

Thermal conductivity of metals:

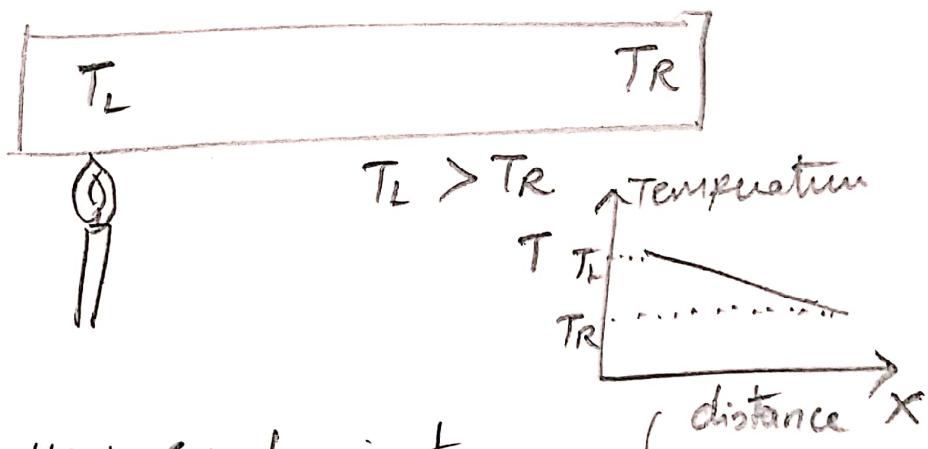
Drude's model was successful in explaining another observation, called the Wiedemann-Franz law, discovered in 1853. It said that the ratio of thermal to electrical conductivities, $\frac{K}{\sigma}$, is proportional to temperature T . That is, $\frac{K}{\sigma T}$ is a constant, called Lorenz number.

Drude derived this constant almost precisely, making everyone believe in Drude's model.

We have already evaluated σ to be $\frac{n e^2 \tau}{m}$, where n is the electronic density & τ is the relaxation time. Thermal conductivity K is evaluated as follows: [This is an example of a quick back-of-the-envelope calculations that you will be asked to perform in good interviews]

Let us first understand what we mean by thermal conductivity.

"Thermal conductivity" measures the ability of a material to equalize the temperature of the material specimen when it is heated unevenly (ie, at one end, for example). The faster it evens out the temperature gradients, we say that it has higher "thermal conductivity". As defined above, the problem is time-dependent. But we can make it time-independent, by assuming steady-state conditions [a common trick used in Physics often].



In steady-state, you supply just enough heat at one end to keep the "temperature profile" of the specimen constant in time. That is, the ability of the material specimen to conduct thermal energy from left to right is precisely counteracted by the supply of thermal energy at the left.

Thus in steady state, the thermal current density [defined as thermal energy flow per unit time per unit area J_q to the energy flow direction]

\vec{J}_q would be proportional to the temperature gradient [which is now time-independent] at all points along the sample \rightarrow thermal conductivity

$$\text{ie } \vec{J}_q = -k \vec{\nabla} T \quad \text{in 3-D.}$$

The -ve sign denotes the fact that thermal current flows in a direction opposite to that of the temperature gradient.

Simplifying this equation to 1-D,

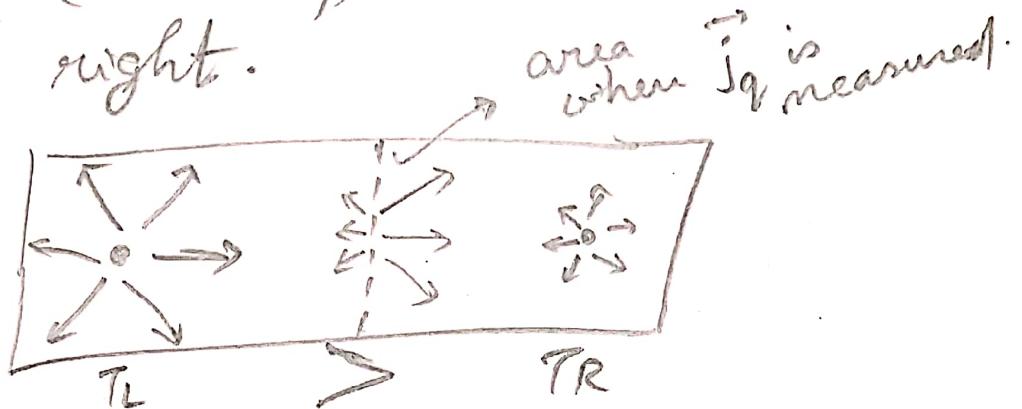
$$\vec{J}_q = -k \frac{dT}{dx}.$$

Let us now apply the assumptions of Drude model to calculate k .

We have assumed in Drude model that $e\vec{s}$ coming out of collisions with ions carry energy proportional to the temperature at that point.

in the form of
velocity

Since T_L is greater than T_R , the electrons coming out of collisions on the left side of the Specimen will have higher kinetic energy (& velocity) than that of the e^- s from the right.



If we assume that the energy of e^- emerging from collision from a place where the temperature is T is $E(T[x])$. [a function of function].

Electrons coming from the left to the central line above will have an energy $E(T[x - vt])$ & e^- s from the right will have $E(T[x + vt])$.
 [we have used the same velocity 'v' for e^- s from left & right] But e^- s from left & right have diff. velocities!
 It turns out that it is a good approximation].

Thus, the energy flux density traveling through the ; area in above picture is

$$J_q = \frac{1}{2} nv [E(T[x - vt]) - E(T[x + vt])]$$

only $\frac{1}{2}$ of e^- s from left move to right.

When the temperature change is very small [we can always reduce the size of our observation area smaller to make this true], the above formula can be approximated using Taylor expansion.

$$\mathcal{E}(T[x - v\tau]) = \mathcal{E}\left(T(x) - v\tau \frac{dT}{dx} + \dots\right)$$

$$\& \mathcal{E}(T[x + v\tau]) = \mathcal{E}\left(T(x) + v\tau \frac{dT}{dx} + \dots\right)$$

$$\mathcal{E}(T(x) - v\tau \frac{dT}{dx}) = \mathcal{E}(T(x)) - (v\tau \frac{dT}{dx}) \frac{d\mathcal{E}}{dT} + \dots$$

$$\& \mathcal{E}(T(x) + v\tau \frac{dT}{dx}) = \mathcal{E}(T(x)) + (v\tau \frac{dT}{dx}) \frac{d\mathcal{E}}{dT} + \dots$$

$$\therefore j_q = \frac{1}{2} nv \left[\mathcal{E}(T[x - v\tau]) - \mathcal{E}(T[x + v\tau]) \right]$$

becomes

$$j_q = -n v^2 \frac{d\mathcal{E}}{dT} \cdot \frac{dT}{dx}$$

Generalizing this to 3-D,

$$\vec{j}_q = -n v^2 \frac{d\mathcal{E}}{dT} \left[V_x^2 \frac{dT}{dx} \hat{i} + V_y^2 \frac{dT}{dy} \hat{j} + V_z^2 \frac{dT}{dz} \hat{k} \right]$$

Assuming the average of V_x , V_y & V_z over all directions is the same [isotropic material],

$$\langle V_x^2 \rangle = \langle V_y^2 \rangle = \langle V_z^2 \rangle = \frac{1}{3} v^2$$

which leads to

$$\vec{J}_q = -\frac{1}{3} n v^2 \tau \frac{dE}{dT} \cdot \vec{\nabla} T$$

giving, $K = \frac{1}{3} n v^2 \tau \frac{dE}{dT}$.

$\frac{dE}{dT}$, the rate of change of kinetic energy of e^-s with temperature is related to specific heat.

$$n \frac{dE}{dT} = \frac{N}{V} \frac{dE}{dT} = \frac{1}{V} \frac{d(NE)}{dT} = \frac{1}{V} \frac{dE}{dT} = C_v$$

C_v is the electronic specific heat, the amount of energy required to raise the temperature of e^-s by $1K$.
(not the whole metal)

Thus,
$$K = \frac{1}{3} \cdot v^2 \tau \cdot C_v$$

For wiedemann-franz law, let us calculate

$$\frac{K}{\sigma} = \frac{\frac{1}{3} v^2 \tau C_v}{n e^2 \kappa} = \frac{\frac{1}{3} C_v \cdot m v^2}{n e^2}$$

Drude again makes the mistake of assigning $C_v = \frac{3}{2} n k_B$, a classical mechanics

result. This is not correct & is about 100 times larger than the correct result derived from QM.

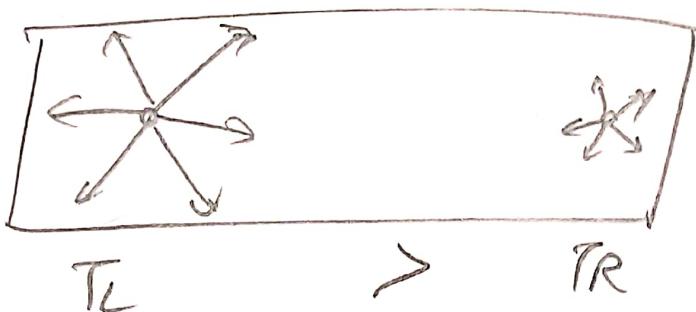
He also assigns for the kinetic energy of $\frac{1}{2}mv^2 \approx \frac{3}{2}k_B T$ from kinetic theory of gases, which is about 100 times smaller than the correct value! These two errors cancel to give an amazingly precise value for the Lorenz constant:

$$\frac{K}{\sigma} = \frac{\frac{2}{3} \cdot eV \cdot \frac{1}{2}mv^2}{ne^2} = \frac{\frac{2}{3} \cdot \left(\frac{eV}{2}\right) k_B T}{ne^2}$$

$$\Rightarrow \boxed{\frac{K}{\sigma} = \frac{3}{2} \left(\frac{k_B}{e} \right)^2 T}$$

This proves Wiedemann-Franz law and also gives us the Lorenz constant, which compared well with the experimental values of various metals.

If you thought a little bit more about the following picture,



you will realize that the electrons from left will move faster to the right than electrons from the right towards left. This will lead to accumulation of electrons to the right, setting up an electric field that will counteract further flow of electrons from left to right.

This appears as voltage across the specimen and has been measured. It is called Seebeck effect. Drude's model can be used to derive an equation describing this scenario as well. But the errors due to Drude's assumption of kinetic theory of gases do not cancel fortuitously like before & his value for thermopower turns out to be larger (by about a factor of 100) than observed.

On to Sommerfeld model.

Sommerfeld Model

= Drude's model + Fermi-Dirac distribution.

Enter QM.

Drude assumed e^- s to be like little billiard balls-particles. Quantum Mechanics says that the e^- s are neither particles nor waves, but behave as either during observation. They are properly described as waves of probability amplitude [square root of probability]. These waves are described by a mathematical quantity called "wave function", $\Psi(\vec{r}, t)$. This is a complex function, with both magnitude and a phase.

The principle that is of fundamental importance in understanding material behavior comes from QM → Pauli's exclusion principle.

→ No two electrons can occupy the same state [ignoring spin].

→ Sounds similar to the classical statement that no two particles can occupy the same position.

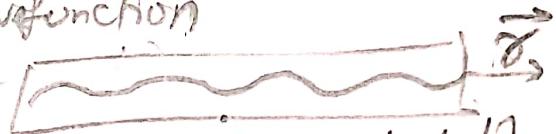
If you want to be proficient in the "machinery" of QM, you have to understand that there are two "representations" of the same object (e , photon etc):

A representation in the real space & a representation in the momentum space.

Going from one representation to another involves Fourier Transforms.

An example:

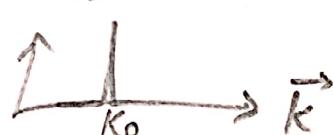
An electron with a precisely defined momentum, $\vec{P} = \hbar \vec{k}_0$, will have a wavefunction

$$\psi(\vec{r}) = e^{i(\vec{k}_0 \cdot \vec{r})}$$


It extends from $-\infty$ to $+\infty$ and the probability of finding the electron at any position is constant.

Here \vec{k}_0 is a parameter & \vec{r} is a variable.

This same wave function can be looked at as

$$\psi(\vec{k}) = \delta(\vec{k} - \vec{k}_0)$$


where \vec{k} is the variable & \vec{k}_0 is the parameter. These two functions "represent" the same particle, are just "Fourier Transforms" of each other.



If it is entirely up to us to choose a representation to work with. Which ever is easier mathematically will be the one we choose. For free electrons, it is easier to work with delta-functions (which are localized to a point) than with extended waves (completely delocalized). Thus, we choose the momentum representation to describe electrons in a material. Instead of drawing an infinitely long wave, we can use a "dot" to represent an electron in the "Momentum space" or "k-space".

With this prelude, we now solve the Schrodinger's equation to work out $\psi(\vec{r}, t)$ or $\psi(\vec{k})$ for electrons in a material. We assume, as in Drude's model, that the electrons don't interact with each other (independent electron approximation). For now, we also assume that the electrons do not interact with the ions either & are only confined within the boundaries of the material.

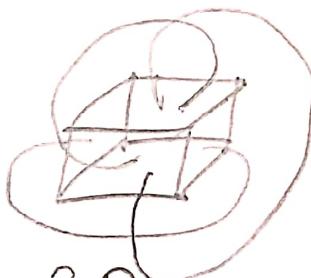
The nature of boundary conditions in solving any differential equations dictates the type of solutions. If we assume that the electrons are confined within a cube, and try to measure current due to applied electric field, we will get 'zero', because the \vec{e} 's are confined within the space & does not have anywhere to move. Thus, we assume "Periodic boundary conditions" or "Born-Von-Karman" boundary conditions:



1-D
loop



2-D
toroid



3-D
???

In 3-D, imagine joining the right face of a cube to the left face, front to back & top to bottom. Mathematically, the electronic wave function would have the boundary conditions

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

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

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

Now, we can have current, because \vec{e} 's can move in circles or closed loops in such a geometry.

(*) It is the geometry that dictates the nature of the wave function.

Because there are no interactions of \vec{e} 's with themselves or ions, the potential term in the schrodinger eqn is zero. Therefore,

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

We are attempting to solve for $\psi(\vec{r})$, i.e., we want to find the wave function in the "real" space or "position space". The solution, with the application of the boundary conditions, is just plane waves appropriately normalized:

$$\boxed{\psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}}}$$

& $E = \frac{\hbar^2 k^2}{2m}$, which is just the kinetic energy of the \vec{e} .

Applying the boundary conditions to the above wavefunction, we witness the emergence of discrete states, a hallmark of QM:

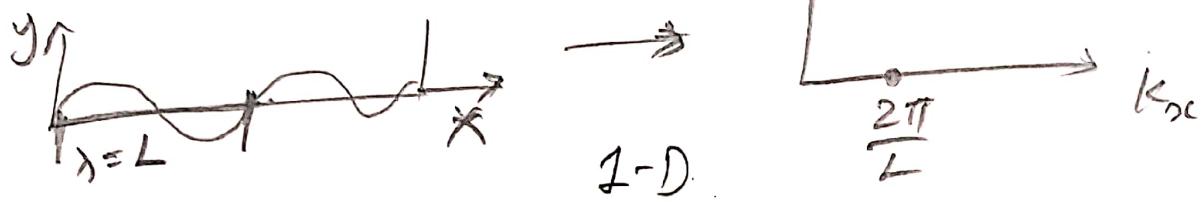
$$\psi(x+L) = \psi(x) \Rightarrow \text{for } x=0, e^{ik_0 L} = 1$$

This means that k_0 can take only discrete values

$$\text{of } \frac{2\pi n_x}{L}, e^{i 2\pi n_x L} = 1, \text{ whenever } n_x = \text{integers.}$$

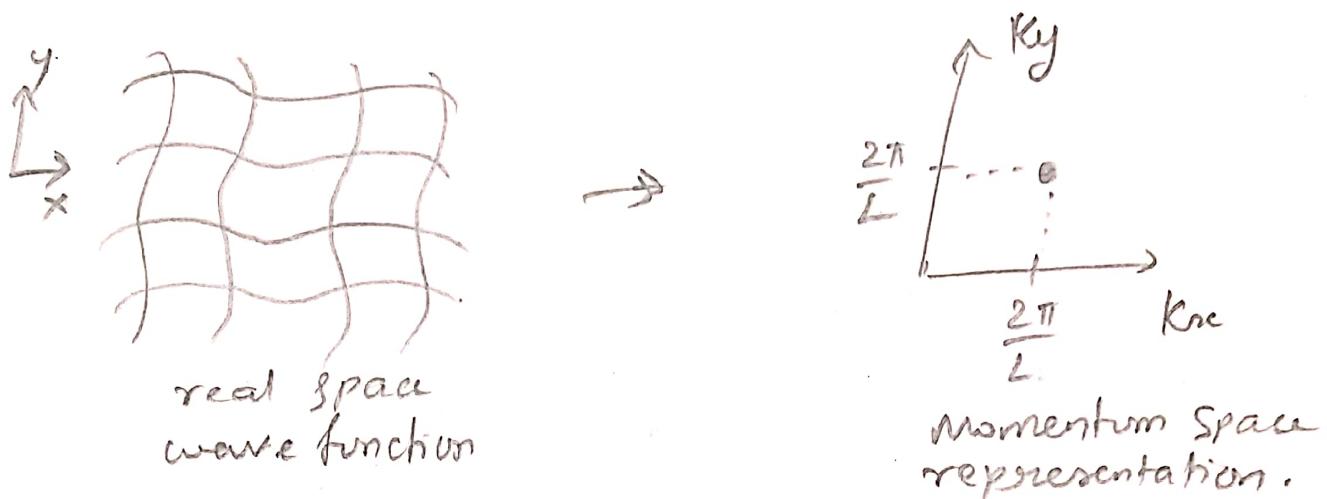
Similarly, $k_y = \frac{2\pi n_y}{L}$ & $k_z = \frac{2\pi n_z}{L}$, where n_x, n_y, n_z are integers.

Going over to momentum space, as we argued awhile ago, the extended real space wavefunctions can be represented by dots in the momentum space.



For those of you who intend to delve deep into QM, the wavefn $e^{i\vec{k}\cdot\vec{r}}$ is a momentum eigenfunction. i.e., when we apply momentum operator on the wavefunction, $-i\hbar\frac{\partial}{\partial\vec{r}}$, we get the same wavefunction multiplied by the momentum eigenvalue, $i\vec{k}$.

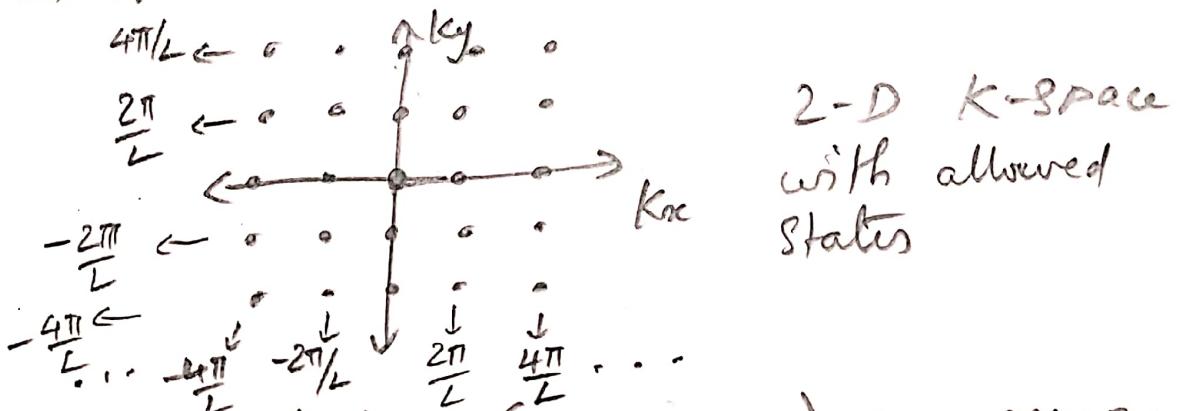
In 2-D



Since any wave function

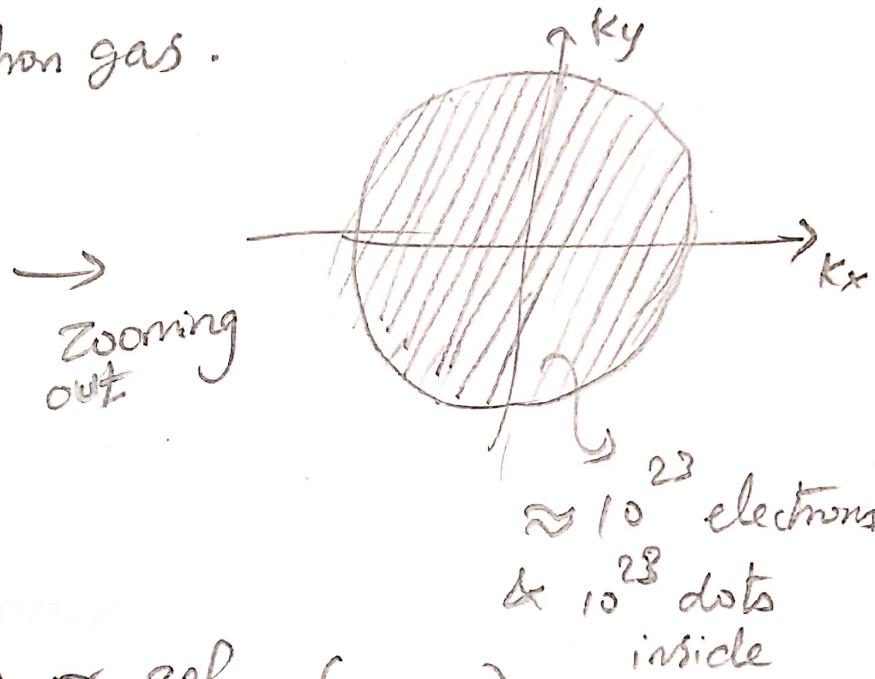
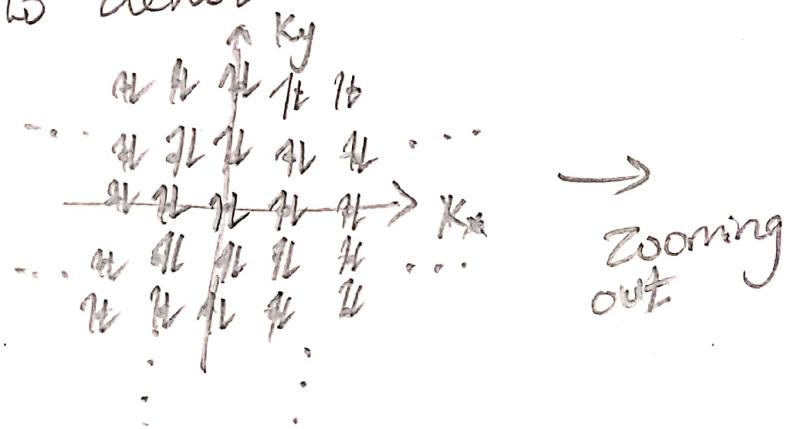
$$\psi(\vec{r}) = e^{i \frac{2\pi}{L} (n_x x + n_y y + n_z z)}$$

with integers n_x, n_y, n_z will satisfy the Schrödinger equation describing electrons in a material, the possible states in which electrons can exist can be denoted as follows:



Only two electrons (\uparrow & \downarrow spins) can occupy each of these dots that represent a state with the wave function above.

The number of electrons that will be occupying these points is of the order of $10^{23}/\text{cm}^3$. This means that we have to fill about 10^{23} "dots" in the k-space diagram to denote an electron gas.



This circle (in 2-D) or sphere (in 3-D) represent the low energy state of an electron gas. [Again, each dot represents a wave function $e^{ik \cdot r}$ and can take only two \bar{e} s. If you want to add more \bar{e} s, you have to go to other "dots" with more momentum & energy]. This representation is for an \bar{e} gas at temperature $T=0$.

This sphere is called Fermi Sphere.
Its radius is called k_F (Fermi wave vector).
Its surface is called Fermi surface.
 $k_F \rightarrow$ Fermi momentum.

$$E_F = \frac{\hbar^2 k_F^2}{2m} \rightarrow \underline{\text{Fermi Energy}}$$

$$v_F = \frac{\hbar k_F}{m} \rightarrow \underline{\text{Fermi velocity}}.$$

This construction is very important in understanding material behavior.

Obviously the radius of the Fermi sphere, k_F , depends on the number of electrons, n , that we are putting inside the sphere. \rightarrow which means $k_F = f(n)$.

What is $f(n)$? or what is $n = g(k_F)$?

Let us calculate how many "dots" are inside a Fermi sphere of radius k_F . Since there is a dot at every $\frac{2\pi}{L}$ distance along the three axes, each dot will take up a volume of $\left(\frac{2\pi}{L}\right)^3$. Thus the number of dots inside a sphere of volume $\frac{4}{3}\pi k_F^3$ is just

$$\# \text{ of dots} = \frac{\frac{4}{3}\pi k_F^3}{\left(\frac{2\pi}{L}\right)^3} = \frac{k_F^3}{\frac{8\pi^3}{L^3}} \cdot V$$

Since each dot will be occupied by two e^- ($\uparrow \downarrow$), the total number of e^- , N , within the Fermi sphere is $2 \times \#$ of dots.

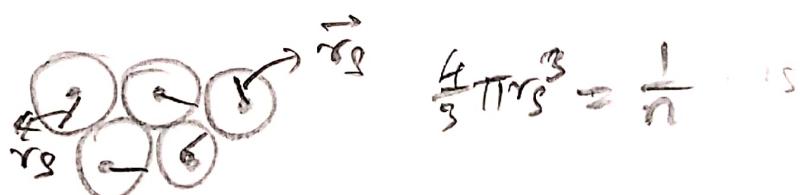
which is,

$$N = \frac{k_F^3}{3\pi^2} \cdot V$$

Thus,

$$\boxed{n = \frac{N}{V} = \frac{k_F^3}{3\pi^2}}.$$

This gives the relation between Fermi radius k_F and electronic density n of a material. We have mentioned before that electronic density may also be measured by evaluating the average distance between electrons (within Drude's picture), by evaluating the radius of a sphere around every e^- .



$$\text{Then, } \frac{1}{\frac{4}{3}\pi r_s^3} = \frac{k_F^3}{3\pi^2}$$

$$\text{or } k_F = \frac{(9\pi/4)^{1/3}}{r_s} = \frac{1.92}{r_s}$$

$$\boxed{k_F = \frac{3.63}{r_s/a_0} \text{ \AA}^{-1}}$$