Free electron gas in 3D

$$\frac{p^2}{2m}\psi_n = E_n\psi_n$$ Schrödinger Eq.

$$\vec{p} = -i\hbar\vec{\nabla}$$

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

If e^- are confined in 3D

$$0<x<L_x \qquad 0<y<L_y \qquad 0<z<L_z$$

The solution is a standing wave

$$\psi_n(\vec{r}) = A_n \sin(k_x x)\sin(k_y y)\sin(k_z z)$$

$$k_x = \frac{n_x\pi}{L_x} \qquad k_y = \frac{n_y\pi}{L_y} \qquad k_z = \frac{n_z\pi}{L_z}$$

n_x, n_y, n_z are positive integers

From Schrödinger Eq.

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

$k^2 = k_x^2+k_y^2+k_z^2$; k: magnitude of $\vec{k}\,(k_x, k_y, k_z)$

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

k is also related to the wavelenght through $k = 2\pi/\lambda$

If we apply the periodic boundary nethod

$$\psi_n(x+L_x, y, z) = \psi_n(x, y, z)$$

analogously for y, and z

The solutions have the form

$$\psi_n(\vec{r}) = A\, e^{i\vec{k}\cdot\vec{r}}$$

$\vec{k} = (k_x, k_y, k_z)$

$\vec{r} = (x, y, z)$

$$k_x = 0;\ \pm\frac{2\pi}{L_x};\ \pm\frac{4\pi}{L_x}\ \ldots$$

similarly for k_y and k_z

Using this solution, we have

$$\vec{p}\,\psi_{\vec{k}} = -i\hbar\left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right) A\, e^{i(k_x x + k_y y + k_z z)}$$

$$= -i\hbar\,(ik_x, ik_y, ik_z)\, A e^{i(k_x x + k_y y + k_z z)}$$

$$\vec{p}\,\psi_{\vec{k}} = \hbar\vec{k}\,\psi_{\vec{k}}$$

A plane wave is an eigenstate of the linear momentum operator with eigenvalue $\hbar\vec{k}$.

A particle with wavevector $\vec{k}$ has a velocity

$$\vec{v} = \frac{\vec{p}}{m} = \frac{\hbar\vec{k}}{m}$$

k-space:
- reciprocal
- momentum

In the ground state of a system of N e^-, the occupied orbitals (energy levels) are represented as points in k-space

$$E_F = \frac{\hbar^2 k_f^2}{2m}$$

k_f: k-Fermi

The number of states with energy $E < E_F$ is given by

$$N = 2 \left(\frac{L_x}{2\pi}\right)\left(\frac{L_y}{2\pi}\right)\left(\frac{L_z}{2\pi}\right) \frac{4\pi k_f^3}{3} = \frac{V}{3\pi^2} k_f^3$$

The factor 2 comes from the possible values of the spin

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

k_f only depends on the particle concentration N/V

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

the velocity at the fermi surface $(k = k_f)$

$$v = \frac{\hbar k_f}{m} = \frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

we could define the Fermi-tempercture T_F

$$E_F = k_B T_F \Rightarrow T_F = \frac{\hbar^2}{2mk_B}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

Now we can the $D(\varepsilon)$:

$$D(\varepsilon) = \frac{\partial N}{\partial \varepsilon}$$

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

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

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

$$\boxed{D(E) = \frac{3N}{2E^{3/2}} E^{1/2} = \frac{3N}{2E}}$$

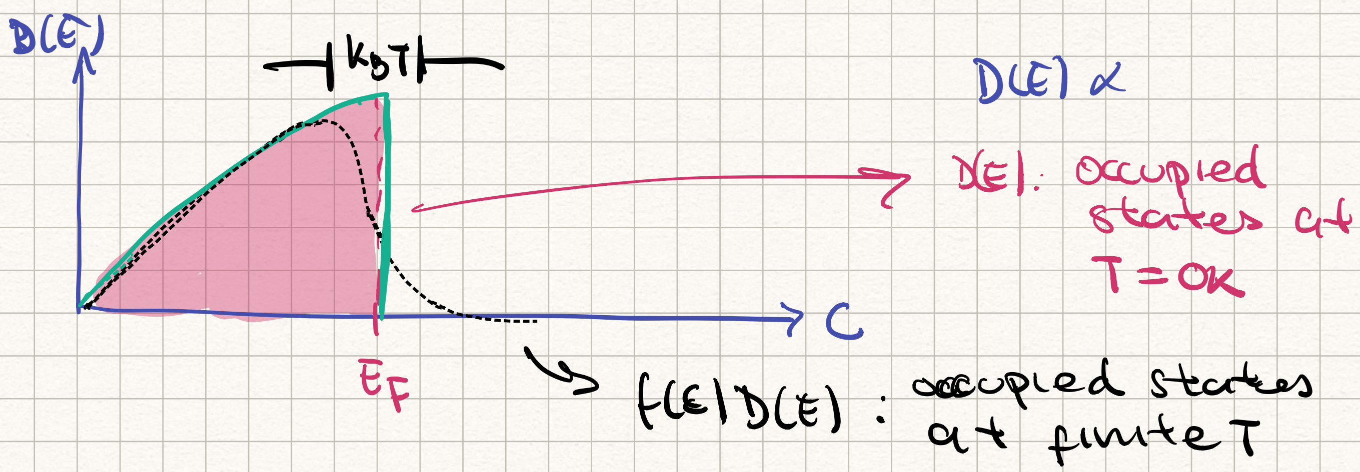
within a factor ~ 1, the number of orbitals per unit energy range at the fermi level is the total number of conduction electrons divided by Fermi Energy.

Classical statistical mechanics predicts that a free particle should have a heat capacity of $3k_B/2$. If N atoms each give electron to the electron gas, then the heat capacity should be $3Nk_B/2$.
However, the observed electronic contribution at room temperature is $\lesssim 1\%$ of this value.

This discrepancy is due the Pauli exclusion principle.

↳ Not all e^- gain an energy $\sim k_B T$
↳ only those who are within $k_B T$ to the Fermi energy.

If N is the total number of electrons, only a fraction T/T_F can be excited thermically, because only these lie within $\sim k_B T$ to the top of the energy distribution



Each of these NT/T_F electrons has energy of the order $k_B T$, so the total electronic thermal kinetic energy U is of the order

$$U_{el} \cong (NT/T_F)\, k_B T$$

So the heat capacity is

$$C_{el} = \frac{\partial U}{\partial T} \approx \frac{N k_B T}{T_F}$$ which is linear in T.

this is in agreement with experiments.

At room T. $C_{el} \approx 0.001\ 3Nk_B/2$. !