

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

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

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

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

Where

$$p_i = \frac{2\pi\hbar}{L} \nu_i \quad (3)$$

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

$$\epsilon_p = \frac{p^2}{2m} \quad (4)$$

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

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

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

$$N = \sum_p n_p \quad (6)$$

And the energy eigenvalue as follows

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

Therefore, the grand canonical partition function will be the following

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

Therefore, summing and considering the difference between bosons and fermions

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

From this we can calculate directly the grand potential

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

With the upper sign referring to bosons and vice versa for fermions.

The average particle number will then be

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

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 $|\bar{\alpha}\rangle$. In order to obtain this result we need to calculate the expectation value of $n_{\bar{\alpha}}$.

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

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

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

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

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

Where g is the degeneracy factor

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

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

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

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

Where g_s, f_s are the generalized ζ -functions, which are defined and analyzed in the mathematical appendix.

From this, taking the grand partition function, we have that

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

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

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

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

$$E = \frac{gVm^{\frac{3}{2}}}{\pi^2\hbar^3\sqrt{2}} \int_0^\infty \frac{\epsilon^{\frac{3}{2}}}{e^{\beta(\epsilon-\mu)} \mp 1} d\epsilon \quad (19)$$

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

$$PV = \frac{2}{3}E \quad (20)$$

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

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

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

$$PV^{\frac{5}{3}} = \eta \in \mathbb{R} \quad (22)$$

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 $T = 0\text{K}$. 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

$$N = g \sum'_{\{p\}} 1 = \frac{gV}{(2\pi\hbar)^3} \int \Theta(p_F - p) d^3p = \frac{gV p_F^3}{6\pi^2 \hbar^3} \quad (23)$$

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

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

From this, we get the *Fermi Energy*

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

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

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

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

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

§§ 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 $T \rightarrow 0$. It's easy to demonstrate that here $\mu \rightarrow \epsilon \rightarrow \epsilon_F$ and therefore

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

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

$$I = \int_0^\mu f(\epsilon) d\epsilon + \int_0^\infty f(\epsilon) (n(\epsilon) - \Theta(\mu - \epsilon)) d\epsilon \quad (29)$$

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

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

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

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

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

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

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

$$C_V = N k_B \frac{\pi^2 T}{2T_F} \quad (33)$$

§ 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

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

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

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

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

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

Therefore, for bosons we get, in terms of generalized ζ -functions and characteristic temperature

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

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

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

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 $z \rightarrow 1$, setting $z = 1$ in N_e , we obtain

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

And defining the *condensate fraction* ν as follows

$$\nu = \lim_{N \rightarrow \infty} \frac{N_0}{N} \quad (40)$$

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.

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

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

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

And, therefore, entropy has the following expression

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