Ground state properties of electron gas
(temperature $T=0$)

N electrons confined to a volume V

electron density $n = N/V \longrightarrow E_F$?

$\boxed{\text{Non-interacting!}}$ $\Rightarrow$ single-particle

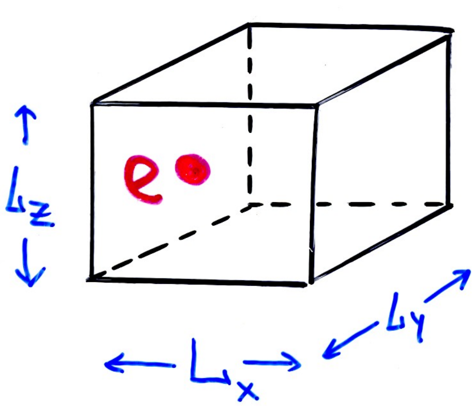
t-independent Schrödinger equation

$$\frac{\hat{\vec{p}}^{\,2}}{2m}\psi(\vec{r}) = \varepsilon\,\psi(\vec{r})$$

$$\hat{\vec{p}}^{\,2} = (-i\hbar\vec{\nabla})^2 = -\hbar^2\cdot\vec{\nabla}^2 = -\hbar^2\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$$

+ boundary conditions

For macroscopically large volumes can be chosen rather arbitrary when bulk properties are studied.



e in a cube of volume $V = L^3$

$$L_x = L_y = L_z = L$$

+ periodic Bound. cond. = $\boxed{\text{Born-von Karman B.cond}}$

$$\psi(\vec{r}+\hat{e}_i L) = \psi(\vec{r})$$
$$i = x, y, z$$

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$$\psi(\vec{r}) = \psi_{\vec{p}}(\vec{r}) = A \cdot \exp\left(i\,\frac{\vec{p}\cdot\vec{r}}{\hbar}\right)$$

① $\int d\vec{r}\,|\psi_{\vec{p}}(\vec{r})|^2 = |A|^2 \cdot V = 1 \qquad A = \frac{1}{\sqrt{V}}$

② momentum $\vec{p} \longrightarrow$ wave vector $\vec{k} = \vec{p}/\hbar$

$\lambda = \frac{2\pi}{k}$, plane waves $\vec{k}\cdot\vec{r} = \text{const}$

③ $\hat{\vec{p}}\,\psi_{\vec{p}}(\vec{r}) = -i\hbar\frac{\partial}{\partial\vec{r}} \cdot \frac{1}{\sqrt{V}} e^{i\frac{\vec{p}\cdot\vec{r}}{\hbar}} = \vec{p}\,\psi_{\vec{p}}(\vec{r})$

$\vec{v} = \vec{p}/m$ momentum eigenvalue

④ $\hat{H}\,\psi_{\vec{p}}(\vec{r}) = \frac{\hat{\vec{p}}^2}{2m}\psi_{\vec{p}}(\vec{r}) = \frac{\vec{p}^2}{2m}\psi_{p}(\vec{r})$

$\hat{H}\,\psi_{\vec{p}}(\vec{r}) = \varepsilon\,\psi_{\vec{p}}(\vec{r}) \qquad \varepsilon = \varepsilon(\vec{p}) = \frac{\vec{p}^2}{2m}$

energy eigenvalue

⑤ Bound. cond.

$$e^{i\vec{k}\cdot(\vec{r}+\hat{e}_i L_i)} = e^{i\vec{k}\cdot\vec{r}}$$

$$L_i\,\hat{e}_i\cdot\vec{k} = k_i \cdot L_i = 2\pi \cdot n_i \qquad n_i = 0, \pm 1, \pm 2, \ldots$$

$i = x, y, z$ (no summation in i !)

$$\boxed{k_i = \frac{2\pi}{L_i}\cdot n_i \;,\; n_i = 0, \pm 1, \pm 2, \ldots}$$

L_i are macroscopic! $\Rightarrow \Delta k_i = 2\pi/L_i$ small

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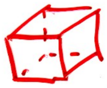
Volume of crystal $V = L_x L_y L_z$.

How many states are contained in the volume $\Omega_{\vec{k}}$ in $\vec{k}$-space?

 $$\Delta\Omega_{\vec{k}} = \Delta k_x \cdot \Delta k_y \cdot \Delta k_z = \frac{(2\pi)^3}{L_x L_y L_z} = \frac{(2\pi)^3}{V}$$

↑ "elementary volume" per one state

$$N = \frac{\Omega_{\vec{k}}}{\Delta\Omega_{\vec{k}}} = \frac{\Omega_{\vec{k}} \cdot V}{(2\pi)^3}$$

$$\sum_{\vec{k}} \ldots \longrightarrow \int \frac{V d^3 k}{(2\pi)^3} \ldots$$

Constructing Fermi-sphere ...

Ground State of an electron system $\equiv$ the state with the lowest possible energy

Only occupied at $T=0$;

Excitations from it are relevant at low T

?

we need to specify this

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Fermi sphere

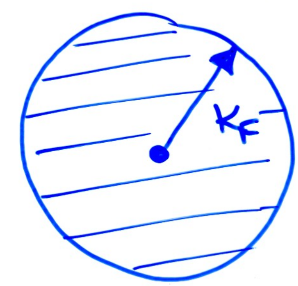
$$k_F = \hbar^{-1} \cdot p_F$$

$$2 \cdot \frac{\frac{4\pi}{3} p_F^3 \cdot V}{(2\pi\hbar)^3} = N = N_\uparrow + N_\downarrow \; ; \; N_\downarrow = N_\uparrow$$

$$k_F^\downarrow = k_F^\uparrow .$$

$$n = n_\uparrow + n_\downarrow = \frac{N}{V} = \frac{k_F^3}{3\pi^2}$$

total electron density



Fermi energy $E_F = \frac{\hbar^2 k_F^2}{2m}$

$$E_F = \frac{\hbar}{2m} \cdot (3\pi^2 n)^{2/3} \sim n^{2/3} \sim 1\text{-}20\,eV$$

Fermi velocity $v_F = \frac{p_F}{m} = \frac{\hbar k_F}{m} \sim 10^8 \frac{cm}{sec}$

Ground state energy

$$E = 2 \cdot \sum_{|\vec{k}| < k_F} \frac{\hbar^2 \vec{k}^2}{2m} = 2 \cdot \int_{|\vec{k}| < k_F} \frac{V d^3 k}{(2\pi)^3} \cdot \frac{\hbar^2 k^2}{2m}$$

$$E = \frac{\hbar^2 k_F^5 \cdot V}{10\pi^2 m} .$$ Energy per electron $\frac{E}{N} = \frac{3}{5} E_F .$

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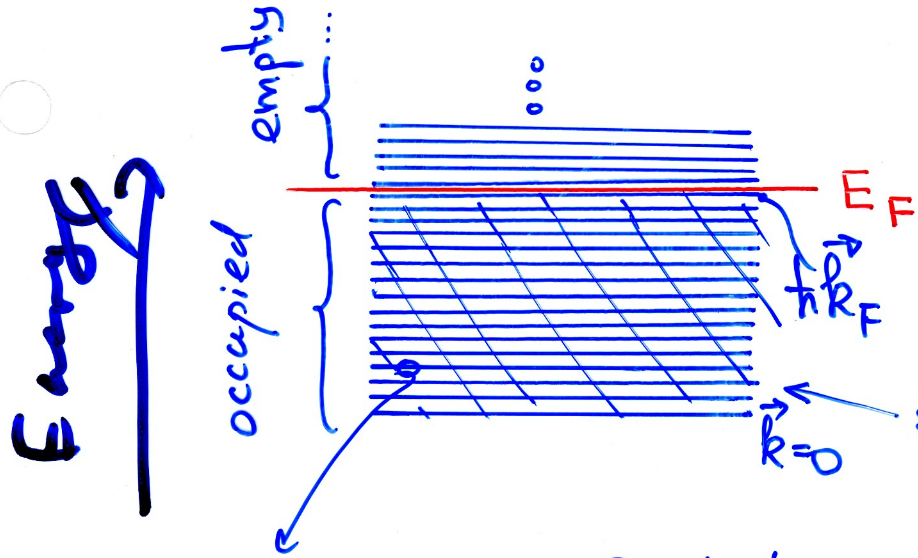
T=0



Fermi energy

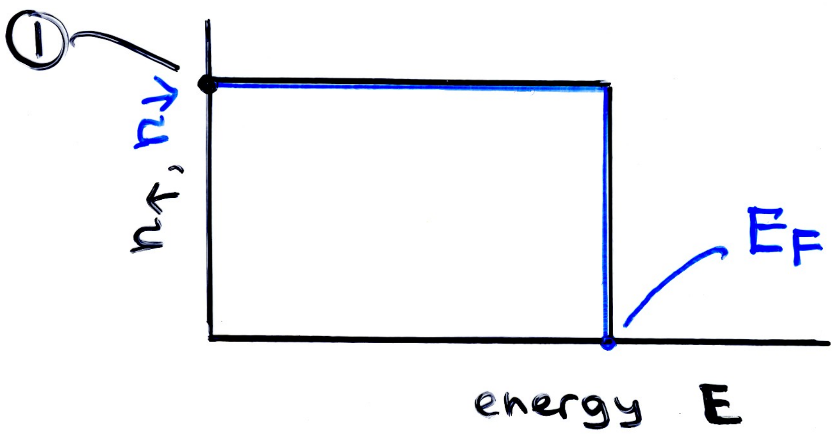
Fermi momentum

single-electron levels

$$\varepsilon = \varepsilon_{\vec{k}_i} = \frac{\hbar \vec{k}_i^{\,2}}{2m}$$

occupied by 2 electrons

$\uparrow$ $\downarrow$ $\quad S_z = \pm \frac{1}{2}\hbar$



$$n_\downarrow = n_\uparrow = \begin{cases} 1 & E < E_F \\ \emptyset & E > E_F \end{cases}$$

Isotropic dispersion $\varepsilon(\vec{k}) = \frac{\hbar \vec{k}^2}{2m} \rightarrow$ DOS $= n(E)$

density of states

$N_\uparrow(E)$ = total # of states with energies $\leq E$

$$g_\uparrow(E) = \frac{dN(E)}{dE}$$

$$N_\uparrow = \frac{V \cdot \frac{4\pi}{3} p^3}{(2\pi\hbar)^3} = \frac{V \cdot (2mE)^{3/2}}{6\pi^2\hbar^3}$$

$p^2 = 2mE$

$$\boxed{g_\uparrow(E) = V \cdot \frac{(2m)^{3/2}}{4\pi^2\hbar^3} \cdot E^{1/2}}$$

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Pressure of the electron gas

$$P = -\left(\frac{\partial E}{\partial V}\right)_N = \frac{2}{3}\cdot\frac{E}{V}$$

$$E = \frac{3}{5} E_F \cdot N \sim \frac{k_F^2}{2m} \sim \left(\frac{N}{V}\right)^{2/3} \sim V^{-2/3}$$

$$B = \frac{1}{K} = -V\frac{\partial P}{\partial V} = \frac{5}{3}P = \frac{2}{3} n \cdot E_F$$

bulk modulus

compressibility

$$P \sim \frac{E}{V} \sim V^{-5/3}$$

Thermal properties of the free electron gas

Probability that a system in thermal equilibrium has energy E_{nN} and number of particles N

$$w = w_{nN} = A \exp\left(-\frac{E_{nN} - \mu N}{k_B T}\right)$$

grand canonical ensemble

μ, chemical potential

↓ Gibbs distribution for a variable number of particles.

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$$A: \quad \sum_{n}\sum_{N} w_{nN} = 1$$

Entropy $\quad S = - \langle \ln w_{nN} \rangle$

$$S = - \left[\ln A + \frac{\mu}{k_B T} \cdot \langle N \rangle - \frac{1}{k_B T} \cdot \langle E_{nN} \rangle \right]$$

$$k_B T \cdot \ln A = - k_B T \cdot S - \mu \langle N \rangle + \langle E \rangle$$

$$k_B T \cdot \ln A = \Omega = \left(\langle E \rangle - k_B T \cdot S \right) - \mu \langle N \rangle = F - \mu \cdot \langle N \rangle$$

↓ thermodynamic potential

$$\Omega = \Omega(T, V, \mu)$$

$$\boxed{w_{nN} = \exp\left(\frac{\Omega + \mu N - E_{nN}}{k_B T} \right)}$$

Let us specify this for the free electron gas:

a gas of $1/2$-spin particles $n_k = 0, 1$.

a system of particles occupying **each** level !

ε_k, n_k

$$\Omega_k = - k_B T \sum_{n_k} \exp\left(\frac{\mu - \varepsilon_k}{k_B T} \right)^{n_k}$$

$n_k = 0, 1$

$$\Omega_k = - k_B T \left(1 + \exp\left[\frac{\mu - \varepsilon_k}{k_B T} \right] \right)$$

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$$\Omega = \sum_k \Omega_k$$ ← contributions of different energy levels

$$f(\varepsilon_k) = \langle n_k \rangle = \sum_{n_k=0,1} n_k \cdot w_{k n_k} = w_{k n_k=1}$$

$$f(\varepsilon_k) = \exp\left(\frac{\Omega_k + \mu - \varepsilon_k}{k_B T}\right)$$

$$\exp(\Omega_k / k_B T) = \frac{1}{1+\exp\left(\frac{\mu-\varepsilon_k}{k_B T}\right)}$$

$$\boxed{f(\varepsilon_k) = \frac{1}{e^{\frac{\varepsilon_k-\mu}{k_B T}}+1}}$$

Fermi-Dirac distribution function

Chemical potential μ

$U = U(S, V, N)$ $\left(\frac{\partial U}{\partial N}\right)_{SV} = \mu$

internal energy

$F = F(T, V, N)$ $\left(\frac{\partial F}{\partial N}\right)_{TV} = \mu$

μ = change of F when 1 particle is added at T = const, V = const

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