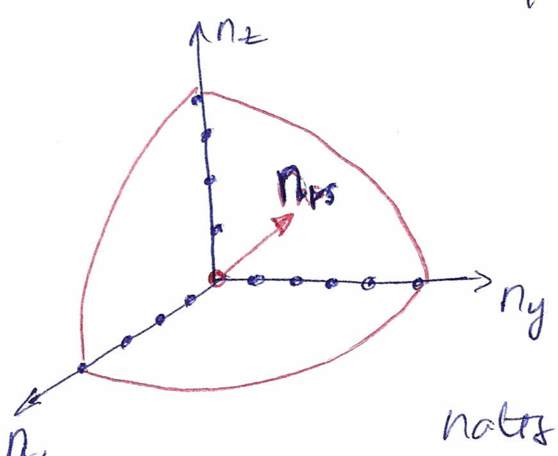
$$E_{n_x,n_y,n_z} = \frac{n_x^2+n_y^2+n_z^2}{2mL^2} \qquad \begin{cases} n_x = 1,2,3,\dots \\ n_y = 1,2,3,\dots \\ n_z = 1,2,3,\dots \end{cases}$$

Density of states

= the number of states per unit energy range:

$$\boxed{g(E) = \frac{dn}{dE}}$$

Consider a 3D space with coordinates n_x, n_y, n_z



The radius n_{rs} of a sphere centered in the origin is:

$$n_{rs} = \sqrt{(n_x^2+n_y^2+n_z^2)}$$

Each point with integer coordinates in this space represents one spatial quantum state $(n_x, n_y, n_z) \longrightarrow \psi_{n_x,n_y,n_z}$.

Thus, each point represents one unit of volume in the space n_x, n_y, n_z and the total number of point with integer coordinates equals the total volume of a sphere, but because n_x, n_y, n_z are only positive we have to count only $\frac{1}{8}$ of volume $\Leftrightarrow$

$$\frac{1}{8}\left(\frac{4\pi n_{rs}^3}{3}\right) = \frac{1}{6}\pi n_{rs}^3 .$$

If the particles are electrons, (we'll see that each state correspond to two states with opposite spin ($m_s = \pm 1/2$) $\Rightarrow$ the total number of states is multiplied by two $\Rightarrow$

$$\underline{n = \frac{\pi n_{rs}^3}{3}}$$

The energy E of states at the surface of the sphere can be expressed in terms of n_{rs}

$$E = \frac{n_{rs}^2 \pi^2 \hbar^2}{2mL^2} \Rightarrow n_{rs} = \left(\frac{2mL^2 E}{\pi^2 \hbar^2}\right)^{3/2}$$

$$\Rightarrow \boxed{n = \frac{(2m)^{3/2} L^3 E^{3/2}}{3\pi^2 \hbar^2} = \frac{(2m)^{3/2} V E^{3/2}}{3\pi^2 \hbar^2}}$$

$V = L^3$

gives the total number of states with energy $\leq E$.

$\Leftrightarrow$ by differentiating both sides

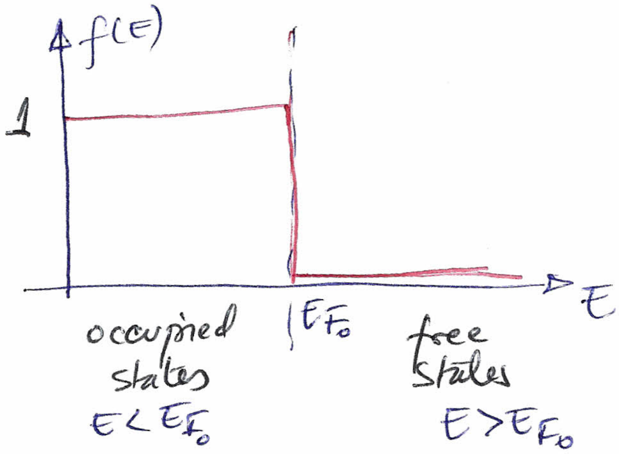
$$dn = \frac{(2m)^{3/2} V E^{1/2}}{2\pi^2 \hbar^3} dE \Rightarrow$$

The density of states for the free electrons is:

$$\boxed{g(E) = \frac{dn}{dE} = \frac{(2m)^{3/2} V}{2\pi^2 \hbar^3} E^{1/2}}$$

Fermi-Dirac distribution

We need to know how the electrons are distributed among the various quantum states at any given temperature



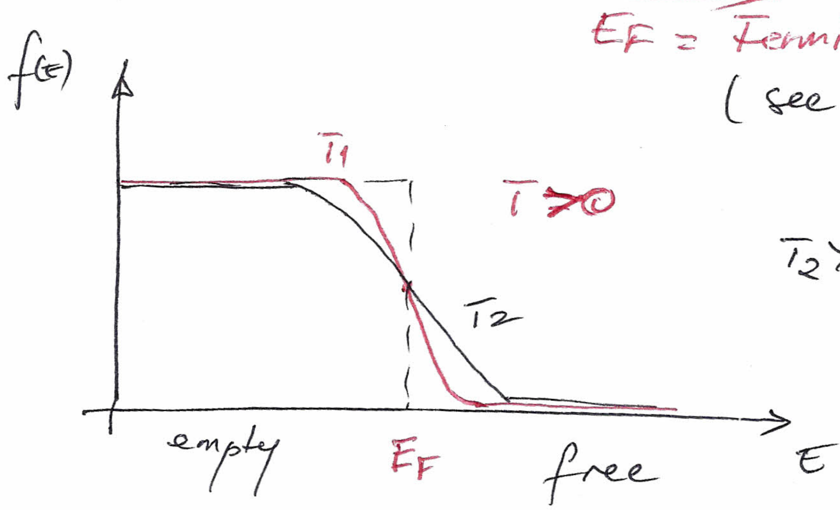
The probability distribution for occupation of free electron states at absolute zero (T=0K)

The statistical distribution function emerges from the exclusion principle and the indistinguishable principle of electrons in metals

$$\boxed{f(E) = \frac{1}{e^{\frac{E-E_F}{KT}} + 1}}$$

Fermi-Dirac distribution function

E_F = Fermi energy or Fermi level (see signification later)



Electron concentration and Fermi-Energy

$$g(E) = \frac{dn}{dE} = \frac{(2m)^{3/2} V E^{1/2}}{2\pi^2 \hbar^3}$$

To get the actual number of electrons in any energy range dE we have to multiply the density of states with the occupation probability of that state $(f(E))$

$$\Rightarrow dN = g(E) f(E) dE = \frac{(2m)^{3/2} V E^{1/2}}{2\pi^2 \hbar^3} \frac{1}{e^{\frac{E-E_F}{kT}}+1} dE$$

The Fermi energy E_F is determined by the total number of N electrons

$\Rightarrow$ at any temperature the electron states are filled up to a point at which all electrons are accomodated

$\Rightarrow$ Fermi level (Fermi energy = energy of last occupied state)

At $T = 0\,K$ $\Rightarrow$

$$N = \frac{(2m)^{3/2} V}{3\pi^2 \hbar^3} E_{F_0}^{3/2} \Rightarrow$$

$$E_{F_0} = \frac{3^{2/3} \pi^{4/3} \hbar^2}{2m} \left(\frac{N}{V}\right)^{2/3}$$

$\frac{N}{V} = n$ = electron concentration

$$\Rightarrow \boxed{E_{F_0} = \frac{3^{2/3} \pi^{4/3} \hbar^2 n^{2/3}}{2m}}$$

Example

The Fermi energy in copper $\qquad$ $n = 8{,}45 \cdot 10^{28}\, m^{-3}$

$$E_F = \frac{3^{2/3}\pi^{4/3} n^{2/3} \hbar^2}{2m} = 1{,}126 \cdot 10^{-18} J = 7{,}03\, eV$$

$$v_F = \sqrt{\frac{2E_F}{m}} \longrightarrow \underline{v_F = 1{,}57 \cdot 10^6\, m/s}$$

Obs.: The density of states, e.g. the density of states at the Fermi-level $g(E_F)$ determines most of the properties of materials (e.g. metals).

The electric conductivity, thermal conductivity, ... are directly related to $g(E_F)$.