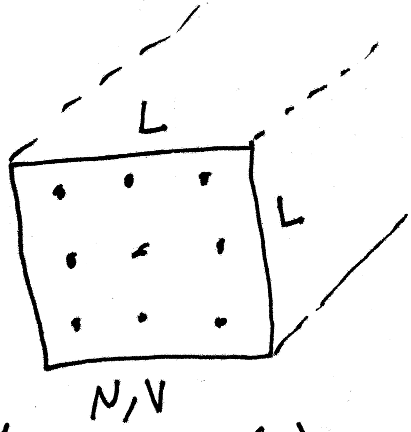
Chapter 6

The free Fermi gas and single electron model

This model applies only to metals and assumes that the Coulomb interactions between electrons and electrons and electrons and nuclei are all turned off; with respecting the Pauli exclusion principle.

- consider a 1 mole of silver metal that has one conduction electron per atom. This leads to 6×10^{23} electrons/cm^3. let us assume that This Ag metal occupy a cube of volume $V=L^3$. the 6×10^{23} electrons are free to move all around the metal and thus called conduction electrons. They form an ideal fermi gas with $s=1/2$ and thus obey Fermi-Dirac statistics.



(Fig 6.1)

let us assume that the wave function of all electrons is $\Psi(\vec{r_1} \cdots \vec{r_N})$, so the schroding equation (time-indep) of all electrons is given by

$H\Psi = \varepsilon\,\Psi$, where $H = \sum_{l=0}^{N} \frac{p_l^2}{2m} = \sum_{l=0}^{N} \frac{-\hbar^2\nabla_l^2}{2m}$, $|p = -i\hbar\nabla_l$

$$-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2\,\psi(\vec{r_1}\cdots\vec{r_N}) = \varepsilon\,\psi(\vec{r_1}--\vec{r_N}) \quad \text{------} \quad (1)$$

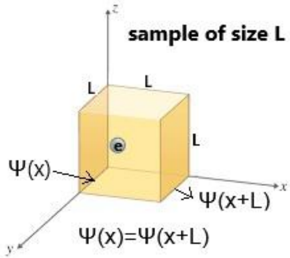
Now because the electrons don't interact with each others, it is sufficent to solve the single electron schrodinger equation

$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\vec{r}) = \varepsilon_i\,\psi_i(\vec{r})$, then the total wave function of this many electron system is just the product of single electron wave functions; i.e

$\psi(\vec{r_1} \cdots \vec{r_N}) = \psi_1(\vec{r_1})\,\psi_2(\vec{r_2}) \cdots \psi_N(\vec{r_N})$ and the total energy is the sum of the single particle energies

$$\varepsilon = \varepsilon_1 + \varepsilon_2 + \cdots \varepsilon_N .$$

- in order to solve the single particle schrodinger eq^n, we must first set up an appropriate B.Cs. the usual choice is to require the wavefunction to vanish at the boundaries of the object (standing wave B.Cs). This is not practicle for calculations. in addition, the bulk properties of the metal is independent of what is happening at the boundaries, specifically when $L \to \infty$ (large object). the other choice is to pick up periodic B.Cs which assumes that an electron leaving the cube on one side returns simultaneously at the opposite side; i.e



Running wave B.Cs

$$\left.\begin{aligned}\psi(x_1+L, y_1, z_1, \cdots z_N) &= \psi(x_1, y_1, z_1 \cdots z_N)\\ \psi(x_1, y_1+L, z_1, \cdots z_N) &= \psi(x_1, y_1, z_1, \cdots z_N)\\ \psi(x_1, y_1, z_1+L, \cdots z_N) &= \psi(x_1, y_1, z_1, \cdots z_N)\end{aligned}\right\}$$

No for a single electron in a box, the wave function is

$\psi_k(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$; $\vec{r} = x\hat{i} + y\hat{j} + z\hat{k}$

$\vec{k} = k_x\hat{i} + k_y\hat{j} + k_z\hat{k}$

because the electron is spacially quantized, this impose specific values on ks, that can be derived from the B.Cs ; i.e $\psi_k(x+L) = \psi_k(x)$

$$\Rightarrow \psi_k(x+L) = \frac{1}{\sqrt{V}} e^{ik_x(x+L)} = \frac{1}{\sqrt{V}} e^{ik_xL} \Rightarrow e^{ik_xL} = 1$$

$$\Rightarrow \cos k_x l = 1 \Rightarrow k_xL = 0, \pm 2\pi, \pm 4\pi, \ldots$$

$$k_x = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \ldots$$

with spacing $\Delta k_x = \frac{2\pi}{L}$

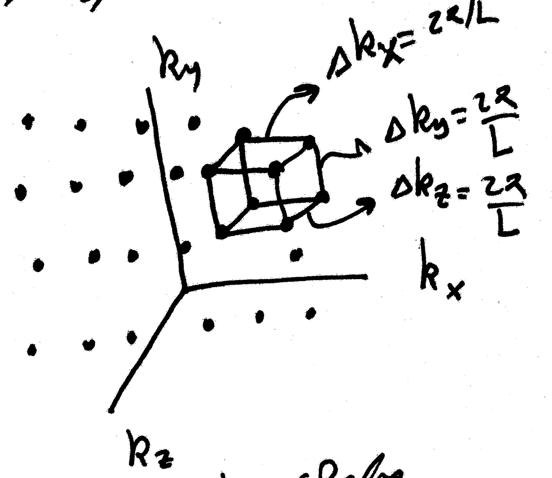
similarly for k_y and k_z $\Rightarrow \vec{k} = \frac{2\pi}{L}(l_x, l_y, l_z)$

l_x, l_y, l_z: integers $0, \pm 1, \pm 2, \ldots$

the energy eigenvalue is

$$\varepsilon^0_{\vec{k}} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2}{2m}\frac{4\pi^2}{L^2}(l_x^2 + l_y^2 + l_z^2).$$

the vectors $\vec{k}$ form a cubic lattice (reciprocal lattice) with spacing of $\frac{2\pi}{L}$ in each direction k_x, k_y, k_z. The volume of the wigner-Seitz cell is $(2\pi/L)^3$.



k- space (reciprocal space)

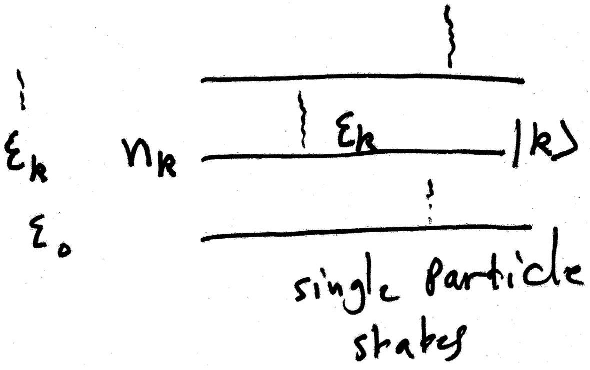
- Non-interacting N electrons with two limits

i) Ground state ($T=0$)

ii) degenerate limit ($T > 0$ and $T << T_F$)

i) Ground state : the N-conduction electrons are to be distributed over the single particle states with respecting the Pauli principle; where every single particle state can't be occupied by more than one electron. So due to spin of the electron ($s = 1/2$; $S_z = \pm 1/2$), the state $|k\rangle$ or ψ_k can have at most two electrons; spin up and spin down. So first, we put two electrons with opposite spins in the lowest energy state $k=0$; then we place two electrons in the second state and so on.

- the mean occupation # $\langle n_k \rangle$ of the single particle state $|k\rangle$ that has an energy $\varepsilon_k = \frac{\hbar^2 k^2}{2m}$ is



$$\langle n_k \rangle = \frac{1}{e^{(\varepsilon_k - \mu)/k_B T} + 1} \quad ; \quad \mu : \text{chemical Potential}$$

at fixed μ and T ; this is called Fermi-Dirac distribution function $f(\varepsilon)$

$$f(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)/kT} + 1}$$

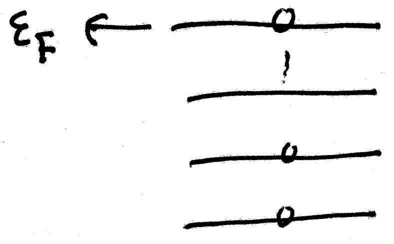
which gives the probability that a single particle state of energy ε is occupied at equilibrium.

- now in general, the chemical Potential μ is temperature dependent. However, at $T = 0$, $\mu = \varepsilon_F$; Fermi energy

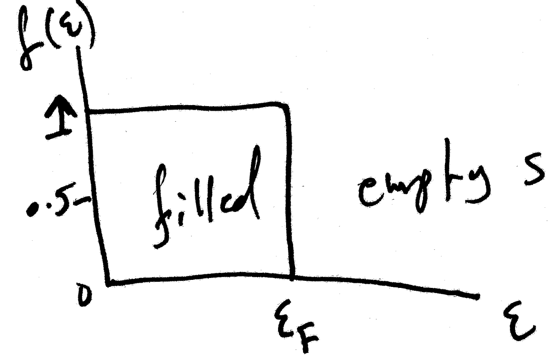
$$\Rightarrow f(\varepsilon) = \frac{1}{e^{(\varepsilon-\varepsilon_F)/k_BT}+1}$$; this is a step function

where ε_F is the energy of the hieghest occupied state.

$$f(\varepsilon) = \begin{cases} 1 & ; \quad \varepsilon < \varepsilon_F \\ 0 & ; \quad \varepsilon > \varepsilon_F \end{cases}$$

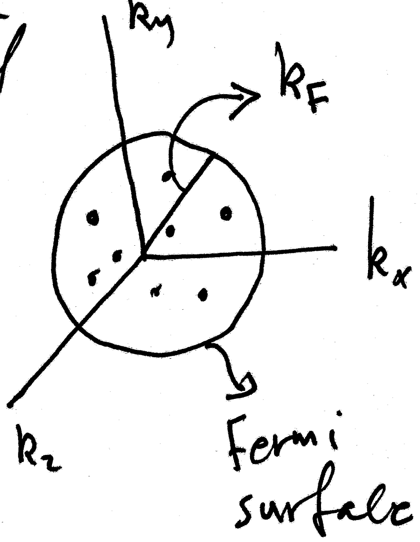


at $T=0$
single-particle states



all states with $\varepsilon \leqslant \varepsilon_F$ are filled and those states with $\varepsilon > \varepsilon_F$ are empty. This is the ground state.

- in reciprocal space (k-space), all occupied states below ε_F, are represented by a points inside a sphere of radius k_F
- the total # of electrons N and the total energy E are calculated by



$$N = \sum_{k\sigma} n_{k\sigma} \quad ; \quad E = \sum_{k\sigma} \varepsilon_k n_{k\sigma}$$

$k\sigma \rightarrow \sigma$: for spin

now in the thermodynamic limit $(L \rightarrow \infty, N \rightarrow \infty)$; $\Delta k = \frac{2\pi}{L} \rightarrow 0$; energy levels get very close to each others such that they can be treated continuously; meaning the sums can be replaced by integrals.

$$\sum_{k\sigma} \to \frac{(2s+1)}{(2\pi)^3}\int d^3\vec{r}\, d^3\vec{k} \;; \quad \sigma = s = 1/2$$

$$\to \frac{2}{(2\pi)^3}\underbrace{\int d^3\vec{r}}_{V}\int d^3\vec{k} \;; \quad d^3\vec{k} = 4\pi k^2 dk$$

in spherical coordinates

$0 < k < \infty$

$$\to \frac{2V}{(2\pi)^3} 4\pi \int k^2 dk \to \frac{V}{\pi^2}\int_0^\infty k^2 dk$$

so $N = \sum_{k\sigma} n_{k\sigma} = \sum_{k\sigma} f_{k\sigma}(\varepsilon)$

$$= \frac{V}{\pi^2}\int_0^\infty dk\, k^2 f(\varepsilon) \;; \quad f(\varepsilon) = \begin{cases} 1, & \varepsilon < \varepsilon_F \\ 0, & \varepsilon > \varepsilon_F \end{cases}$$

$$N = \frac{V}{\pi^2}\int_0^{k_F} dk\, k^2 = \frac{V}{\pi^2}\frac{1}{3}k_F^3 = \frac{V}{3\pi^2}k_F^3$$

$$\Rightarrow \frac{N}{V} = n = \frac{k_F^3}{3\pi^2} \Rightarrow k_F^3 = 3\pi^2 n \Rightarrow k_F = (3\pi^2 n)^{1/3}$$

$$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3} \;; \quad p_F = \hbar k_F = m v_F$$

↳ Fermi energy

$$\Rightarrow v_f = \frac{\hbar}{m}(3\pi^2 n)^{1/3}$$

↳ Fermi velocity

and let $\varepsilon_F = k_B T_F$

$\Rightarrow T_F = \frac{\varepsilon_F}{k_B}$ Fermi temperature

Energy: $E = \sum_{k\sigma} \varepsilon_k n_{k\sigma} = \sum_{k\sigma} \varepsilon_k f_{k\sigma}$; $\varepsilon_k = \frac{\hbar^2 k^2}{2m}$

$$\to \frac{V}{\pi^2}\int_0^\infty dk\, k^2\, \varepsilon_k\, f(\varepsilon_k)$$

; again $f(\varepsilon_k) = 1;\ \varepsilon < \varepsilon_F$
$= 0,\ \varepsilon > \varepsilon_F$

$$= \frac{V}{\pi^2}\int_0^{k_F} dk\, k^2\, \frac{\hbar^2 k^2}{2m}$$

$$= \frac{\hbar^2 V}{2m\pi^2}\int_0^{k_F} k^4\, dk = \frac{\hbar^2 V}{2m\pi^2}\,\frac{k_F^5}{5}$$

$$= \frac{V k_F^3}{5\pi^2}\,\frac{\hbar^2 k_F^2}{2m} = \frac{V k_F^3}{5\pi^2}\,\varepsilon_F \times \frac{3}{3} = \frac{3}{5}\underbrace{\frac{V k_F^3}{3\pi^2}}_{N}\,\varepsilon_F$$

(see problem 4 in HW#4)

in 2D: E/N = $\frac{\varepsilon_F}{2}$

in 1D : E/N = $\frac{\varepsilon_F}{3}$

$$E = \frac{3}{5} N \varepsilon_F \Rightarrow \frac{E}{N} = \bar{\varepsilon} = \frac{3}{5}\varepsilon_F$$

average energy per electron

- **Energy density of states:** the # of states in the energy interval $\varepsilon \to \varepsilon + d\varepsilon$ (per unit energy)

The density of states $D(\varepsilon)$ can be counted using a the delta function due to the discreteness nature of the levels i.e $D(\varepsilon) = \frac{1}{L^d}\sum_{k\sigma} \delta(\varepsilon - \varepsilon_k)$; $\varepsilon_k = \frac{\hbar^2 k^2}{2m}$

(DOS per unit volume) ; d: dimensionality 1,2,3

in 3D

$$D(\varepsilon) = \frac{V}{\pi^2}\int_0^\infty dk\, k^2\, \delta(\varepsilon - \varepsilon_k) \ ;$$

DOS (not per unit volume)

$$\left\{ \begin{aligned} k^2 &= \frac{2m}{\hbar^2}\varepsilon_k, \\ 2k\,dk &= \frac{2m}{\hbar^2}\, d\varepsilon_k \\ dk &= \frac{m}{\hbar^2 k}\, d\varepsilon_k \\ &= \frac{m}{\hbar}\,\frac{1}{(2m)^{1/2}}\,\frac{1}{\varepsilon_k^{1/2}}\, d\varepsilon_k \end{aligned} \right.$$

$$= \frac{V}{\pi^2}\,\frac{m}{\hbar(2m)^{1/2}}\int_0^\infty \frac{d\varepsilon_k}{\varepsilon_k^{1/2}}\,\frac{2m\varepsilon_k}{\hbar^2}\,\delta(\varepsilon - \varepsilon_k)$$

$$= \frac{V}{\pi^2\hbar^3}\, m(2m)^{1/2}\int_0^\infty d\varepsilon_k\, \varepsilon_k^{1/2}\, \delta(\varepsilon - \varepsilon_k)$$

$$\Rightarrow D(\varepsilon) = \frac{V}{\pi^2 \hbar^3}\, m\,(2m)^{1/2}\, \varepsilon^{1/2} \times \frac{2}{2} \,;$$

in textbook (Marder) it is defined as $\frac{D(\varepsilon)}{V}$ per unit volume and per unit energy

$m^{-3}.\,J^{-1}$ ...

$$= \frac{V}{2\pi^2 \hbar^3}\,(2m)^{3/2}\, \varepsilon^{1/2}$$

$$\boxed{D(\varepsilon) = K\, V\, \varepsilon^{1/2}} \longrightarrow J^{-1} \;;\quad K = \text{constant} = \frac{(2m)^{3/2}}{2\pi^2 \hbar^3} = 1.062 * 10^{56}\ m^{-3}.\,J^{-3/2}$$

Now using $D(\varepsilon)$, one can recalculate N and E using

$$N = \int_0^\infty d\varepsilon\, D(\varepsilon)\, f(\varepsilon) = \frac{2}{3} K\, V\, \varepsilon_F^{3/2} \quad \text{and} \quad E = \int_0^\infty d\varepsilon\, D(\varepsilon)\, \varepsilon\, f(\varepsilon) = \frac{2}{5} K\, V\, \varepsilon_F^{5/2}$$

same results will be obtained as before.

note that
$$D(\varepsilon_F) = \frac{V}{2\pi^2\hbar^3}\,(2m)^{3/2}\, \varepsilon_F^{1/2} \times \frac{3\,\varepsilon_F}{3\,\varepsilon_F}$$

$$= \frac{3}{2}\, \underbrace{\frac{V}{3\pi^2\hbar^3}\,(2m\,\varepsilon_F)^{3/2}}_{N}\, \frac{1}{\varepsilon_F} = \frac{3\,N}{2\,\varepsilon_F} \equiv \text{constant}$$

Recall that $\varepsilon_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3} \Rightarrow \frac{2m\,\varepsilon_F}{\hbar^2} = (3\pi^2 n)^{2/3}$

$$\Rightarrow \frac{(2m\,\varepsilon_F)^{3/2}}{\hbar^3} = 3\pi^2 n \;; \quad \text{but } n = \frac{N}{V} \Rightarrow N = \frac{V}{3\pi^2\hbar^3}\,(2m\,\varepsilon_F)^{3/2}$$

Caution!! : in Marder textbook, $D(\varepsilon_F) = \frac{3\,n}{2\,\varepsilon_F}$ as he defined $D(\varepsilon)$ per unit volume

for silver and using the values of n and fermi energy from table 6.1, one gets for D(fermi level) $=1 * 10^{47}\ m.^{-3}\,J^{-1}$

huge number !! ... lots of charge carriers ... Ag is a good electric conductor density of states in 1D and 2D

- the same procedure can be followed to find $D(\varepsilon)$ in 1D and 2D

using the general definition $\rightarrow D(\varepsilon) = \frac{2}{(2\pi)^d} \int dq^d dk^d \delta(\varepsilon - \varepsilon_p)$

in 2D: $D(\varepsilon) = \frac{mA}{\pi \hbar^2}$; A: area (see problem 4)

(see problem 4 in HW#4)

in 1D: $D(\varepsilon) = \frac{L}{\pi \hbar} \sqrt{\frac{2m}{\varepsilon}}$; L: Length (see problem 7)

- **r_s - Parameter:** The density of electrons is sometimes defined by finding the volume per electron $\frac{V}{N}$ and defining the free electron sphere to be one with the same volume; i.e

$$\frac{V}{N} = \frac{4}{3}\pi r_s^3 \Rightarrow r_s = \left(\frac{3}{4\pi}\frac{V}{N}\right)^{1/3} = \left(\frac{3}{4\pi n}\right)^{1/3}$$

Table 6.1 lists n, k_F, ε_F, T_F, v_F, and r_s/a_0

$\downarrow$ Bhor radius

n was measured at 300K and the rest were calculated using n as a given quantity

Example: electrons in Copper metal

$n = 8.49 \times 10^{28}/m^3$; $k_F = 1.36 \times 10^{10} m^{-1}$, $\varepsilon_F = 7.04$ eV

$v_F = 1.57 \times 10^6 m/s$; $T_F = 8.17 \times 10^4 K$; $\frac{r_s}{a_0} = 2.67$

when $\hbar = 6.58 \times 10^{-16}$ eV.s and $m_e = 9.1 \times 10^{-31}$ kg were used.

stabistical mechanics of Non interacting electrons:

- let us consider that the system of conduction electrons in a metal is in contact with a thermal and particle bath such that Both E and N of the conduction electrons are variables. The bath usually has an infinit heat capacity so that it can provides any amount of energy or any # of electrons to the system without changing its chemical Potential and temperature. i.e the big bath has a fixed μ and T such that it fixes the μ and T of the system at equilibrium. so once the system of the conduction electrons reaches the state of equilibrium, it will have an average energy $\bar{E}$ and an average # of electrons $\bar{N}$.

- Grand Partion function $Z_1 = \prod_k (1+e^{\beta(\mu-\varepsilon_k)})$ ----(2)

- Grand Potential $\Omega = -k_BT \sum_k \ln(1+e^{\beta(\mu-\varepsilon_k)})$

---(3)

where I used $\Omega = -k_BT \ln Z_1$

$\downarrow$

symbole used in mader II

Note that using Z_1, one can calculate $\langle n_k \rangle$ of state $\underline{k}$ using the relation $\langle n_k \rangle = -k_B T \dfrac{\partial \ln Z_1}{\partial \varepsilon_k} = -\dfrac{1}{\beta} \dfrac{\partial \ln Z_1}{\partial \varepsilon_k}$

<u>check!:</u> $\ln Z_1 = \ln \prod_k (1 + e^{\beta(\mu - \varepsilon_k)})$

$$= \sum_k \ln (1 + e^{\beta(\mu - \varepsilon_k)})$$

for specific state $|k\rangle$ with energy ε_k ; we get

$\dfrac{\partial \ln Z_1}{\partial \varepsilon_k} = \dfrac{-\beta e^{\beta(\mu - \varepsilon_k)}}{1 + e^{\beta(\mu - \varepsilon_k)}}$; Recall that $\dfrac{\partial \ln Z_1}{\partial \varepsilon_j} = 0$; if $\varepsilon_j \neq \varepsilon_k$

$$\Rightarrow \langle n_k \rangle = -\frac{1}{\beta} \left(\frac{-\beta e^{\beta(\mu - \varepsilon_k)}}{1 + e^{\beta(\mu - \varepsilon_k)}} \right) = \frac{e^{\beta(\mu - \varepsilon_k)}}{1 + e^{\beta(\mu - \varepsilon_k)}}$$

$$= \frac{1}{e^{\beta(\varepsilon_k - \mu)} + 1} \equiv f(\varepsilon_k) \equiv f_k$$

F-D distribution function as expected.

- furthermore, one can also find the average # of particles at equilibrium from Ω using $N = \bar{N} = -\dfrac{\partial \Omega}{\partial \mu}$

$$N = k_B T \frac{\partial \ln Z_1}{\partial \mu} = \frac{1}{\beta} \frac{\partial \ln Z_1}{\partial \mu} =$$

$$= \frac{1}{\beta} \sum_k \frac{\beta e^{\beta(\mu - \varepsilon_k)}}{1 + e^{\beta(\mu - \varepsilon_k)}} = \sum_k \frac{1}{e^{\beta(\varepsilon_k - \mu)} + 1} = \sum_k \langle n_k \rangle$$

as expected.

The Grand Potential Ω is an important quantity in statistical mechanics. We can rewrite over energy as

$$\Omega = -k_BT \sum_k \ln(1+e^{\beta(\mu-\varepsilon_k)}) \; ; \quad \sum_k \to \frac{V}{\pi^2}\int_0^\infty k^2 dk$$

thermodynamics limit

$$= -k_BT\frac{V}{\pi^2}\int_0^\infty dk\, k^2 \ln(1+e^{\beta(\mu-\varepsilon)}) \; ;$$

$$= -k_BT\frac{V}{\pi^2}\frac{1}{2\hbar}\frac{(2m)^{3/2}}{}\frac{2m}{\hbar^2}\int_0^\infty d\varepsilon\, \varepsilon^{1/2}\ln(1+e^{\beta(\mu-\varepsilon)})$$

$$= -k_BT\int_0^\infty d\varepsilon\, \underbrace{\frac{V}{2\pi^2\hbar^3}(2m)^{3/2}\varepsilon^{1/2}}_{D(\varepsilon)} \ln(1+e^{\beta(\mu-\varepsilon)})$$

$\varepsilon = \frac{\hbar^2k^2}{2m}$

$k^2 = \frac{2m\varepsilon}{\hbar^2}$

$2k\,dk = \frac{2m}{\hbar^2}d\varepsilon$

$\Rightarrow dk = \frac{1}{2\hbar}\frac{(2m)^{3/2}}{\varepsilon^{1/2}}d\varepsilon$

$$\boxed{\Omega = -k_BT\int_0^\infty d\varepsilon\, D(\varepsilon)\ln(1+e^{\beta(\mu-\varepsilon)})} \quad \text{----} \; (4)$$

So at $T=0$, and using $D(\varepsilon) = KV\varepsilon^{1/2}$, one can easily show that (using integration by parts)

$$\Omega = -k_BT\, KV\int_0^{\varepsilon_F} d\varepsilon\, \varepsilon^{1/2}\ln(1+e^{(\varepsilon_F-\varepsilon)/kT}) \; ;$$

$$= -\frac{2}{5}\,\frac{2}{3}KV\varepsilon_F^{5/2} = -\frac{2}{3}\underbrace{\frac{2}{5}KV\varepsilon_F^{5/2}}_{E} = -\frac{2}{3}E \equiv -PV$$

and $S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu} = 0$ as expected at $T=0$

$\Rightarrow PV = \frac{2}{3}E$ equation of state

also $N = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{V,T} = -\left(\frac{\partial\Omega}{\partial\varepsilon_F}\right)_{V,T} = \frac{2}{3}KV\varepsilon_F^{3/2}$ as obtained before

see problem 6.3

$$P = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu} = \frac{4}{15}K\,\varepsilon_F^{\frac{5}{2}} = \frac{2}{5}n\,\varepsilon_F$$

ii) $T > 0$ (degenerate limit; $T \ll T_F$)

in this case $\mu(T) \neq \varepsilon_F$ and $f(\varepsilon)$ is no longer 1 or zero for $\varepsilon < \varepsilon_F$ and $\varepsilon > \varepsilon_F$, respectively. so we need to calculate N and E using

$$N = \int_0^\infty d\varepsilon \, D(\varepsilon) f(\varepsilon) = K V \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{e^{\beta(\varepsilon-\mu)} + 1} \quad \text{----} \quad (5)$$

$$E = \int_0^\infty d\varepsilon \; \varepsilon \, D(\varepsilon) f(\varepsilon) = K V \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{\beta(\varepsilon-\mu)} + 1} \quad \text{----} \quad (6)$$

before calculation of these two integrals, let us talk about Heat capacity of electron gas in metals. Classically, (at high T and low n), the expected $C_V \approx 3 N k_B$. However, the observed electronic C_V in metals is less than 0.01 of this expected value. this discrepancy was answered after the discovery of the Pauli principle and the F-D distribution function $f(\varepsilon)$. when a metal is heated up from $(T=0)$, not every electron among the conduction electrons gains an energy $k_B T$ as expected classically, but only those electrons in states within an energy range $k_B T$ of the Fermi level are excited thermally. so if N is the total # of conduction electrons, then only a fraction of the order $N\left(\frac{T}{T_F}\right)$ can be excited thermally, at a temperature T.

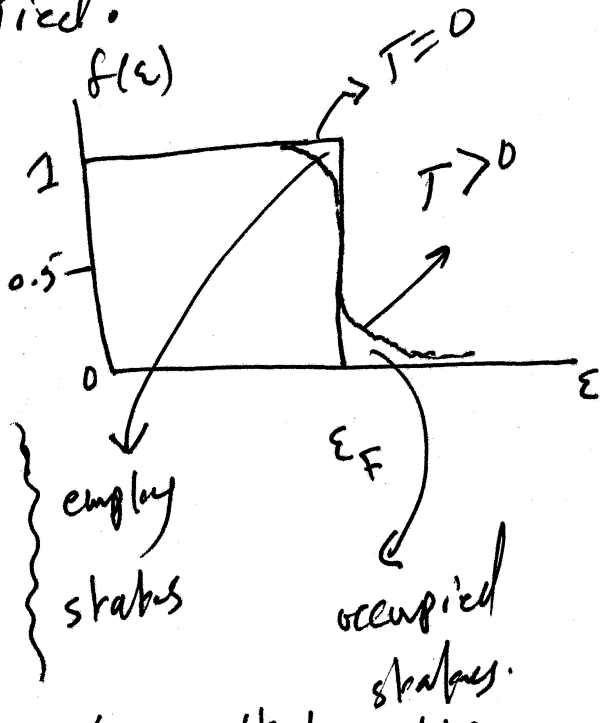
so $U_{ele} = \left(N\frac{T}{T_F}\right)k_BT \Rightarrow C_{ele} = \frac{\partial U}{\partial T} = Nk_B\frac{T}{T_F}$

in agreement with experimental results. $\Rightarrow C_{ele} \propto T$

- typical value of ε_F in metals is around severals eVs $\Rightarrow T_F = \frac{\varepsilon_F}{k_B}$ gives values of several tens of thousands of kelvins. so at RT, typical $k_BT \approx 0.0257$ eV, meaning that $k_BT \ll \varepsilon_F$ or $(T \ll T_F)$. so we expect that $f(\varepsilon)$ at RT is still close to a step function. This limit is called the degenerate limit, meaning at RT still most levels are doubly occupied.

k_B = 8.6 *10^-5 eV/K

- Calculating the integrals in eqns 5 and 6 is not an easy task. However, they can be solved with an approximation, sommerfeld expansion



$$\int_0^\infty \frac{F(\varepsilon)\,d\varepsilon}{e^{\beta(\varepsilon-\mu)}+1} = \int_0^\mu F(\varepsilon)\,d\varepsilon + \frac{\pi^2}{6}(k_BT)^2 F'(\mu)$$

$F(\varepsilon)$ is not Fermi function and in our textbook labeled as $H(\varepsilon)$. F' is 1st derivative.

so eqn 5 becomes

$$N = KV\int_0^\infty \frac{\varepsilon^{1/2}\,d\varepsilon}{e^{\beta(\varepsilon-\mu)}+1} = KV\left[\frac{2}{3}\mu^{3/2} + \frac{\pi^2}{6}(k_BT)^2\cdot\frac{1}{2}\mu^{-1/2}\right]; \cdots (7)$$

when $F(\varepsilon) = \varepsilon^{1/2}$

Now at $T=0$, we found that

$$N=\frac{2}{3}KV\varepsilon_F^{3/2} \Rightarrow KV=\frac{3N}{2\varepsilon_F^{3/2}}$$, so eq^n (7) now reads

$$\cancel{N}=\frac{3\cancel{N}}{2\varepsilon_F^{3/2}}\left[\frac{2}{3}\mu^{3/2}+\frac{\pi^2}{6}(k_BT)^2\cdot\frac{1}{2}\mu^{-1/2}\right]$$

$$\Rightarrow \varepsilon_F^{3/2}=\mu^{3/2}+\frac{\pi^2}{8}\frac{(kT)^2}{\mu^{1/2}}=\mu^{3/2}\left[1+\frac{\pi^2}{8}\frac{(kT)^2}{\mu^2}\right]$$

$\hookrightarrow$ can be replaced by ε_F

$$\Rightarrow \varepsilon_F=\mu\left[1+\frac{\pi^2}{8}\left(\frac{k_BT}{\varepsilon_F}\right)^2\right]^{2/3}$$

$$\approx\mu\left[1+\frac{2}{3}\frac{\pi^2}{8}\left(\frac{kT}{\varepsilon_F}\right)^2\right]$$; $(1+x)^n\approx 1+nx$ when $x\ll 1$

$$\varepsilon_F=\mu\left[1+\frac{\pi^2}{12}\left(\frac{kT}{\varepsilon_F}\right)^2\right]$$

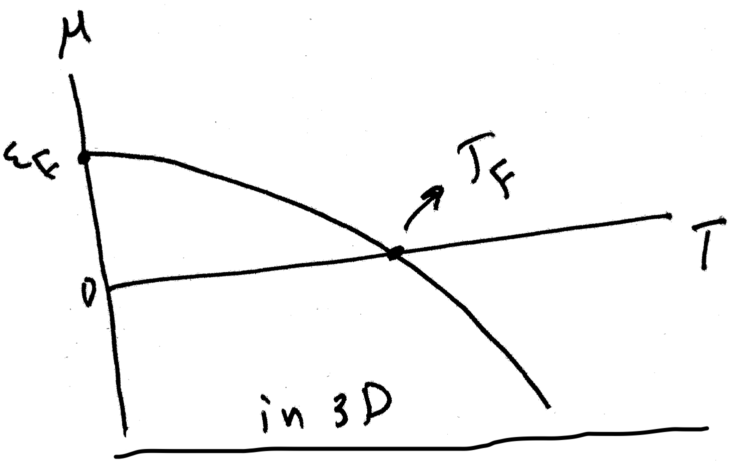
$$\Rightarrow \mu=\varepsilon_F\left[1+\frac{\pi^2}{12}\left(\frac{kT}{\varepsilon_F}\right)^2\right]^{-1}\approx\varepsilon_F\left[1-\frac{\pi^2}{12}\left(\frac{kT}{\varepsilon_F}\right)^2\right]$$

using $D(\varepsilon)=KV\varepsilon^{1/2}$, it can be written as $=\varepsilon_F-\frac{\pi^2}{6}(k_BT)^2\frac{D'(\varepsilon_F)}{D(\varepsilon_F)}$ as in textbook

$$=\varepsilon_F-\frac{\pi^2}{12}\frac{(k_BT)^2}{\varepsilon_F}=\varepsilon_F+\delta\mu$$;

when $\delta\mu=-\frac{\pi^2}{12}\frac{(kT)^2}{\varepsilon_F}$

i.e $\mu(T)=\varepsilon_F+\delta\mu$, so $\mu>0$ when $T<T_F$, which is good enough as T_F is several thousands of kelvins. So for all practical purposes, $\mu>0$ for an ideal Fermi gas.



valid only at very low temperatures (see problem 6 in HW#4 for the full temperature dependence)

Note that in 2D, $D'(\varepsilon_F)=0 \Rightarrow$ we always have $\mu(T)=\varepsilon_F$ in 2D for energy

$$E = KV \underbrace{\int_0^{\infty} \frac{\varepsilon^{3/2}\, d\varepsilon}{e^{\beta(\varepsilon-\mu)}+1}}_{I} \quad \text{----} \quad (8)$$

$$I = \int_0^{\infty} \frac{\varepsilon^{3/2}\, d\varepsilon}{e^{\beta(\varepsilon-\mu)}+1} = \int_0^{\mu} \varepsilon^{3/2}\, d\varepsilon + \frac{\pi^2}{6}(k_B T)^2 \cdot \frac{3}{2}\mu^{1/2}$$

$$= \frac{2}{5}\mu^{5/2} + \frac{\pi^2}{4}(k_B T)^2 \mu^{1/2} \quad \text{-----} \quad (9)$$

now find $\mu^{1/2}$ and $\mu^{5/2}$

$$\mu(T) = \mu(T=0) + \delta\mu = \varepsilon_F + \delta\mu = \varepsilon_F\left(1 + \frac{\delta\mu}{\varepsilon_F}\right)$$

$$\Rightarrow \mu^n = \varepsilon_F^n\left(1+\frac{\delta\mu}{\varepsilon_F}\right)^n = \varepsilon_F^n\left(1 + n\frac{\delta\mu}{\varepsilon_F}\right) \quad ; \text{ as } \delta\mu \ll \varepsilon_F$$

$$= \varepsilon_F^n + n\,\delta\mu\,\varepsilon_F^{n-1}$$

so $\mu^{1/2} = \varepsilon_F^{1/2} + \frac{1}{2}\delta\mu\,\varepsilon_F^{-1/2}$ and $\mu^{5/2} = \varepsilon_F^{5/2} + \frac{5}{2}\delta\mu\,\varepsilon_F^{3/2}$

$$\Rightarrow I = \frac{2}{5}\varepsilon_F^{5/2} + \varepsilon_F^{3/2}\delta\mu + \frac{\pi^2}{4}(kT)^2\left[\varepsilon_F^{1/2} + \frac{1}{2}\delta\mu\,\varepsilon_F^{-1/2}\right]$$

$$= \frac{2}{5}\varepsilon_F^{5/2} + \varepsilon_F^{3/2}\delta\mu + \frac{\pi^2}{4}(kT)^2\varepsilon_F^{1/2} + \frac{\pi^2}{8}\frac{(kT)^2}{\varepsilon_F^{1/2}}\delta\mu$$

Now using $\delta\mu = -\frac{\pi^2}{12}\frac{(kT)^2}{\varepsilon_F}$

$$\Rightarrow I = \frac{2}{5}\varepsilon_F^{5/2} - \frac{\pi^2}{12}(kT)^2\varepsilon_F^{1/2} + \frac{\pi^2}{4}(kT)^2\varepsilon_F^{1/2} - \frac{\pi^4}{96}(kT)^4\varepsilon_F^{-3/2}$$

very small as $kT \ll \varepsilon_F$

$$= \frac{2}{5}\varepsilon_F^{5/2} + \frac{\pi^2}{6}(kT)^2\varepsilon_F^{1/2}$$

so eq^n (8) reads

$$E = KV\left[\frac{2}{5}\varepsilon_F^{5/2} + \frac{\pi^2}{6}(kT)^2\varepsilon_F^{1/2}\right]$$

$$= \frac{2}{5}KV\varepsilon_F^{5/2} + \underbrace{KV\frac{\pi^2}{6}(kT)^2\varepsilon_F^{1/2}} \nearrow \times \text{ multiply by } \frac{\varepsilon_F}{\varepsilon_F}\times\frac{2}{3}\times\frac{3}{2}$$

$$= \underbrace{\frac{2}{5}KV\varepsilon_F^{5/2}}_{E\,(T=0)} + \underbrace{\frac{2}{3}KV\varepsilon_F^{3/2}}_{N}\cdot\frac{\pi^2}{4}\frac{(k_BT)^2}{\varepsilon_F}$$

$$E = E(T=0) + N\frac{\pi^2}{4}\frac{k_B^2T^2}{k_BT_F} \quad ; \text{ where } \varepsilon_F = k_BT_F$$

$$E = \underbrace{E(T=0)}_{\text{constant}} + \frac{\pi^2}{4}Nk_B\frac{T^2}{T_F}$$

$$\Rightarrow C_{ele} = \frac{\partial E}{\partial T} = \frac{\pi^2}{2}Nk_B\frac{T}{T_F} \propto T$$ in agreement with experimental results

$$C_{ele} \downarrow C_V$$

Note that $C_{ele} = C_V = \frac{\pi^2}{2}Nk_B\frac{T}{T_F}\times\frac{k_B\times 3}{k_B\times 3} = \frac{\pi^2}{3}\underbrace{\frac{3N}{2\varepsilon_F}}_{D(\varepsilon_F)}k_B^2T$

$$= \frac{\pi^2}{3}k_B^2D(\varepsilon_F)T$$

Note that: $C_{ele} = \frac{\pi^2}{2}Nk_B\frac{T}{T_F} = \gamma T \; ; \; \gamma = \frac{\pi^2}{2}N\frac{k_B}{T_F}$

So by measuring γ experimentally, one can find T_F of the metal from the slope of C_{ele} vs T

see problem 4 in HW#8

so $\gamma = \frac{\pi^2}{2} N \frac{k_B}{T_F} = \frac{\pi^2}{2} N \frac{k_B^2}{\varepsilon_F}$

Now # of moles $n = \frac{N}{N_A}$; so for 1 mole $\Rightarrow N = N_A = 6.02\times10^{23} \frac{\text{atom}}{\text{mol}}$

$\Rightarrow \gamma = \frac{\pi^2}{2} N_A \frac{k_B^2}{\varepsilon_F}$; $k_B = 1.38\times10^{-23} \frac{J}{K}$

$= \frac{\pi^2}{2} \times 6.02\times10^{23} \frac{}{\text{mol}} \times \frac{(1.38\times10^{-23})^2 \frac{J^2}{K^2}}{\varepsilon_F(eV)\times1.6\times10^{-19}\, J}$ ε_F : from table 6.1

theory ← $= \frac{3.536}{\varepsilon_F(eV)} \boxed{\frac{mJ}{mol.K^2}}$ → standard unit

table 6.2 shows a comparison between theoritical and experimental values of γ

metal	γ_{exp}	γ_{th}
Li	1.65	0.75
Na	1.38	1.09

see other values in table 6.2

Clearly from table 6.2, γ_{th} is not that good, indicating that this model (free electron model) need improvement.

to find the equation of state and the pressure in the degenerate limit, let us first find Ω

$$\Omega = -k_B T \int_0^\infty d\varepsilon \; D(\varepsilon) \ln\left(1 + e^{(\mu-\varepsilon)/kT}\right) ;$$

$$= -k_B T K V \int_0^\infty d\varepsilon \; \varepsilon^{1/2} \ln\left(1 + e^{(\mu-\varepsilon)/kT}\right)$$

integrate by parts

$$\text{let } u = \ln\left(1 + e^{(\mu-\varepsilon)/kT}\right) \quad ; \quad dv = \varepsilon^{1/2} d\varepsilon$$

$$du = -\frac{1}{kT} \frac{e^{(\mu-\varepsilon)/kT}}{1 + e^{(\mu-\varepsilon)/kT}} \quad ; \quad v = \frac{2}{3} \varepsilon^{3/2}$$

$$= -\frac{1}{kT} \frac{1}{e^{(\varepsilon-\mu)/kT} + 1} \; ;$$

$$\text{so } \Omega = -k_B T K V \left[\overbrace{\frac{2}{3} \varepsilon^{3/2} \ln\left(1 + e^{(\mu-\varepsilon)/kT}\right) \Big|_0^\infty}^{0} + \frac{2}{3} \frac{1}{kT} \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{(\varepsilon-\mu)/kT} + 1} \right.$$

$\Downarrow$

at $\varepsilon = 0$, it vanishes because the factor $\varepsilon^{3/2}$

at $\varepsilon = \infty$, $\frac{\mu - \varepsilon}{kT} \to -\infty$, whatever μ and T

so $e^{-\infty} = \frac{1}{e^{\infty}} = 0 \Rightarrow \ln 1 = 0$

$\therefore$

$$\Omega = -\frac{2}{3} K V \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{(\varepsilon-\mu)/kT} + 1}$$

$$\therefore\quad \Omega = -\frac{2}{3}\underbrace{KV\int_0^\infty \frac{\varepsilon^{3/2}\,d\varepsilon}{e^{(\varepsilon-\mu)/kT}+1}}_{E(T)} = -\frac{2}{3}\left[E(T=0) + \frac{\pi^2}{4}Nk_B\frac{T^2}{T_F}\right]$$

$$= -\frac{2}{3}\underbrace{E(T=0)}_{\text{constant}} - \frac{\pi^2}{6}Nk_B\frac{T^2}{T_F}$$

so $\underset{\substack{\downarrow\\ \text{entropy}}}{S} = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu} = \frac{\pi^2}{3}Nk_B\frac{T}{T_F} \propto T$

Note that $\Omega = -\frac{2}{3}E \equiv -PV \Rightarrow \boxed{PV = \frac{2}{3}E}$

$\Downarrow$ equation of state

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similar calculations can be done in 1D and 2D

<u>in 2D</u>: $D(\varepsilon) = \frac{Am}{\pi\hbar^2}$ = constant $\Rightarrow \quad E = \frac{1}{2}N\varepsilon_F + \frac{\pi^2}{6}Nk_B\frac{T^2}{T_F}$

$$\Rightarrow C_V = C_{el} = \left(\frac{\partial E}{\partial T}\right)_V = \frac{\pi^2}{3}Nk_B\frac{T}{T_F} \quad \propto T$$

<u>in 1D</u>: $D(\varepsilon) = \frac{L}{\pi\hbar}\left(\frac{2m}{\varepsilon}\right)^{1/2} \Rightarrow C_V = \frac{\pi^2}{6}Nk_B\frac{T}{T_F} \propto T$

classical limit (low n and high T);

$$\frac{\mu}{k_B T} <<1 \Rightarrow \beta\mu << 1 \Rightarrow e^{-\beta\mu} >> 1$$

so $N = \int_0^\infty d\varepsilon \, D(\varepsilon)\, f(\varepsilon)$; $f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} \underline{\underline{+1}}} \rightarrow e^{-\beta(\varepsilon-\mu)}$ Boltzmann dist

$\underline{\underline{+1}} \rightarrow$ can be ignored

$$= K V \int_0^\infty d\varepsilon \, \varepsilon^{1/2} e^{-\beta(\varepsilon-\mu)}$$

$$= K V \, e^{\beta\mu} \int_0^\infty d\varepsilon \, \varepsilon^{1/2} e^{-\beta\varepsilon} \quad ; \text{ let } \beta\varepsilon = x, \; \beta d\varepsilon = dx$$

$$= K V \frac{e^{\beta\mu}}{\beta^{3/2}} \underbrace{\int_0^\infty dx \, x^{1/2} e^{-x}}_{\Gamma(3/2) = \frac{\sqrt{\pi}}{2}} \quad ; \quad \Gamma(n) = \int_0^\infty x^{n-1} e^{-x} dx$$

$$= K V \frac{e^{\beta\mu}}{\beta^{3/2}} \frac{\sqrt{\pi}}{2} ;$$

$$E = \int_0^\infty d\varepsilon \, \varepsilon \, D(\varepsilon)\, f(\varepsilon) = K V \int_0^\infty d\varepsilon \, \varepsilon^{3/2} e^{-\beta(\varepsilon-\mu)}$$

$$= K V e^{\beta\mu} \int_0^\infty d\varepsilon \, \varepsilon^{3/2} e^{-\beta\varepsilon} = K V \frac{e^{\beta\mu}}{\beta^{5/2}} \underbrace{\int_0^\infty dx \, x^{3/2} e^{-x}}_{\Gamma(5/2) = \frac{3\sqrt{\pi}}{4}}$$

$$= \underbrace{K V \frac{e^{\beta\mu}}{\beta^{3/2}} \frac{\sqrt{\pi}}{2}}_{N} \cdot \frac{3}{2} \cdot \frac{1}{\beta}$$

$= \frac{3}{2} N k_B T$ as expected.