FERMI_DIRAC GASSES

Fermions: Are particles of half-integer spin that obey Fermi-Dirac statistics. Fermions obey the Pauli exclusion principle, which prohibits the occupancy of an available quantum state by more than one particle.

Ideal fermion gas: Consisting of *N* non-interacting and indistinguishable fermions in a container of volume *V* held at absolute temperature *T*.
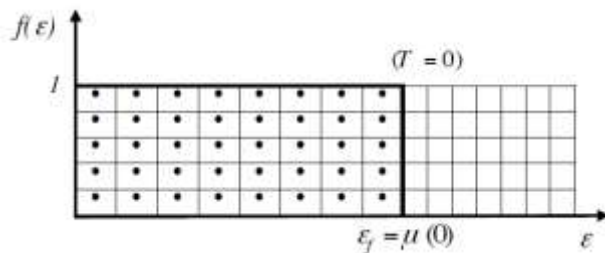
Fermi-Dirac distribution: For an ideal FD gas (non-interactions between the indistinguishable particles) of N molecules in a volume V, the most probable number of particles with ε_i energy is:

$$f(\varepsilon_i) = \frac{n_i^*}{g_i} = \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1}$$
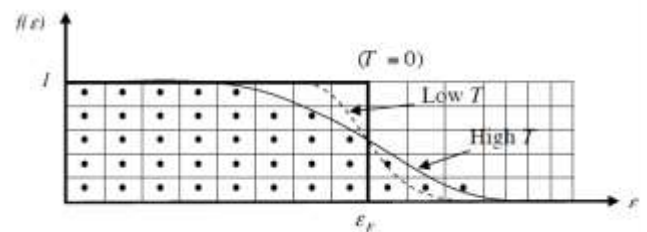
and the continuum is:

$$f(\varepsilon) = \frac{N(\varepsilon)}{g(\varepsilon)} = \frac{1}{e^y + 1}, \qquad y = \beta(\varepsilon - \mu)$$

Fermi function gives the probability that a single particle state ε_i will be occupied by a fermion. Clearly, $0 \le f(\varepsilon) \le 1$.

The Fermi function at T = 0 $f(\varepsilon)$ at three different temperatures in FD statistics

Notes:

1- μ no need to be negative, due to the +1 in the denominator. μ may be positive or negative.

2- If $\mu\beta \ll 0$, then $e^{\beta(\varepsilon - \mu)} \gg 1$, and $f(\varepsilon)$ reduces to the Maxwell-Boltzmaan distribution.

3- If $\mu\beta \gg 0$

  i- if $\varepsilon \ll \mu \implies \beta(\varepsilon - \mu) \ll 0 \implies f(\varepsilon) = 1$

  ii- if $\varepsilon \gg \mu \implies \beta(\varepsilon - \mu) \gg 0 \implies f(\varepsilon) = e^{-\beta(\varepsilon - \mu)}$ and fall off exponentially like Maxwell-Boltzmaan distribution.

  iii- if $\varepsilon = \mu \implies f(\varepsilon) = \frac{1}{2}$

  iv- In the limit of $T \to 0$ we have sharp drop and

$$f(\varepsilon) = \begin{cases} 1 & \varepsilon < \mu_o \\ 0 & \varepsilon > \mu_o \end{cases} \implies N = \begin{cases} \int_0^{\mu_o} g(\varepsilon)d\varepsilon & T = 0 \\ \int_0^{\mu_o} g(\varepsilon)f(\varepsilon)d\varepsilon & T \ne 0 \end{cases}$$

Where

$$g(\varepsilon) = g_s \left(\frac{2\pi V}{h^3}\right)(2m)^{3/2}\sqrt{\varepsilon}, \qquad\qquad g_s = 2s + 1$$

$$= 4\pi V \left(\frac{2m}{h^2}\right)^{3/2}\sqrt{\varepsilon}, \qquad \text{for electrons}$$

Exclusion principle implies that a FD gas has a large mean energy even at absolute zero, $0 < \varepsilon < \mu_o (\equiv \varepsilon_f(0))$. [**Note that**: *Degenerate here means filled, not as the case of QM*]

$$
T = \begin{cases}
0 & \mu_o > 0, \quad \varepsilon < \mu_o & \text{Very low temperature} & \text{Completely degenerate} \\
T \ll T_f & \mu_o > 0 & \text{Low temperature} & \text{degenerate} \\
T \approx T_f & \mu_o = 0 & \text{Intermediate temperature} & \text{Slightly degenerate} \\
T \gg T_f & \mu < 0 & \text{High temperature} & \text{Classical limit}
\end{cases}
$$

At absolute zero, due to exclusion principle, all the states with $0 < \varepsilon \leq \mu_o (\equiv \varepsilon_f(0))$ are completely filled and all the states with $\varepsilon > \mu_o$ are completely empty.

Completely Degenerate Fermi-Gas
Total number of particles:

$$
N = \int_0^{\mu_o} g(\varepsilon) f(\varepsilon) d\varepsilon = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^{\mu_o} \sqrt{\varepsilon}\, d\varepsilon = \frac{8\pi V}{3} \left(\frac{2m}{h^2}\right)^{3/2} \mu_o^{3/2}
$$

$$
\Rightarrow \mu_o = \frac{h^2}{2m} \left(\frac{3N}{8\pi V}\right)^{2/3}
$$

For convenience, we introduce a Fermi temperature T_f such that $\mu_o = \varepsilon_F = k_B T_f$. This can be written as:

$$
T_f = \frac{\mu_o}{k_B} = \frac{h^2}{2mk_B} \left(\frac{3}{8\pi} \frac{N}{V}\right)^{2/3}
$$

Example: Metallic potassium has $\rho = 0.86 \times 10^3 \text{ kg/m}^3$ and atomic weight of $M = 39 \text{ kg/kmole}$. Find μ_o, T_f, and v_f.

Solution: We will consider one free electron per atom for monovalent atoms. Thus the concentration is:

$$
\frac{N}{V} = \frac{N_a \rho}{M} = \frac{(6.02 \times 10^{26} \text{ atoms/kmole})(0.86 \times 10^3 \text{ kg/m}^3)}{39 \text{ kg/kmole}} = 1.33 \times 10^{28} \text{ atoms/m}^3,
$$

$$
\mu_o = \frac{h^2}{8m} \left(\frac{3}{\pi} \frac{N}{V}\right)^{2/3} = \frac{(hc)^2}{8mc^2} \left(\frac{3}{\pi} \frac{N}{V}\right)^{2/3} = \frac{(12.4 \times 10^{-7} \text{ eV.m})^2}{8(0.511 \times 10^6 \text{ eV})} \left(\frac{3}{\pi} \times 1.33 \times 10^{28} \frac{\text{atoms}}{\text{m}^3}\right)^{2/3} = 2.05 \text{ eV}
$$

Then

$$
T_f = \frac{\mu_o}{k_B} = \frac{2.05 \text{ eV}}{8.617 \times 10^{-5} \dfrac{\text{eV}}{\text{K}}} = 23790 \text{ K}
$$

So, even at room temperature we have to treat the metallic potassium quantum mechanically. Use

$$
\mu_o = \frac{p_f^2}{2m} \quad \Rightarrow \quad p_f^2 = 2m\mu_o
$$

$$
\Rightarrow v_f^2 = \frac{2\mu_o}{m} = \frac{2\mu_o c^2}{mc^2} = \frac{2(2.05 \text{ eV}) \times (3.0 \times 10^8 \text{ m/s})^2}{(0.511 \times 10^6 \text{ eV})} = 7.22 \times 10^{11} \text{ m}^2/\text{s}^2
$$

$$
\Rightarrow v_f = 8.5 \times 10^5 \text{ m/s}
$$

The speed of the electron in metals is 10 times the speed of sound.
Internal energy:

$$U_o = \int_0^{\mu_o} \varepsilon g(\varepsilon) f(\varepsilon) d\varepsilon$$

$$= 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^{\mu_o} \varepsilon^{3/2} d\varepsilon = \frac{8\pi V}{3}\left(\frac{2m}{h^2}\right)^{3/2} \mu_o^{5/2}$$

$$= \frac{3}{5} N \mu_o$$

Other thermodynamic functions are:

$$S_o = 0,$$

$$\Omega_o = -PV = U_o - S_o - \mu_o N = -\frac{2}{5}\mu_o N,$$

$$P = -\frac{\Omega_o}{V} = \frac{2}{5}\mu_o \left(\frac{N}{V}\right) \quad = 2.71\times 10^7 \rho \text{ atm for electrons)}$$

Thus at $T = 0$ K a fermion gas exerts a pressure. If the electrons in a metal were neutral they would exert a pressure of about 10^6 atm. Given this tremendous pressure, we can appreciate the role of the surface potential barrier in keeping the electrons from evaporating from the metal. In other words, the Coulomb attraction to the ions counterbalances the pressure. For $T = 0$ K the value of $\varepsilon_f(0)$ is positive and large.

H.W.
Prove that

$$\mu(T) \approx \mu_o \left[1 - \frac{\pi^2}{12}\left(\frac{T}{T_f}\right)^2\right], \qquad\qquad T \ll T_f$$

Notes:
1. $\mu(T)$ is positive for temperature below the Fermi temperature and negative for higher temperature.
2. As the temperature increases above, more and more of the fermions are in the excited states and the mean occupancy of the ground state falls below 1/2. In this region,

$$f(0) = \frac{1}{e^{-\beta\mu}+1} < \frac{1}{2}$$

   which implies that

$$\frac{\mu}{k_B T} < 0$$

   or $\mu < 0$.

For boson gas $\mu(T)$ is negative at all temperatures and is zero at absolute zero.
AT high temperature the fermion gas approximates the classical ideal gas. In the classical limit:

$$\mu = -k_B T \ln(z) = -k_B T \ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{V}{N}\right]$$

Example: for   kilo-mole   of   the   fermion ^3He gas   atoms   at   STP,

$T_f = 0.069$ K, so that $\dfrac{T}{T_f} = 3900$, then classically

$$\frac{\mu}{kT} = -\ln\left(\frac{z}{N}\right) = -\ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\frac{V}{N}\right] = -12.7$$

And $e^{-\beta\mu} = 3.3\times10^5$. The average occupancy of single particle states is very small, as in the case of an ideal gas obeying the Maxwell-Boltzmann distribution.

(Strongly degenerate gas)

$$N = \int_0^\infty g(\varepsilon) f(\varepsilon) d\varepsilon = G_s V \int_0^\infty \frac{\sqrt{\varepsilon}\, d\varepsilon}{e^{\beta(\varepsilon - \mu(T))} + 1} = G_s V (k_B T)^{3/2} \int_0^\infty \frac{\sqrt{x}\, dx}{e^{(x - x_o)} + 1}$$

Where we used $x_o = \beta \mu(T)$ and $x = \beta \varepsilon$.

Our target is the calculation of $\mu(T)$ as a function of the absolute temperature.

Mathematical Note: Somerfield's integral
The standard integral in the above equation could be solved with the help of Somerfield's integral, i.e.

$$\int_0^\infty f(x - x_o) x^s dx = \frac{x_o^{s+1}}{s+1} \left[1 + \frac{\pi^2}{6} \frac{s(s+1)}{x_o^2} + \cdots \right],$$

For the case of the analytic function $f(x - x_o) = \dfrac{1}{e^{(x - x_o)} + 1}$ and $s = 1/2$, we have

$$\int_0^\infty \frac{x^{1/2}}{e^{(x - x_o)} + 1} dx = \frac{2}{3} x_o^{3/2} \left[1 + \frac{\pi^2}{8 x_o^2} + \cdots \right]$$

$$\int_0^\infty \frac{\sqrt{x}\, dx}{e^{(x - x_o)} + 1} = \frac{2}{3} x_0^{3/2} \left[1 + \frac{\pi^2}{8 x_0^2} + \cdots \right] = \frac{2}{3} \left(\frac{\mu}{k_B T} \right)^{3/2} \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 + \cdots \right]$$

So the total number will be

$$N = \frac{2}{3} G_s V \mu^{3/2} \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 + \cdots \right]$$

Using $N = \dfrac{2}{3} G_s V \mu_o^{3/2}$, one finds

$$\mu_o^{3/2} = \mu^{3/2}(T) \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 + \cdots \right]$$

As a first order approximation, we put $\mu = \mu_o$ in the square bracket to have

$$\mu_o^{3/2} = \mu^{3/2}(T) \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu_o} \right)^2 + \cdots \right]$$

Then, using $\mu_o = k_B T_F$, we get

$$\mu_o^{3/2} = \mu^{3/2}(T) \left[1 + \frac{\pi^2}{8} \left(\frac{T}{T_F} \right)^2 + \cdots \right]$$

Now, we can calculate $\mu(T)$ as a function of μ_o as the following:

$$\because \mu^{3/2}(T) = \mu_o^{3/2} \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu_o} \right)^2 + \cdots \right]^{-1}$$

$$\therefore \quad \mu(T) = \mu_o \left[1 + \frac{\pi^2}{8} \left(\frac{T}{T_F} \right)^2 + \cdots \right]^{-2/3} \approx \mu_o \left[1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 + \cdots \right]$$

Example: Calculate $\mu(T)$ of potassium at $T = 3.0 \times 10^2$ K. Note that for potassium, $\mu_o = 2.05$ eV at $T_F = 2.3 \times 10^4$ K.

Answer:

$$\mu(T) = \mu_o\left[1 - \frac{\pi^2}{12}\left(\frac{T}{T_F}\right)^2 + \cdots\right] = 2.05\left[1 - \frac{\pi^2}{12}\left(\frac{3.0\times10^3}{2.3\times10^4}\right)^2 + \cdots\right] = 2.05 \times 0.986 \approx 2.02 \text{ eV}$$

Which is a slight change with respect to $\mu_o = 2.05$ eV. This is because T_F is high for potassium and we can consider $\mu(T) = \mu_o$.
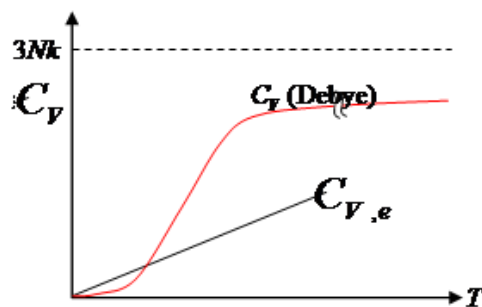
H.W. Prove

i- the internal energy

$$U \approx \underbrace{\frac{3}{5}N\mu_o}_{U_o}\left[1 + \frac{5\pi^2}{12}\left(\frac{T}{T_F}\right)^2 + \frac{\pi^4}{16}\left(\frac{T}{T_F}\right)^4 - \cdots\right]$$

ii- Specific heat

$$C_{V,e} = \left(\frac{\partial U}{\partial T}\right)_V = \frac{5\pi^2}{12}U_o\left(\frac{T}{T_F^2}\right) + \cdots \approx \frac{\pi^2}{2}\left(\frac{Nk_B}{T_F}\right)T$$

Total specific heat of metal could be written as:

$$\left(C_V\right)_{total} = C_{V,e} + C_V(\text{Debye})$$
$$= \underset{\text{free electron}}{AT} + \underset{\text{Deby's}}{BT^3}$$

The following figure is a comparison between the specific heat in the three distribution
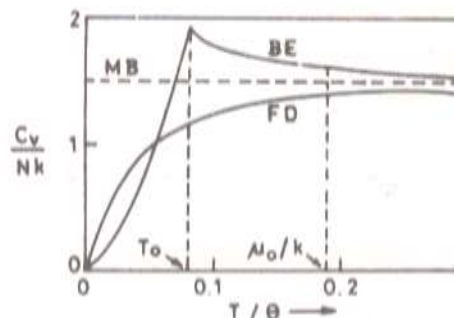

Fig. 7.5 Comparison of heat capacity of a gas according to the three statistics,
$\theta = (h^2/mk)(\overline{N}/gV)^{2/3}$.

Example: Calculate the specific heat of potassium at $T = 3.0 \times 10^2$ K. Note that for potassium $T_F = 2.3 \times 10^4$ K.

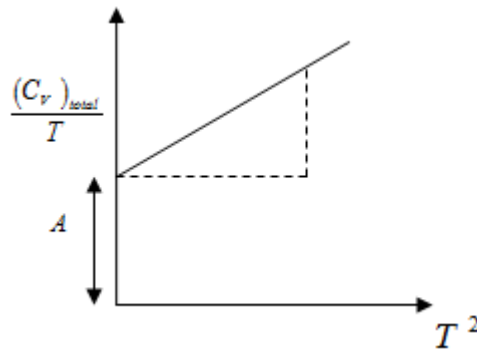**Answer:**

$$C_{V,e} = \frac{\pi^2}{2}\left(\frac{Nk_B}{T_F}\right)T = \frac{\pi^2}{2}\left(\frac{T}{T_F}\right)Nk_B = 4.93\times\left(\frac{3.0\times10^2 \text{ K}}{2.3\times10^4 \text{ K}}\right)Nk_B$$

$$= 6.44\times10^{-2} \, Nk_B$$

Which is very small compare to $3 \, Nk_B$ at room temperature.

To calculate the values of A and B in the equation $\left(C_V\right)_{total} = AT + BT^3$, one can treat it as a linear equation, see the following figure.

ii- Entropy

$$S = \int_0^T \frac{C_{V,e}}{T}\, dT = \frac{\pi^2}{2}Nk_B\left[\left(\frac{T}{T_F}\right) - \frac{\pi^2}{10}\left(\frac{T}{T_F}\right)^3 + \cdots\right]$$

So, $S = 0$ as $T = 0$.

iii- Helmholtz

$$F = U - TS = Nk_B T_F\left[\frac{3}{5} - \frac{\pi^4}{4}\left(\frac{T}{T_F}\right)^2 + \frac{\pi^4}{80}\left(\frac{T}{T_F}\right)^4 + \cdots\right]$$

iv- Pressure

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{2}{5}\frac{Nk_B T_F}{V}\left[1 + \frac{5\pi^4}{12}\left(\frac{T}{T_F}\right)^2 + \frac{\pi^4}{80}\left(\frac{T}{T_F}\right)^4 + \cdots\right] = \frac{2}{3}\frac{U}{V}$$