In this chapter we will derive with quantum statistical mechanics, all the thermodynamic properties of non interacting quantum gases of fermions and bosons. We begin by defining the grand potential for N non interacting and non relativistic particles confined inside a box with volume $V = L^3$. The Hamiltonian of the system is

$$\hat{\mathcal{H}} = \sum_{i=1}^{N} \frac{\hat{p}_i^2}{2m} \tag{1}$$

Applying periodic boundary conditions to the associated differential equation we obtain the following solution

$$\langle x_i | p_i \rangle = \phi_{p_i}(x_i) = \frac{1}{\sqrt{V}} e^{\frac{i p_i x^i}{\hbar}} \tag{2}$$

Where

$$p_i = \frac{2\pi\hbar}{L} \nu_i \tag{3}$$

Where we have $\nu_i \in \mathbb{Z}$. The single particle energy ϵ_p will be, obviously

$$\epsilon_p = \frac{p^2}{2m} \tag{4}$$

Now, if we consider particle spin, we find ourselves in a particular situation. As we have seen in the chapter for identical particles, we have that a multi-particle factorisable eigenket of the Hamiltonian (1) can then be written as follows

$$|p_1, \cdots, p_N\rangle = \mathcal{N} \sum_P (\pm 1)^P \hat{P} \bigotimes_{i=1}^{N} |p_i\rangle \tag{5}$$

Where $\hat{P}$ is the permutation operator, with eigenvalue 1^P and normalization $\mathcal{N} = (\prod_i N! n_{p_i}!)^{-1/2}$ for bosons, and eigenvalue $(-1)^P$ and normalization $\mathcal{N} = (N!)^{-1/2}$ for fermions. For an N-particle system, we can define the particle number as follows

$$N = \sum_p n_p \tag{6}$$

And the energy eigenvalue as follows

$$E(\{n_p\}) = \sum_p n_p \epsilon_p \tag{7}$$

Therefore, the grand canonical partition funtion will be the following

$$\begin{aligned} Z_G = \sum_{N=0}^{\infty} \sum_{\{n_p\}} e^{-\beta(E(\{n_p\}) - \mu N)} = \sum_{\{n_p\}} e^{-\beta \sum_p n_p(\epsilon_p - \mu)} = \\ = \prod_p \sum_{n_p} e^{-\beta n_p(\epsilon_p - \mu)} \end{aligned} \tag{8}$$

Therefore, summing and considering the difference between bosons and fermions

$$Z_G = \prod_p \sum_{n_p} e^{-\beta n_p(\epsilon_p - \mu)} = \begin{cases} \displaystyle\prod_p \frac{1}{1 - e^{-\beta(\epsilon_p - \mu)}} & m_s \in \mathbb{Z} \\ \displaystyle\prod_p (1 + e^{-\beta(\epsilon_p - \mu)}) & m_s \in \mathbb{F} := \left\{ m_s \in \mathbb{Q} \middle| m_s = \frac{n}{2},\ n \in \mathbb{Z} \right\} \end{cases} \tag{9}$$

From this we van calculate directly the grand potential

$$\Phi = -\frac{1}{\beta} \log(Z_G) = \pm \frac{1}{\beta} \sum_p \log\left(1 \mp e^{-\beta(\epsilon_p - \mu)}\right) \tag{10}$$

With the upper sign referring to bosons and vice versa for fermions.
The average particle number will then be

$$N = -\frac{\partial \Phi}{\partial \mu} = \sum_p \frac{1}{e^{\beta(\epsilon_p - \mu)} \mp 1} = \sum_p n(\epsilon_p) \tag{11}$$

The last function $n(\epsilon_p)$ is called the Bose-Einstein distribution (for bosons) or the Fermi-Dirac distributions (for fermions). From this, we can find that it's actually the *average occupation number* of a state $|\overline{\alpha}\rangle$. In order to obtain this result we need to calculate the expectation value of $n_{\overline{\alpha}}$.

$$\langle n_{\overline{\alpha}} \rangle = \mathrm{Tr}(\hat{\rho}_G n_{\overline{\alpha}}) = \frac{\sum_{\{n_p\}} n_{\overline{\alpha}} e^{-\beta \sum_p n_p(\epsilon_p - \mu)}}{\sum_{\{n_p\}} e^{-\beta \sum_p n_p(\epsilon_p - \mu)}} = -\frac{\partial}{\partial x} \log\left(\sum_n e^{-nx}\right) = n(\epsilon_{\overline{\alpha}}) \tag{12}$$

From the grand potential we then get the energy of the quantum gas

$$E = \left(\frac{\partial(\Phi\beta)}{\partial\beta}\right)_{\mu\beta} = \sum_p \epsilon_p n(\epsilon_p) \tag{13}$$

Considering that free particles can be considered as being confined to a space $\Delta = 2\pi\hbar V^{-1} \to \infty$, we can choose to approximate the sum over the discrete p to an integral for large volumes, using the following substitution

$$\sum_{\mathbf{p}} [\cdot] \to \frac{gV}{(2\pi\hbar)^3} \int [\cdot]\ \mathrm{d}^3 p \tag{14}$$

Where g is the degeneracy factor
Using this approximation for calculating the number of particles $N = \sum_p n_p(\epsilon_p)$, we get

$$\begin{aligned} N &= \frac{gV}{(2\pi\hbar)^3} \int n(\epsilon_p)\ \mathrm{d}^3 p = \frac{gV}{2\pi^2\hbar^3} \int_0^\infty n(\epsilon_p) p^2\ \mathrm{d}p \\ &= \frac{gV}{2\pi^2\hbar^3} \int_0^\infty \frac{p^2}{e^{\beta(\epsilon-\mu)} \mp 1}\ \mathrm{d}p = \frac{gVm^{\frac{3}{2}}}{\pi^2\hbar^3\sqrt{2}} \int_0^\infty \frac{\sqrt{\epsilon}}{e^{\beta(\epsilon-\mu)}}\ \mathrm{d}\epsilon \end{aligned} \tag{15}$$

Where we substituted in the energy eigenvalue density. Defining the specific volume $v = V/N$ and substituting $x = \beta\epsilon$, we get

$$\frac{1}{v} = \frac{2g}{\lambda^3\sqrt{\pi}} \int_{\mathbb{R}_+} \frac{\sqrt{x}}{e^x z^{-1} \mp 1} = \frac{g}{\lambda^3} \begin{cases} g_{3/2}(z) & s \in \mathbb{Z} \\ f_{3/2}(z) & s = \frac{n}{2},\ n \in \mathbb{Z} \end{cases} \tag{16}$$

Where g_s, f_s are the generalized $\zeta-$functions, which are defined and analyzed in the mathematical appendix.
From this, taking the grand partition function, we have that

$$\begin{aligned} \Phi &= \pm \frac{gV}{\beta(2\pi\hbar)^3} \int \log\left(1 \mp e^{-\beta(\epsilon-\mu)}\right) \mathrm{d}^3 p \\ &= \pm \frac{gVm^{\frac{3}{2}}}{\beta\pi^2\hbar^3\sqrt{2}} \int_0^\infty \log\left(1 \mp e^{\beta(\epsilon-\mu)}\right)\sqrt{\epsilon}\ \mathrm{d}\epsilon \end{aligned} \tag{17}$$

Integrating by parts and remembering that $PV = -\Phi$ we get

$$-\Phi = PV = \frac{gm^{\frac{3}{2}}V\sqrt{2}}{3\pi^2\hbar^3} \int_0^\infty \frac{\epsilon^{\frac{3}{2}}}{e^{\beta(\epsilon-\mu)} \mp 1}\ \mathrm{d}\epsilon = \frac{gV}{\beta\lambda^3} \begin{cases} g_{\frac{5}{2}}(z) \\ f_{\frac{5}{2}}(z) \end{cases} \tag{18}$$

We also can obtain the energy E of the system as follows

$$E = \frac{gVm^{\frac{3}{2}}}{\pi^2\hbar^3\sqrt{2}} \int_{,}^\infty \frac{\epsilon^{\frac{3}{2}}}{e^{\beta(\epsilon-\mu)} \mp 1} \tag{19}$$

A quick comparison with the equation (18), gives the same relation that we got for the classical ideal gas

$$PV = \frac{2}{3}E \tag{20}$$

From the homogeneity of Φ in T, μ we can derive from the previous equations other relations, as follows

$$\begin{aligned} P &= -\frac{\Phi}{V} = -T^{\frac{5}{2}}\phi\left(\frac{\mu}{T}\right) \\ N &= VT^{\frac{3}{2}}n\left(\frac{\mu}{T}\right) \\ S &= -\frac{\partial\Phi}{\partial T} = VT^{\frac{3}{2}}s\left(\frac{\mu}{T}\right) \\ \frac{S}{N} &= \frac{s}{n} \end{aligned} \tag{21}$$

For an adiabatic expansion, i.e. setting $S = \alpha,\ \mu/T = \beta,\ VT^{\frac{3}{2}} = \gamma,\ PT^{-\frac{5}{2}} = \delta$, with $\alpha, \beta, \gamma, \delta \in \mathbb{R}$, we get the adiabatic equation for an ideal quantum gas

$$PV^{\frac{5}{3}} = \eta \in \mathbb{R} \tag{22}$$

Note how this differs from the classical version, since $c_p/c_v \neq 5/3$

§ 0.1 Degenerate Fermi Gas

Let's consider now the ground state of N fermions. It will correspond to a fermion gas at temperature $T = 0\mathrm{K}$. In this situation, every single particle state will be occupied g fold, thus all momenta inside a sphere of radius p_F (the maximum momentum possible, the *Fermi momentum*) will be occupied.
The number of particles therefore will be

$$N = g \sum_{\{|p\rangle\}}{}' 1 = \frac{gV}{(2\pi\hbar)^3} \int \Theta(p_F - p) \, \mathrm{d}^3 p = \frac{gV p_F^3}{6\pi^2 \hbar^3} \tag{23}$$

Therefore, using the particle density $n = N/V$ we get our Fermi momentum

$$p_F = \hbar \sqrt[3]{\frac{6\pi^2 n}{g}} \tag{24}$$

From this, we get the *Fermi Energy*

$$\epsilon_{p_F} = \frac{p_F^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{6\pi^2 n}{g} \right)^{\frac{2}{3}} \tag{25}$$

The ground state energy, from these relations, will therefore be

$$E = \frac{gV}{(2\pi\hbar)^3} \int \frac{p^2}{2m} \Theta(p_F - p) \, \mathrm{d}^3 p = \frac{gV p_F^5}{20 m \pi^2 \hbar^3} = \frac{3}{5} N \epsilon_F \tag{26}$$

Using what we found in the previous section, we find that the pressure of such gas will be the following

$$P = \frac{2}{5} \epsilon_F n = \frac{\hbar^2 n^{\frac{5}{2}}}{5m} \left(\frac{6\pi^2}{g} \right)^{\frac{2}{3}} \tag{27}$$

§§ 0.1.1 Complete Degeneracy Limit

Having calculated the thermodynamic properties of a quantum gas of fermions in the case of complete degeneracy (i.e., $T = 0$), we can start calculating the same properties in the *limit* of complete degeneracy, i.e. for $T \to 0$. It's easy to demonstrate that here $\mu \to \epsilon \to \epsilon_F$ and therefore

$$\begin{aligned} \Phi &= -N \epsilon_F^{-\frac{3}{2}} \int_0^\infty n(\epsilon) \epsilon^{\frac{3}{2}} \, \mathrm{d}\epsilon \\ N &= \frac{3}{2} N \epsilon_F^{-\frac{3}{2}} \int_0^\infty n(\epsilon) \epsilon^{\frac{1}{2}} \, \mathrm{d}\epsilon \end{aligned} \tag{28}$$

From this, knowing already the solution of these integrals, as discussed in appendix (**??**), we can solve these integrals approximately in the limit $\beta\mu \to \infty$, and deduce some

approximated conclusions for what happens thermodynamically in a Fermi gas for really low temperatures.
We begin writing our integrals (called *Sommerfield integrals*) as a sum of two integrals as follows

$$I = \int_0^\mu f(\epsilon)\ \mathrm{d}\epsilon + \int_0^\infty f(\epsilon)\left(n(\epsilon) - \Theta(\mu-\epsilon)\right)\ \mathrm{d}\epsilon \tag{29}$$

Using a $x-$substitution with $x = \beta(\epsilon-\mu)$, extending the integral's domain over the whole real line, and Taylor approximating the function $f(\epsilon)$ around μ, we get

$$\begin{aligned} I &= \int_0^\mu f(\epsilon)\ \mathrm{d}\epsilon + \int_{\mathbb{R}} \left(\frac{1}{e^x+1} - \Theta(-x)\right) \sum_{k=0}^{\infty} \frac{\beta^{-(k+1)}}{k!} \left.\frac{\partial^k f}{\partial x^k}\right|_{x=\mu} x^k\ \mathrm{d}x \\ &= \int_0^\mu f(\epsilon)\ \mathrm{d}\epsilon + 2\sum_{k=0}^{\infty} \frac{\beta^{-(k+1)}}{k!} \frac{\partial^k f}{\partial \mu^k} \int_0^\infty \frac{x^k}{e^x+1}\ \mathrm{d}x \end{aligned} \tag{30}$$

Applying this approximation till $\mathcal{O}(T^4)$ we can write for the integrals (28)

$$\begin{aligned} \mu &= \epsilon_F\left(1 - \frac{\pi^2}{12\beta^2} + \mathcal{O}\Big(T^4\Big)\right) \\ \Phi &= -\frac{2}{5}N\epsilon_F\left(1 + \frac{5\pi^2}{12\beta^2\epsilon_F^2} + \mathcal{O}\Big(T^4\Big)\right) \end{aligned} \tag{31}$$

Using $P = -\Phi/V$ we obtain immediately the energy of such gas

$$E = \frac{3}{2}PV = \frac{3}{5}N\epsilon_F\left(1 + \frac{5\pi^2}{12\epsilon_F^2\beta^2} + \mathcal{O}\Big(T^4\Big)\right) \tag{32}$$

And introducing the Fermi temperature as $T_F = \epsilon_F/k_B$ we get the heat capacity of this gas as

$$C_V = Nk_B\frac{\pi^2 T}{2T_F} \tag{33}$$

§ 0.2 Bose-Einstein Condensation

After having studied the Fermi gas, we begin studying a Boson gas at low temperatures, which has a particular behavior called *Bose-Einstein condensation*. This gas has $s = 0$ and $g = 1$. Due to this, in the ground state all the non-interacting bosons occupy the lowest single particle state.
In the previous sections, we found that for the particle density we have

$$\frac{\lambda}{v} = g_{\frac{3}{2}}(z) \tag{34}$$

This function has a maximum for a value of fugacity $z = 1$, and it's equal to $g_{\frac{3}{2}}(1) = \zeta(\frac{3}{2}) = 2.612$. Thanks to this we can define a characteristic temperature T_c, which has the following value

$$\beta_c^{-1} = \frac{2\pi\hbar^2}{m(v\zeta(\frac{3}{2}))^{\frac{2}{3}}} \tag{35}$$

In this case, we have that the limit $\sum_p \to \int \, \mathrm{d}^3p$ isn't anymore a good approximation for $z \to 1$, since the term $p = 0$ diverges for $z = 1$. Treating it separately, we get for the particle number

$$N = \frac{1}{z^{-1} - 1} + \sum_{p \neq 0} n(\epsilon_p) \to \frac{1}{z^{-1} - 1} + \frac{V}{(2\pi\hbar)^3} \int n(\epsilon_p) \, \mathrm{d}^3p \tag{36}$$

Therefore, for bosons we get, in terms of generalized $\zeta-$functions and characteristic temperature

$$\begin{aligned} N &= \frac{1}{z^{-1} - 1} + \frac{Nv}{\lambda^3} g_{\frac{3}{2}}(z) \\ N &= \frac{1}{z^{-1} - 1} + N \left(\frac{T}{T_c}\right)^{\frac{3}{2}} \frac{g_{\frac{3}{2}}(z)}{g_{\frac{3}{2}}(1)} \end{aligned} \tag{37}$$

This can be seen as a sum of the number of particles in the ground state N_0 and the number of particles in excited states N_e, where

$$\begin{aligned} N_0 &= \frac{1}{z^{-1} - 1} \\ N_e &= N \left(\frac{T}{T_c}\right)^{\frac{3}{2}} \frac{g_{\frac{3}{2}}(z)}{g_{\frac{3}{2}}(1)} \end{aligned} \tag{38}$$

We have that for $T > T_c$, N yields a value of $z < 1$, hence N_0 is finite and can be neglected with respect to N. For $T < T_c$ we have $z = 1 - \mathcal{O}(N^{-1})$, and when $z \to 1$, setting $z = 1$ in N_e, we obtain

$$N_0 = N \left(1 - \left(\frac{T}{T_c}\right)^{\frac{3}{2}}\right) \tag{39}$$

And defining the *condensate fraction* ν as follows

$$\nu = \lim_{N \to \infty} \frac{N_0}{N} \tag{40}$$

We get, in summary, what's called the *Bose-Einstein Condensation*, for which, at $T < T_c$ the ground state at $p = 0$ is macroscopically occupied.

$$\nu = \begin{cases} 0 & T > T_c \\ 1 - \left(\frac{T}{T_c}\right)^{\frac{3}{2}} & T < T_c \end{cases} \tag{41}$$

Evaluating the other thermodynamic quantities, we get the pressure of a Bose gas as

$$P = \begin{cases} \dfrac{1}{\beta\lambda^3} g_{\frac{5}{2}}(z) & T > T_c \\ \dfrac{1}{\beta\lambda}\zeta\left(\dfrac{5}{2}\right) = \dfrac{1}{\beta\lambda^3}1.342 & T < T_c \end{cases} \tag{42}$$

And, therefore, entropy has the following expression

$$S = \frac{\partial PV}{\partial T} = \begin{cases} Nk_B\left(\dfrac{5v}{2\lambda^3} g_{\frac{5}{2}}(z) - \log(z)\right) & T > T_c \\ Nk_B\dfrac{5}{2}\left(\dfrac{T}{T_c}\right)^{\frac{3}{2}} \dfrac{g_{\frac{5}{2}}(1)}{g_{\frac{3}{2}}(1)} \end{cases} \tag{43}$$