

## IDEAL 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  $\varepsilon_i$  energy is:

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

Fermi function,  $f(\varepsilon_i)$ , gives the probability that a single particle state  $\varepsilon_i$  will be occupied by a fermion. In the continuum we can have:

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

Clearly,  $0 \leq f(\varepsilon) \leq 1$ .  $\mu$  no need to be negative, as in BEC, due to the +1 in the denominator, i.e.  $-\infty \leq \mu \leq \infty$ .

### From Wikipedia

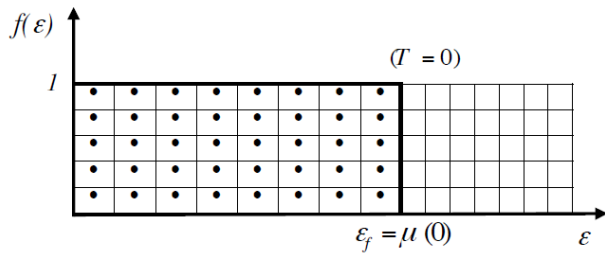
The **Fermi energy** is a concept in [quantum mechanics](#) usually referring to the energy difference between the highest and lowest occupied single-particle states in a quantum system of non-interacting [fermions](#) at [absolute zero temperature](#). In a [Fermi gas](#), the lowest occupied state is taken to have zero kinetic energy, whereas in a metal, the lowest occupied state is typically taken to mean the bottom of the [conduction band](#).

Confusingly, the term "Fermi energy" is often being used for referring to a different yet closely related concept, the [Fermi level](#) (also called [electrochemical potential](#)). There are a few key differences between the Fermi level and Fermi energy, at least as they are used in here:

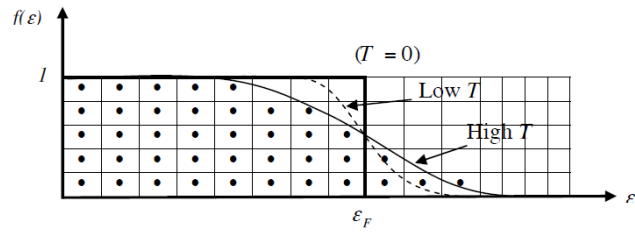
- The Fermi energy is only defined at absolute zero, while the Fermi level is defined for any temperature.
- The Fermi energy is an energy *difference* (usually corresponding to a [kinetic energy](#)), whereas the Fermi level is a total energy level including kinetic energy and potential energy.
- The Fermi energy can only be defined for [non-interacting fermions](#) (where the potential energy or band edge is a static, well defined quantity), whereas the Fermi level (the electrochemical potential of an electron) remains well defined even in complex interacting systems, at thermodynamic equilibrium.

Since the Fermi level in a metal at absolute zero is the energy of the highest occupied single particle state, then the Fermi energy in a metal is the energy difference between the Fermi level and lowest occupied single-particle state, at zero-temperature.

- **Fermi energy:** is often defined as the highest occupied energy level of a material at absolute zero temperature. In other words, all electrons in a body occupy energy states at or below that body's Fermi energy at 0K. The fermi energy is the difference in energy, mostly **kinetic**.
- **Chemical potential ( $\mu$ ):** May be regarded as the Lagrangian multiplier introduced to satisfy the constraint of a fixed number of particles. Also, can be defined as the change in the energy of the system as a result of the change in its number of particles, when every other thermodynamical variable that describes the state of the system, such as entropy, volume, etc., is kept constant. It has the units of energy/molecule, or otherwise stated, for a single species of particles in a grand canonical ensemble, the chemical potential can be defined as the change in internal energy gained per particles added to the system when all other thermodynamic variables are held constant.  $-\infty < \mu < 0$  for Bosons, and  $-\infty < \mu < \infty$  for Fermions.
- **Density of states:** It is the number of microstates (i.e. the number of independent quantum states) of an  $N$  particle system per unit energy range. In other words, the density of states, denoted by  $g(E)$ , indicates how densely packed quantum states in a particular system. Macroscopically, the density of states can be treated as a continuous function of the internal energy of the system.



The Fermi function at T = 0



$f(\epsilon)$  at three different temperatures in FD statistics

### Classification according to the chemical potential

In the expression  $\beta(\epsilon - \mu)$

- i- If  $\epsilon = \mu \Rightarrow f(\epsilon) = \frac{1}{2}$  (at all temperature). Thus, the probability of finding an electron with energy equal to the Fermi-energy in a metal is  $\frac{1}{2}$  at any temperature.
- ii- If  $\beta(\epsilon - \mu) \ll 0 \Rightarrow f(\epsilon) = 1$
- iii- If  $\mu \ll \beta$  or  $\mu \approx 0$ ,  $\Rightarrow f(\epsilon) = e^{-\beta(\epsilon - \mu)}$  and fall off exponentially like Maxwell-Boltzmaan distribution.

### Total number of particles as $T \rightarrow 0$

In the limit of  $T \rightarrow 0$  we have sharp drop and

$$f(\epsilon) = \begin{cases} 1 & \epsilon < \mu_0 \\ 0 & \epsilon > \mu_0 \end{cases} \Rightarrow N = \begin{cases} \int_0^{\mu_0} g(\epsilon) d\epsilon & T = 0 \\ \int_0^{\mu_0} g(\epsilon) f(\epsilon) d\epsilon & T \neq 0 \end{cases}$$

Where

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

$$= VG_s \sqrt{\epsilon}, \quad \text{for electrons,} \quad G_s = 4\pi \left(\frac{2m}{h^2}\right)^{3/2}$$

### Classification according to the Temperature

Exclusion principle implies that a FD gas has a large mean energy even at absolute zero,  $0 < \epsilon < \mu_0 (\equiv \epsilon_f(0))$ . [**Note that:** Degenerate here means filled, not as the case of QM]

$T =$	{	$T = 0$	$\mu_0 > 0, \quad \epsilon < \mu_0$	Very low temperature	Completely degenerate
		$T \ll T_f$	$\mu(T) > 0$	Low temperature	degenerate
		$T \approx T_f$	$\mu(T) \sim 0$	Intermediate temperature	Slightly degenerate
		$T \gg T_f$	$\mu(T) < 0$	High temperature	Classical limit

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.

### Fermi temperature $T_f$ in Completely Degenerate Fermi-Gas

i- Total number of particles:

$$N = \int_0^{\mu_o} g(\varepsilon) f(\varepsilon) d\varepsilon = V G_s \int_0^{\mu_o} \sqrt{\varepsilon} d\varepsilon = \frac{2V}{3} G_s \mu_o^{3/2}$$

ii- Fermi energy

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

iii- Fermi temperature

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

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

where  $n = N/V$  is the concentration.

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

i-  $\mu_o$ , ii-  $T_f$  and iii-  $v_f$ .

**Solution:**

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

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

consequently,

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

ii-

$$T_f = \frac{\mu_o}{k_B} = \frac{2.05 \text{ eV}}{8.617 \times 10^{-5} \frac{\text{eV}}{\text{K}}} = \underline{2.379 \times 10^4 \text{ K}}$$

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

iii- Use

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

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

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

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

**Internal energy:**

$$U_o = \int_0^{\mu_o} \epsilon g(\epsilon) f(\epsilon) d\epsilon = 4\pi V \left( \frac{2m}{h^2} \right)^{3/2} \int_0^{\mu_o} \epsilon^{3/2} d\epsilon = \frac{8\pi V}{3} \left( \frac{2m}{h^2} \right)^{3/2} \underbrace{\mu_o^{5/2}}_{\frac{3}{5} N \mu_o^{-3/2}} = \frac{3}{5} N \mu_o$$

Other thermodynamic functions are:

$$S_o = 0,$$

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

$$P = -\frac{\Omega_o}{V} = \frac{2}{5} \mu_o \left( \frac{N}{V} \right) = \frac{2}{5} n \mu_o, \quad n = \text{concentration}$$

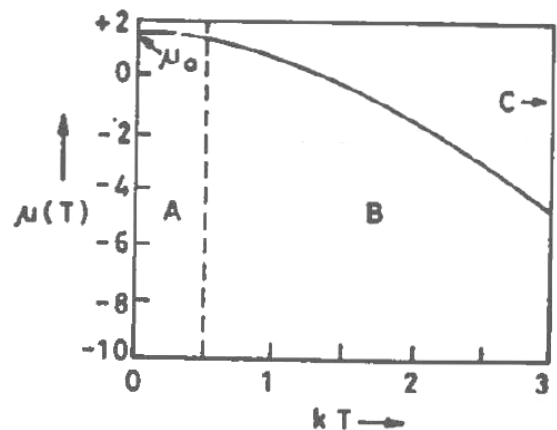
Thus at  $T = 0$  K a fermions' gas exerts a pressure.

**Example:** For silver, if we take the concentration  $n = N/V = 6 \times 10^{28}$  electron/m<sup>3</sup> and Fermi energy of  $\mu_o = 10^{-18}$  J. Calculate the pressure.

$$p = \frac{2}{5} \times (6 \times 10^{28} \text{ electron/m}^3) \times (10^{-18} \text{ J}) \approx 2.4 \times 10^{10} \text{ N/m}^2 = 2.4 \times 10^5 \text{ atm.}$$

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.

Variation of the chemical potential with  $T$  for an ideal FD gas in 3-region.  $\mu_o$  and  $N/V$  are chosen here to give  $\mu_o = (1.5)^{2/3}$ . The region A corresponds to the degenerate quantum FD gas, B to slightly degenerate FD gas, and C indicates the region of classical gas.



**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

$$\frac{\mu}{k_B T} < 0 \quad \text{or} \quad \mu < 0.$$

At high temperature the fermion gas approximates the classical ideal gas. In the classical limit:

$$\mu = \left( \frac{\partial U}{\partial N} \right)_{V,S} = -k_B T \ln(z) = -k_B T \ln \left[ \left( \frac{2\pi m k T}{h^2} \right)^{3/2} \frac{V}{N} \right]$$

**Example:** for kilo-mole of the fermion  ${}^3\text{He}$  gas atoms at STP,

(a) What is the Fermi temperature of the gas?

$$T_F = \frac{h^2}{2\pi m k_B} \left( \frac{N}{1.504V} \right)^{2/3} = \frac{(6.626 \times 10^{-34})^2}{2\pi \times 4.98 \times 10^{-27} \times 1.38 \times 10^{-23}} \left( \frac{6.023 \times 10^{26}}{1.504 \times 22.4} \right)^{2/3}$$

$$= 0.069\text{K} \approx 0.07\text{K}$$

So, the room temperature is considered as classical temperature.

(b) Calculate  $\mu / k_B T$  and  $e^{-\mu/k_B T}$

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

$$= -\ln \left[ 2 \left( \frac{2\pi \times 4.98 \times 10^{-27} \times 1.38 \times 10^{-23} \times 273}{(6.626 \times 10^{-34})^2} \right)^{3/2} \frac{22.4}{6.023 \times 10^{26}} \right] = -12.7$$

$$\Rightarrow e^{-\mu/k_B T} = 3.3 \times 10^5$$

(c) Find the average occupancy  $f(\varepsilon)$  of a single particle state that has energy of  $(3/2)k_B T$ .

Energy:  $\varepsilon = 1.5 k_B T$

Chemical Potential:  $\mu = -12.7 k_B T$

$$\text{Average Occupancy } f(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/k_B T} + 1} = \frac{1}{e^{(1.5+12.7)k_B T/k_B T} + 1} = \frac{1}{1.469 \times 10^6} = 6.8 \times 10^{-7}$$

The average occupancy of single particle states is very small,  $6.8 \times 10^{-7}$  (dilute), as in the case of an ideal gas obeying the Maxwell-Boltzmann distribution.

### Strongly Degenerate Fermi-Gas

With the help of total number of fermions particle in the form:

$$N = \int_0^\infty g(\varepsilon) f(\varepsilon) d\varepsilon = G_s V \int_0^\infty \frac{\sqrt{\varepsilon} d\varepsilon}{e^{\beta(\varepsilon-\mu(T))} + 1} = G_s V (k_B T)^{3/2} \underbrace{\int_0^\infty \frac{\sqrt{x} dx}{e^{(x-x_0)} + 1}}_I, \quad G_s = 4\pi \left( \frac{2m}{h^2} \right)^{3/2}$$

where we used  $x_0 = \beta\mu(T)$  and  $x = \beta\varepsilon$ .

**In the following, it is our main objective is the calculation of  $\mu(T)$  as a function of the absolute temperature:**

$$\mu(T) \approx \mu_0 \left[ 1 - \frac{\pi^2}{12} \left( \frac{T}{T_f} \right)^2 \right], \quad T \ll T_f$$

**Mathematical integral: Sommerfeld's integral**

The standard integral in the above equation could be solved with the help of Sommerfeld's integral, i.e.

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

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

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

➤ With the help of , one gets

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

So the total number will be

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

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

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

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

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

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

i- Rearrange the above equation:  $\mu^{3/2}(T) = \mu_o^{3/2} \left[ 1 + \frac{\pi^2}{8} \left( \frac{k_B T}{\mu_o} \right)^2 + \dots \right]^{-1}$

ii- Simplify and use the binomial expansion for the square racket, we have

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

As expected, for  $T = 0$  K the last equation gives  $\mu(T) = \mu_o$ . However, as temperature increases,  $\mu(T)$  is lowered slightly. For example as  $T/T_F = 0.2$ , we find that the chemical potential changes by about 4%.

**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:**

$$\mu(T) = \mu_o \left[ 1 - \frac{\pi^2}{12} \left( \frac{T}{T_F} \right)^2 + \dots \right] = 2.05 \left[ 1 - \frac{\pi^2}{12} \left( \frac{3.0 \times 10^2}{2.3 \times 10^4} \right)^2 + \dots \right] = 2.05 \times 0.986 \approx 2.02 \text{ eV}$$

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 the following:**

**i- the internal energy**

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

**ii- Specific heat**

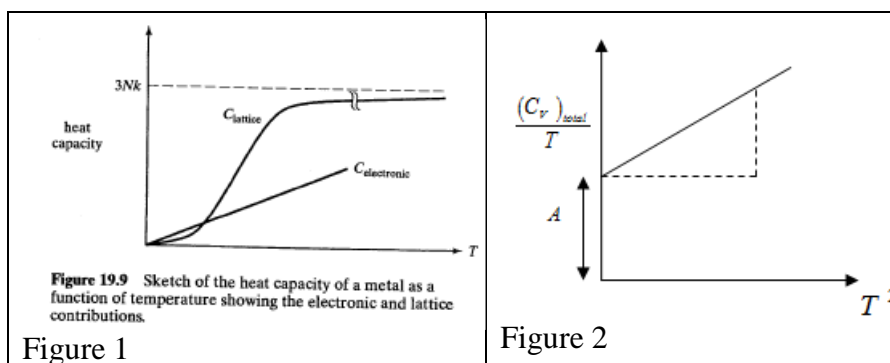
$$C_{V,e} = \left( \frac{\partial U}{\partial T} \right)_V = \frac{5\pi^2}{6} U_o \left( \frac{T}{T_F} \right) + \dots \approx \frac{\pi^2}{2} N k_B \left( \frac{T}{T_F} \right)$$

**Comment:** Metals have a specific heat capacity of about  $3R$ , the same as for other solids. It was originally believed that their free electrons should contribute an additional  $(3/2)R$  associated with their three translational degrees of freedom. Our last calculation shows that the contribution is negligible. *Why* is it so small? While the kinetic energy of the electrons is much greater than the thermal energy' of electrons in a gas, the energy of the electrons *changes* only slightly with temperature ( $dU/dT$  is small). Only those electrons near the Fermi level can increase their energies as the temperature is raised, and there are precious few of them.

At very low temperatures the picture is different. From the Debye theory,  $C_V \propto T^3$  and so the heat capacity of a metal takes the form

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

where the first term is the electronic contribution and the second is associated with the crystal lattice. At sufficiently low temperatures, the former can dominate, as indicates in Figure 1. To calculate the values of  $A$  and  $B$  in the equation  $(C_V)_{total} = AT + BT^3$ , one can treat it as a linear equation, see figure 2. The intercept will be  $A$  and the slope is  $B$ .



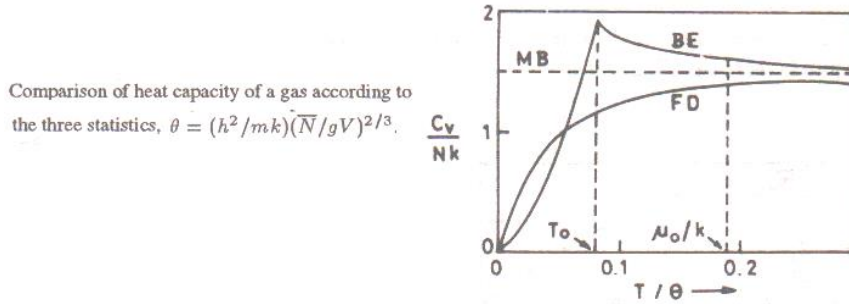
**Example:** Calculate the specific heat of potassium at  $T = 3.0 \times 10^2$  K. Note that for potassium  $T_F = 2.3 \times 10^4$  K.

**Answer:**

$$C_{V,e} = \frac{\pi^2}{2} \left( \frac{Nk_B}{T_F} \right) T = \frac{\pi^2}{2} \left( \frac{T}{T_F} \right) Nk_B = 4.93 \times \left( \frac{3.0 \times 10^2 \text{ K}}{2.3 \times 10^4 \text{ K}} \right) Nk_B = 6.44 \times 10^{-2} Nk_B$$

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

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



### ii- Entropy

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

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

### iii- Helmholtz

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

### iv- Pressure

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



**Appendix 1 to IV.10: Sommerfeld's expansion**  
Statistical Physics  
Lecture J. Fabian

Consider integral,

$$I(\mu) = \int_0^\infty d\varepsilon \frac{\varphi(\varepsilon)}{e^{\beta(\varepsilon-\mu)} + 1}, \quad (1)$$

where  $\varphi(\varepsilon)$  is some well behaved function. Let us introduce a new variable  $x$ ,

$$x = \beta(\varepsilon - \mu), \quad \varepsilon = \mu + k_B T x. \quad (2)$$

The integral transforms to

$$I(\mu) = k_B T \int_{-\mu/k_B T}^\infty dx \frac{\varphi(\mu + k_B T x)}{e^x + 1} = k_B T \int_{-\mu/k_B T}^0 dx \frac{\varphi(\mu + k_B T x)}{e^x + 1} + k_B T \int_0^\infty dx \frac{\varphi(\mu + k_B T x)}{e^x + 1}. \quad (3)$$

Let us work little bit on the first integral on the right,

$$\int_{-\mu/k_B T}^0 dx \frac{\varphi(\mu + k_B T x)}{e^x + 1} = |x \rightarrow -x| = \int_0^{\mu/k_B T} dx \frac{\varphi(\mu - k_B T x)}{e^{-x} + 1} = \quad (4)$$

$$= \left| \frac{1}{e^{-x} + 1} = 1 - \frac{1}{e^x + 1} \right| = \frac{1}{k_B T} \int_0^\mu dz \varphi(z) - \int_0^{\mu/k_B T} dx \frac{\varphi(\mu - k_B T x)}{e^x + 1}. \quad (5)$$

We have introduced new variable  $z$ , by

$$z = \mu - k_B T x, \quad (6)$$

in the first integral on the right. Our original integral now reads,

$$I(\mu) = \int_0^\mu dz \varphi(z) + k_B T \int_0^\infty dx \frac{\varphi(\mu + k_B T x)}{e^x + 1} - k_B T \int_0^{\mu/k_B T} dx \frac{\varphi(\mu - k_B T x)}{e^x + 1} \quad (7)$$

Thus far we have made no approximation. In the following, we make two: (i) In the degenerate limit, we have

$$\frac{\mu}{k_B T} \approx \frac{\varepsilon_F}{k_B T} \gg 1, \quad (8)$$

so that we can extend the integration in the last term of Eq. 7 to infinity; note that the integrand of this term decreases rapidly with increasing  $x$ —this is why the upper limit of that integral is irrelevant. We cannot do the same with the first term, for example. We obtain:

$$I(\mu) = \int_0^\mu dz \varphi(z) + k_B T \int_0^\infty dx \frac{1}{e^x + 1} [\varphi(\mu + k_B T x) - \varphi(\mu - k_B T x)]. \quad (9)$$

(ii) As a second approximation, we expand  $\varphi(\mu \pm k_B T x)$  in Taylor series about  $k_B T x = 0$ , again for the reason that the integrand decreases exponentially with increasing  $x$  as well as that  $k_B T \ll \mu$ :

$$\varphi(\mu + k_B T x) - \varphi(\mu - k_B T x) \approx \varphi(\mu) + k_B T x \frac{d\varphi(\mu)}{d\mu} + \dots - \varphi(\mu) + k_B T x \frac{d\varphi(\mu)}{d\mu} - \dots = 2k_B T x \frac{d\varphi(\mu)}{d\mu} + \dots \quad (10)$$

Substituting to our integral, Eq. 11, we get

$$I(\mu) = \int_0^\mu dz \varphi(z) + 2(k_B T)^2 \frac{d\varphi(\mu)}{d\mu} \int_0^\infty dx \frac{x}{e^x + 1}. \quad (11)$$