6. Applications of the grand canonical ensemble

In this section we will apply the grand canonical ensemble to the study of quantum ideal gases for which the number of particles n_r in a given state $|r\rangle$ fluctuates.

I. Identical particles, symmetry requirements and statistical problem

Let us consider a gas of N identical particles within a container of volume V.

- each particle : $\psi_r(Q) \equiv$ One-particle wave function for a single particle (with coordinate Q (orbital + spin)) in state $|r\rangle$

- whole gas :

$$\Psi_{\{r_1, r_2, \ldots, r_N\}}(Q_1, Q_2, \ldots, Q_N) = \underbrace{\psi_{r_1}(Q_1) \cdots \psi_{r_N}(Q_N)}$$

Restricted to specific symmetry requirements when two identical particles are exchanged

* Symmetry requirements : There are three possible situations

a) Distinguishable particles [Maxwell-Boltzmann]: This is the analogue of the "classical case"

- Any number of particles can be in the same one-particle state $|r\rangle$
- No symmetry requirement when two particles are exchanged
- Quantum gases do not follow MB statistics

b) Indistinguishable particles of integer spin [Bose-Einstein]: This is an actual "quantum behaviour"

- Any number of particles can be in the same one-particle state $|r\rangle$
- Exchanging two particles does not produce a new state of the whole gas

$$\Psi(\ldots Q_j \ldots Q_i \ldots) = +\Psi(\ldots Q_i \ldots Q_j \ldots)$$

- One must specify how many particles $n_r = 0, 1, 2, \ldots$ there are in each one-particle state $|r\rangle$

c) Indistinguishable particles of half-integer spin [Fermi-Dirac]: This is an actual "quantum behaviour"

- Only one or zero particles can be in a one-particle state $|r\rangle$

  $\Rightarrow$ Pauli's exclusion principle

- Exchanging two particles does **not** produce a new state of the whole gas

$$\Psi(\dots Q_j \dots Q_i \dots) = -\Psi(\dots Q_i \dots Q_j \dots)$$

- One must specify how many particles $n_r = 0, 1$ there are in each one-particle state $|r\rangle$

Example : Gas of two particles A and B with $r = 1, 2, 3$ one-particle states $|r\rangle$

a) MB statistics : In this case $A \neq B$

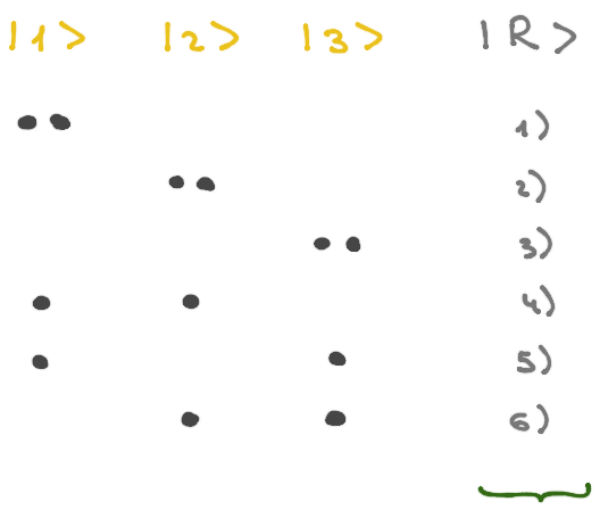
$\|1\rangle$	$\|2\rangle$	$\|3\rangle$	$\|R\rangle$
AB			1)
	AB		2)
		AB	3)
A	B		4)
B	A		5)
A		B	6)
B		A	7)
	A	B	8)
	B	A	9)

$\langle \equiv \rangle \quad \Psi = \psi_r(Q_A) \cdot \psi_s(Q_B)$

with $r = 1, 2, 3$
$s = 1, 2, 3$

9 possible states for the whole gas

b) BE statistics : In this case $A = B \equiv \bullet$



$\Leftrightarrow \quad \Psi = \psi_r(Q_A) \cdot \psi_s(Q_B) + \psi_r(Q_B) \cdot \psi_s(Q_A)$

with $r = 1,2,3$, $s = 1,2,3$

6 possible states for the whole gas

c) FD statistics : In this case $A = B \equiv \bullet$

$\Leftrightarrow \quad \Psi = \psi_r(Q_A) \cdot \psi_s(Q_B) - \psi_r(Q_B) \cdot \psi_s(Q_A)$

with $r = 1,2,3$, $s = 1,2,3$

3 possible states for the whole gas

It is interesting to look at the following quantity :

$$\zeta \equiv \frac{\text{Probability that two particles are found in the same state}}{\text{Probability that two particles are found in different states}}$$

$$\Rightarrow \quad \underbrace{\zeta_{MB} = \frac{3}{6} = \frac{1}{2}}_{\text{"Classical" behaviour}} \quad , \quad \underbrace{\zeta_{BE} = \frac{3}{3} = 1}_{\text{Tendency for particles to bunch together w.r.t. MB}} \quad , \quad \underbrace{\zeta_{FD} = \frac{0}{3} = 0}_{\text{Tendency for particles to remain apart w.r.t MB}}$$

* Statistical problem : We consider the gas at a temperature $\beta = \frac{1}{kT}$. The total energy of a state $|R\rangle$ of the whole gas is

$$\underbrace{E_R}_{\text{energy of whole-gas state } |R\rangle} \overset{\text{additivity}}{=} n_1 \epsilon_1 + n_2 \epsilon_2 + \ldots = \sum_r \overbrace{n_r}^{\text{number of particles in state } |r\rangle} \underbrace{\epsilon_r}_{\text{energy of one-particle state } |r\rangle}$$

with

$$\sum_r n_r = N \qquad [\text{total number fixed}]$$

The partition function is then given by

$$Z = \sum_R e^{-\beta E_R} = \underbrace{\sum_R}_{\text{Sum over all the permitted values of the occupation numbers } (n_1, n_2, \ldots)} e^{-\beta (n_1 \epsilon_1 + n_2 \epsilon_2 + \ldots)}$$

$\Rightarrow$ $(n_1, n_2, \dots)$ changes in different microstates $|R\rangle$ of the whole gas and therefore

$$\overline{n_r} = \frac{\sum_R n_r\, e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)}}{\sum_R e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)}} = \frac{1}{Z}\sum_R \left(-\frac{1}{\beta}\frac{\partial}{\partial \epsilon_r}\right) e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)}$$

$$= -\frac{1}{\beta Z}\frac{\partial Z}{\partial \epsilon_r} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \epsilon_r}$$

The permitted values of $(n_1, n_2, \dots)$ depend on the particular statistics :

a) MB statistics : $n_r = 0, 1, 2, 3, \dots$ with $\sum_r n_r = N$

$\oplus$ possible permutations of particles in different states $|r\rangle$ [distinguishable]

$|r\rangle_{AB} = |r\rangle_{BA}$

b) BE statistics : $n_r = 0, 1, 2, 3, \dots$ with $\sum_r n_r = N$

This condition can be relaxed if particles can be emited-absorbed $\Rightarrow$ photon statistics

c) FD statistics : $n_r = 0$ or 1 with $\sum_r n_r = N$

The goal will then be to compute

$$\boxed{\overline{n_r} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \epsilon_r}}$$

from the partition function $Z = \sum_R e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)}$ and also the dispersion

↳ Sum over permitted $(n_1, n_2, \dots)$

$$\overline{(\Delta n_r)^2} = \overline{n_r^2} - \overline{n_r}^2 = \frac{1}{\beta^2}\frac{\partial^2 \ln Z}{\partial \epsilon_r^2} = -\frac{1}{\beta}\frac{\partial \overline{n_r}}{\partial \epsilon_r}$$

NOTE: $\overline{n_r^2} = \frac{1}{Z}\sum_R \left(-\frac{1}{\beta}\frac{\partial}{\partial \epsilon_r}\right)\left(-\frac{1}{\beta}\frac{\partial}{\partial \epsilon_r}\right) e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)}$

$$= \frac{1}{Z}\frac{1}{\beta^2}\frac{\partial^2 Z}{\partial \epsilon_r^2} = \frac{1}{\beta^2}\left[\frac{\partial}{\partial \epsilon_r}\left(\frac{1}{Z}\frac{\partial Z}{\partial \epsilon_r}\right) + \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \epsilon_r}\right)^2\right]$$

$$= \frac{1}{\beta^2}\left[\frac{\partial}{\partial \epsilon_r}\left(\frac{\partial \ln Z}{\partial \epsilon_r}\right) + \beta^2 \overline{n_r}^2\right] = \frac{1}{\beta^2}\frac{\partial^2 \ln Z}{\partial \epsilon_r^2} + \overline{n_r}^2$$

II. Maxwell - Boltzmann statistics

For a given sequence $(n_1, n_2, \dots)$ there are $\frac{N!}{n_1!\, n_2! \cdots}$ possible ways of distributing N distinguishable particles. Therefore (N balls in boxes $|r\rangle$'s)

$$Z = \sum_R e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)} = \sum_{n_1, n_2, \dots} \underbrace{\frac{N!}{n_1!\, n_2! \cdots}}_{\text{multiplicity}} e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)}$$

$$\Downarrow$$

$$n_r = 0, 1, 2, 3, \dots$$

$$= \sum_{n_1, n_2, \ldots} \frac{N!}{n_1!\, n_2! \cdots} \left(e^{-\beta\epsilon_1}\right)^{n_1} \left(e^{-\beta\epsilon_2}\right)^{n_2} \cdots$$

$$\Gamma = \left[e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2} + \ldots \right]^N = \left[\underbrace{\sum_r e^{-\beta\epsilon_r}}_{z_{1\text{-particle canonical}}} \right]^N$$

$\sum_r n_r = N$

Multinomial theorem (restriction on n_r)

$$\Rightarrow \quad \ln Z = N \ln \left[\sum_s e^{-\beta\epsilon_s} \right]$$

$$\Rightarrow \quad \overline{n_r} = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_r} = N \frac{e^{-\beta\epsilon_r}}{\sum_s e^{-\beta\epsilon_s}} \equiv \text{"Maxwell-Boltzmann distribution"}$$

* Dispersion : The computation of $\overline{(\Delta n_r)^2}$ gives

$$\overline{(\Delta n_r)^2} = -\frac{1}{\beta} \frac{\partial \overline{n_r}}{\partial \epsilon_r} = -\frac{1}{\beta} N \left[-\beta \underbrace{\frac{e^{-\beta\epsilon_r}}{\sum_s e^{-\beta\epsilon_s}}}_{\frac{1}{N}\overline{n_r}} + \beta \underbrace{\frac{e^{-\beta\epsilon_r}\, e^{-\beta\epsilon_r}}{\left(\sum_s e^{-\beta\epsilon_s}\right)^2}}_{\frac{1}{N^2}\overline{n_r}^2} \right]$$

$$= \overline{n_r} - \frac{1}{N}\overline{n_r}^2 = \overline{n_r}\left(1 - \frac{\overline{n_r}}{N}\right) \underset{N \gg \overline{n_r}}{\approx} \overline{n_r}$$

⇓

This is true except if $T \to 0$ and $\overline{n_0} \approx N$

$$\Rightarrow \quad \frac{\overline{(\Delta n_r)^2}}{\overline{n_r}^2} \approx \frac{1}{\overline{n_r}}$$

[relative dispersion arbitrary small if $\overline{n_r} \gg 1$]

III. Photon statistics

This time particles are indistinguishable and the total number is indetermined. This implies that

$$n_r = 0, 1, 2, \dots \quad \text{without any restriction on } \sum_r n_r$$

and therefore

$$Z = \sum_R e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)} = \sum_{n_1, n_2, \dots} e^{-\beta n_1 \epsilon_1} \cdot e^{-\beta n_2 \epsilon_2} \cdots$$

(n_r unrestricted) $= \left(\sum_{n_1=0}^{\infty} e^{-\beta n_1 \epsilon_1} \right) \cdot \left(\sum_{n_2=0} e^{-\beta n_2 \epsilon_2} \right) \cdots$

geometric series : $1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon} + \dots = \underbrace{\frac{1}{1 - e^{-\beta\epsilon}}}$

Each $|r\rangle$ is an harmonic oscillator !!

$$= \frac{1}{1 - e^{-\beta\epsilon_1}} \cdot \frac{1}{1 - e^{-\beta\epsilon_2}} \cdots = \prod_r \frac{1}{1 - e^{-\beta\epsilon_r}}$$

$$\Rightarrow \ln Z = -\sum_r \ln\left(1 - e^{-\beta\epsilon_r}\right)$$

$$\Rightarrow \overline{n_r} = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_r} = \frac{1}{\beta} \frac{1}{1 - e^{-\beta\epsilon_r}} \left(-e^{-\beta\epsilon_r}\right)(-\beta)$$

$$= \frac{e^{-\beta\epsilon_r}}{1 - e^{-\beta\epsilon_r}} = \frac{1}{e^{\beta\epsilon_r} - 1} \equiv \text{"Planck distribution"}$$

* Dispersion : The computation of $\overline{(\Delta n_r)^2}$ gives

$$\overline{(\Delta n_r)^2} = -\frac{1}{\beta}\frac{\partial \bar{n}_r}{\partial \epsilon_r} = +\frac{1}{\beta}\frac{1}{(e^{\beta\epsilon_r}-1)^2}e^{\beta\epsilon_r}\beta = \frac{e^{\beta\epsilon_r}}{(e^{\beta\epsilon_r}-1)^2}$$

$$= \frac{e^{\beta\epsilon_r}-1+1}{(e^{\beta\epsilon_r}-1)^2} = \underbrace{\frac{1}{e^{\beta\epsilon_r}-1}}_{\bar{n}_r} + \underbrace{\frac{1}{(e^{\beta\epsilon_r}-1)^2}}_{\bar{n}_r^2}$$

$$= \bar{n}_r\,(1+\bar{n}_r)$$

$$\Rightarrow \frac{\overline{(\Delta n_r)^2}}{\bar{n}_r^2} = \frac{1}{\bar{n}_r} + 1$$ [relative dispersion not arbitrarily small even if $\bar{n}_r \gg 1$]

NOTE: $\overline{(\Delta n_r)^2}_{\text{Photon}} = \bar{n}_r(1+\bar{n}_r) > \bar{n}_r\left(1-\frac{\bar{n}_r}{N}\right) = \overline{(\Delta n_r)^2}_{MB}$

IV. Bose - Einstein statistics

In order to describe this quantum gas we will make use of the grand canonical ensemble.

Idea : For each one-particle state $|r\rangle$ we have a realisation of the grand canonical ensemble in the whole gas.

$$|r\rangle : \sum_{n_r=0}^{\infty} e^{\underbrace{-\beta E_r}_{n_r\epsilon_r}} e^{-\alpha n_r} = \sum_{n_r=0}^{\infty} e^{-(\alpha+\beta\epsilon_r)n_r}$$

↳ n_r unrestricted but $\alpha \equiv$ Lagrange multiplier

The full partition function $\mathcal{Z}$ is then given by

$$\mathcal{Z} = \sum_{n_1, n_2, \ldots} e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \ldots)} \cdot e^{-\alpha \underbrace{(n_1 + n_2 + \ldots)}_{N}} = e^{-\alpha N} \underbrace{Z}_{\text{canonical } (\alpha\text{-independent})}$$

$$= \sum_{n_1, n_2, \ldots} e^{-(\alpha+\beta\epsilon_1)n_1 - (\alpha+\beta\epsilon_2)n_2 - \ldots}$$

$$= \underbrace{\sum_{n_1=0}^{\infty} e^{-(\alpha+\beta\epsilon_1)n_1}}_{\text{geometric series}} \cdot \sum_{n_2=0}^{\infty} e^{-(\alpha+\beta\epsilon_2)n_2} \cdots \quad [\text{see NOTES}]$$

$$= \left(\frac{1}{1 - e^{-(\alpha+\beta\epsilon_1)}}\right)\left(\frac{1}{1 - e^{-(\alpha+\beta\epsilon_2)}}\right) = \prod_r \frac{1}{1 - e^{-(\alpha+\beta\epsilon_r)}}$$

$$\Rightarrow \ln \mathcal{Z} = -\sum_r \ln\left[1 - e^{-(\alpha+\beta\epsilon_r)}\right]$$

NOTE 1: Summing over all energies $E_r = n_r \epsilon_r$ requires to sum over all numbers of particles n_r

NOTE 2: In the same way as β brings us back to the right energy of the system, α brings us back to the right number of particles $\approx$> "Lagrange multipliers"

NOTE 3: $\mathcal{Z} = e^{-\alpha N} Z \Rightarrow \underbrace{\ln Z}_{\epsilon_r} = \underbrace{\ln \mathcal{Z}}_{(\epsilon_r, \alpha[\epsilon_r])} + \underbrace{\alpha N}_{\alpha[\epsilon_r]}$

Moreover one has that $\frac{\partial}{\partial \alpha}(\ln Z + \alpha N) = \frac{\partial \ln Z}{\partial \alpha} = 0$

$$\bar{n}_r = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \epsilon_r} = -\frac{1}{\beta}\frac{\partial \ln Z_1}{\partial \epsilon_r} - \frac{1}{\beta}\underbrace{\left(\frac{\partial \ln Z_1}{\partial \alpha} + N\right)}\frac{\partial \alpha}{\partial \epsilon_r}$$

$$= \frac{e^{-(\alpha+\beta\epsilon_r)}}{1 - e^{-(\alpha+\beta\epsilon_r)}} = \frac{1}{e^{\alpha+\beta\epsilon_r} - 1} \equiv \text{“Bose-Einstein distribution”}$$

Since the partition function Z of the whole gas has factorised one has

$$\underbrace{\sum_r n_r = N = -\frac{\partial \ln Z}{\partial \alpha}} = \sum_r \frac{e^{-(\alpha+\beta\epsilon_r)}}{1 - e^{-(\alpha+\beta\epsilon_r)}} = \sum_r \frac{1}{e^{\alpha+\beta\epsilon_r} - 1}$$

$$\sum_r \bar{n}_r = N$$

$$\Rightarrow \sum_r \left(\bar{n}_r - \frac{1}{e^{\alpha+\beta\epsilon_r} - 1}\right) = 0 \qquad (i)$$

- Determination of $\alpha(\epsilon_r)$: The quantity $\alpha(\epsilon_r)$ is fixed by the condition (i)

(ii) $\sum_r \bar{n}_r = N = \sum_r \frac{1}{e^{\alpha+\beta\epsilon_r} - 1} \equiv\!>$ Conservation of particles [unlike photon gas]

NOTE: Photon gas is recovered if $\alpha = 0$ [no particle conservation]

* Dispersion : The computation of $\overline{(\Delta n_r)^2}$ gives

$$\overline{(\Delta n_r)^2} = -\frac{1}{\beta}\frac{\partial \bar{n}_r}{\partial \epsilon_r} = -\frac{1}{\beta}\frac{\partial}{\partial \epsilon_r}\left(\frac{1}{e^{\alpha+\beta\epsilon_r}-1}\right)$$

$$= -\frac{1}{\beta}\left[-\underbrace{\frac{e^{\alpha+\beta\epsilon_r}}{(e^{\alpha+\beta\epsilon_r}-1)^2}}\left(\beta+\frac{\partial\alpha}{\partial\epsilon_r}\right)\right]$$

$$\frac{e^{\alpha+\beta\epsilon_r}-1+1}{(e^{\alpha+\beta\epsilon_r}-1)^2} = \underbrace{\frac{1}{e^{\alpha+\beta\epsilon_r}-1}}_{\bar{n}_r} + \underbrace{\frac{1}{(e^{\alpha+\beta\epsilon_r}-1)^2}}_{\bar{n}_r^2}$$

$$= \bar{n}_r\,(1+\bar{n}_r)$$

$$= \bar{n}_r\,(1+\bar{n}_r)\left[1+\underbrace{\frac{1}{\beta}\frac{\partial\alpha}{\partial\epsilon_r}}_{\text{correction to photon statistics } [\alpha=0]}\right]$$

$$\Rightarrow \frac{\overline{(\Delta n_r)^2}}{\bar{n}_r^2} = \left(\frac{1}{\bar{n}_r}+1\right)\left[1+\frac{1}{\beta}\frac{\partial\alpha}{\partial\epsilon_r}\right]$$

- Correction to photon statistics : Let us start from the conservation condition (ii) and take a derivative with respect to ϵ_r

$$\frac{\partial N}{\partial \epsilon_r} = 0 = -\underbrace{\frac{e^{\alpha+\beta\epsilon_r}}{(e^{\alpha+\beta\epsilon_r}-1)^2}}_{\bar{n}_r(1+\bar{n}_r)}\beta - \sum_s \underbrace{\frac{e^{\alpha+\beta\epsilon_s}}{(e^{\alpha+\beta\epsilon_s}-1)^2}}_{\bar{n}_s(1+\bar{n}_s)}\left(\frac{\partial \alpha}{\partial \epsilon_r}\right)$$

$$= -\beta\,\bar{n}_r(1+\bar{n}_r) - \sum_s \bar{n}_s(1+\bar{n}_s)\left(\frac{\partial \alpha}{\partial \epsilon_r}\right)$$

$$\Rightarrow \quad \frac{\partial \alpha}{\partial \epsilon_r} = -\beta\,\frac{\bar{n}_r(1+\bar{n}_r)}{\sum_s \bar{n}_s(1+\bar{n}_s)}$$

$$\Rightarrow \quad \frac{\overline{(\Delta n_r)^2}}{\bar{n}_r^2} = \left(\frac{1}{\bar{n}_r}+1\right)\left[1 - \underbrace{\frac{\bar{n}_r(1+\bar{n}_r)}{\sum_s \bar{n}_s(1+\bar{n}_s)}}_{\text{Correction with respect to photon statistics}}\right]$$

Important : The correction factor becomes relevant at $T \to 0$ where $\bar{n}_0 \approx N$ and $\bar{n}_r \approx 0$ $(r \neq 0)$ so that

$$\overline{(\Delta n_0)^2} \approx N(1+N)\left[1-1\right] = 0$$

$\Rightarrow$ Fluctuation in the number of particles in the ground state goes to zero

V. Fermi - Dirac statistics

This case works similarly as for the BE quantum gas except for the restriction (Pauli's principle) that

$$n_r = 0 \quad \text{or} \quad 1 \qquad \text{for each } |r\rangle$$

The full partition function $\mathcal{Z}$ is then given by

$$\mathcal{Z} = \sum_{n_1, n_2, \ldots} e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \ldots)} \cdot e^{-\alpha \underbrace{(n_1 + n_2 + \ldots)}_{N}} = e^{-\alpha N} \underbrace{Z}_{\substack{\text{canonical} \\ (\alpha\text{-independent})}}$$

$$= \sum_{n_1, n_2, \ldots} e^{-(\alpha + \beta\epsilon_1) n_1 - (\alpha + \beta\epsilon_2) n_2 - \ldots}$$

$$= \underbrace{\sum_{n_1=0}^{1} e^{-(\alpha+\beta\epsilon_1) n_1}}_{\text{finite sum}} \cdot \underbrace{\sum_{n_2=0}^{1} e^{-(\alpha+\beta\epsilon_2) n_2}}_{\text{finite sum}} \cdots$$

$$= \left[1 + e^{-(\alpha+\beta\epsilon_1)}\right]\left[1 + e^{-(\alpha+\beta\epsilon_2)}\right] \cdots$$

$$\Rightarrow \ln \mathcal{Z} = \sum_r \ln\left[1 + e^{-(\alpha+\beta\epsilon_r)}\right]$$

Moreover one has that $\frac{\partial}{\partial \alpha}(\ln Z + \alpha N) = \frac{\partial \ln Z}{\partial \alpha} = 0$

$$\bar{n}_r = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \epsilon_r} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \epsilon_r} - \frac{1}{\beta}\underbrace{\left(\frac{\partial \ln Z}{\partial \alpha} + N\right)}\frac{\partial \alpha}{\partial \epsilon_r}$$

$$= \frac{e^{-(\alpha+\beta\epsilon_r)}}{1+e^{-(\alpha+\beta\epsilon_r)}} = \frac{1}{e^{\alpha+\beta\epsilon_r}+1} \equiv \text{"Fermi-Dirac distribution"}$$

Since the partition function Z has factorised one again has

$$\underbrace{\sum_r n_r = N}_{\sum_r \bar{n}_r = N} = -\frac{\partial \ln Z}{\partial \alpha} = \sum_r \frac{e^{-(\alpha+\beta\epsilon_r)}}{1+e^{-(\alpha+\beta\epsilon_r)}} = \sum_r \frac{1}{e^{\alpha+\beta\epsilon_r}+1}$$

$$\Rightarrow \sum_r \left(\bar{n}_i - \frac{1}{e^{\alpha+\beta\epsilon_r}+1}\right) = 0 \quad (i)$$

- Determination of $\alpha(\epsilon_r)$: The quantity $\alpha(\epsilon_r)$ is fixed by the condition (i)

(ii) $\sum_r \bar{n}_r = N = \sum_r \frac{1}{e^{\alpha+\beta\epsilon_r}+1}$ $\equiv$> Conservation of particles

Remark : Note that everything is as for BE except for a "−" sign that becomes a "+"

* Dispersion : The computation of $\overline{(\Delta n_r)^2}$ gives

$$\overline{(\Delta n_r)^2} = -\frac{1}{\beta}\frac{\partial \bar{n}_r}{\partial \epsilon_r} = -\frac{1}{\beta}\frac{\partial}{\partial \epsilon_r}\left(\frac{1}{e^{\alpha+\beta\epsilon_r}+1}\right)$$

$$= -\frac{1}{\beta}\left[-\frac{e^{\alpha+\beta\epsilon_r}}{(e^{\alpha+\beta\epsilon_r}+1)^2}\left(\beta + \frac{\partial \alpha}{\partial \epsilon_r}\right)\right]$$

$$\frac{e^{\alpha+\beta\epsilon_r}+1-1}{(e^{\alpha+\beta\epsilon_r}+1)^2} = \underbrace{\frac{1}{e^{\alpha+\beta\epsilon_r}+1}}_{\bar{n}_r} - \underbrace{\frac{1}{(e^{\alpha+\beta\epsilon_r}+1)^2}}_{\bar{n}_r^2}$$

$$= \bar{n}_r\,(1-\bar{n}_r)$$

$$= \bar{n}_r\,(1-\bar{n}_r)\left[1 + \frac{1}{\beta}\frac{\partial \alpha}{\partial \epsilon_r}\right]$$

$$\Rightarrow \quad \frac{\overline{(\Delta n_r)^2}}{\bar{n}_r^2} = \left(\frac{1}{\bar{n}_r} - 1\right)\left[1 + \underbrace{\frac{1}{\beta}\frac{\partial \alpha}{\partial \epsilon_r}}\right]$$

Correction due to $\alpha \neq 0$

• Correction due to $\alpha \neq 0$: Let us start from the conservation condition (ii) and take a derivative with respect to ϵ_r

$$\frac{\partial N}{\partial \epsilon_r} = 0 = -\underbrace{\frac{e^{\alpha+\beta\epsilon_r}}{(e^{\alpha+\beta\epsilon_r}+1)^2}}_{\bar{n}_r(1-\bar{n}_r)}\beta - \sum_s \underbrace{\frac{e^{\alpha+\beta\epsilon_s}}{(e^{\alpha+\beta\epsilon_s}+1)^2}}_{\bar{n}_s(1-\bar{n}_s)}\left(\frac{\partial \alpha}{\partial \epsilon_r}\right)$$

$$= -\beta\,\bar{n}_r(1-\bar{n}_r) - \sum_s \bar{n}_s(1-\bar{n}_s)\left(\frac{\partial \alpha}{\partial \epsilon_r}\right)$$

$$\approx> \frac{\partial \alpha}{\partial \epsilon_r} = -\beta\,\frac{\bar{n}_r(1-\bar{n}_r)}{\sum_s \bar{n}_s(1-\bar{n}_s)}$$

$$\Rightarrow \frac{\overline{(\Delta n_r)^2}}{\bar{n}_r^2} = \left(\frac{1}{\bar{n}_r} - 1\right)\left[1 - \frac{\bar{n}_r(1-\bar{n}_r)}{\sum_s \bar{n}_s(1-\bar{n}_s)}\right]$$

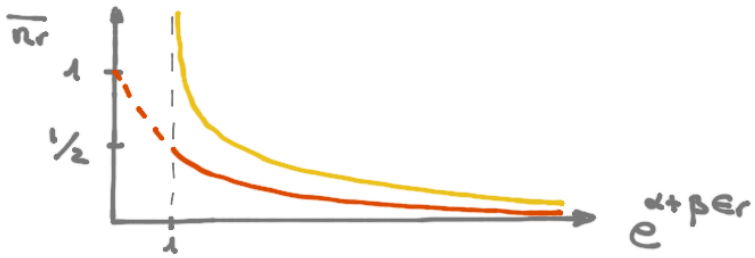
Important : For a state $|r\rangle$ with $\bar{n}_r = 1$ (occupied) then the dispersion vanishes

VI. Regimes of quantum BE and FD gases

Let us start from de BE and FD statistics

$$\bar{n}_r = \frac{1}{e^{\alpha+\beta\epsilon_r} \pm 1} = \frac{1}{e^{\beta(\epsilon_r-\mu)} \pm 1}$$

NOTE : $\mu = -\frac{\alpha}{\beta}$ and $\underbrace{z}_{\text{fugacity}} = e^{-\alpha} = e^{\beta\mu}$



$\alpha + \beta\epsilon_r < 0 \Rightarrow \alpha < 0 \Leftrightarrow \boxed{\mu > 0}$??

NOTE: Chemical potential $\mu < 0$ for a classic gas [see exercises]

subject to the conservation of particle condition

$$\sum_r \bar{n}_r = \sum_r \frac{1}{e^{\alpha+\beta\epsilon_r} \pm 1} = \sum_r \frac{1}{e^{\beta\epsilon_r}\frac{1}{z} \pm 1} = N$$

and with associated partition functions

$$\ln Z = \alpha N \pm \sum_r \ln\left[1 \pm \underbrace{e^{-(\alpha+\beta\epsilon_r)}}_{z\, e^{-\beta\epsilon_r}}\right]$$

* **Classical regime:** We discussed before that the classical limit is recovered at high temperature ($\beta \to 0$) and low density (N small) $\Rightarrow$ $\bar{L} \gg \bar{\lambda}$ [no wave function superposition]

i) Low density: N small $\Rightarrow$ $\bar{n}_r \ll 1$ $\Rightarrow$ $e^{\alpha+\beta\epsilon_r} \gg 1$

ii) High temperature: $\beta \to 0$ $\Rightarrow$ α large $\Rightarrow$ $\bar{n}_r \ll 1$ for not to exceed N $\Rightarrow$ $e^{\alpha+\beta\epsilon_r} \gg 1$

Therefore

$$\underbrace{\frac{1}{z} e^{\beta\epsilon_r}}_{e^{\alpha+\beta\epsilon_r}} \gg 1 \quad \Leftrightarrow \quad \bar{n}_r \ll 1$$

Classical limit $\Leftrightarrow$

NOTE: $\frac{1}{z} e^{\beta\epsilon_r} \gg 1$ seems to require $\begin{cases} z \ll 1 : \text{Low fugacity} \ \checkmark \\ \beta \gg 1 : \text{Low } T \text{ [contradiction?]} \end{cases}$

↳ see quantum regime !!

$z = z(\beta)$

In this limit both BE and FD reduce to

$$\bar{n}_r = e^{-(\alpha+\beta\epsilon_r)} \qquad \text{[classical limit]}$$

and the conservation of particles requires

$$\sum_r \bar{n}_r = N = \sum_r e^{-(\alpha+\beta\epsilon_r)} = e^{-\alpha} \sum_r e^{-\beta\epsilon_r}$$

so that

$$e^{-\alpha} = \frac{N}{\sum_r e^{-\beta\epsilon_r}} \quad \Rightarrow \quad \bar{n}_r = N \frac{e^{-\beta\epsilon_r}}{\sum_s e^{-\beta\epsilon_s}} \equiv \text{"MB distribution"}$$

At the level of partition functions we have that

$$\ln Z = \alpha N \pm \sum_r \ln\left[1 \pm e^{-(\alpha+\beta\epsilon_r)}\right]$$

NOTE: $\ln(1 \pm x) \underset{|x|<1}{\approx} \pm x - \frac{x^2}{2} \pm \frac{x^3}{3} - \dots$

$$= \alpha N + \sum_r \underbrace{e^{-(\alpha+\beta\epsilon_r)}}_{\bar{n}_r} = \alpha N + N$$

NOTE: $e^{-\alpha} = \frac{N}{\sum_r e^{-\beta\epsilon_r}} \Rightarrow \alpha = -\ln N + \ln\left[\sum_r e^{-\beta\epsilon_r}\right]$

$$= -N \ln N + N + \underbrace{N \ln\left[\sum_r e^{-\beta\epsilon_r}\right]}_{\ln Z_{MB}}$$

$$= \ln Z_{MB} \underbrace{- (N \ln N - N)}_{\text{missmatch !!}} = \ln Z_{MB} - \ln N!$$

↳ Stirling's formula

$$= \ln \left[\frac{Z_{MB}}{N!} \right]$$

$$\Rightarrow \quad \ln Z = \ln \left[\underbrace{\frac{Z_{MB}}{N!}} \right] \qquad \text{[classical limit]}$$

- The $\frac{1}{N!}$ factor associated with the indistinguishability of particles arises naturally in the classical limit of quantum gases. We had to introduce it ad-hoc when we treated the gas classically to avoid the Gibbs paradox

* Quantum regime: From the discussion above, the quantum regime must correspond with low temperature ($\beta \to \infty$)

$$\Rightarrow \quad \bar{L} \ll \bar{\lambda} \qquad \text{[wave function superposition !!]}$$

Let us start from the quantum gas result

$$\bar{n}_r = \frac{1}{e^{\alpha + \beta \epsilon_r} \pm 1} = \frac{1}{e^{\beta(\epsilon_r - \mu)} \pm 1}$$

so that

$$N = \sum_r \bar{n}_r = \sum_r \frac{1}{e^{\beta(\epsilon_r - \mu)} \pm 1} \qquad (i)$$

Q: How do we evaluate this sum (i) ??

- Density of states $\omega(\epsilon)$: We start from a free particle in Quantum Mechanics within a box of volume $V = L^3$

$$\hat{H}\,|\psi_{\vec{n}}\rangle = \epsilon_{\vec{n}}\,|\psi_{\vec{n}}\rangle \quad \Rightarrow \text{ Schrödinger equation}$$

with $\hat{H} = \frac{\hat{p}^2}{2m}$ and $\hat{p} = -i\hbar\vec{\nabla}$

Then the boundary conditions are compatible with

$$\psi_{\vec{n}} \propto e^{i\vec{k}\vec{x}} \quad \text{with} \quad \vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$$

$\vec{n} \in \mathbb{Z}$ (discretised)

so that

$$\boxed{\Delta k_{x,y,z} = \frac{2\pi}{L}} \quad \text{(discretised)}$$

The energy of a solution $\psi_{\vec{n}}$ is then given by

$$\boxed{\epsilon_{\vec{n}} = \frac{\hbar^2 \vec{k}^2}{2m} = \left(\frac{2\pi}{L}\right)^2 \frac{\hbar^2}{2m}\,\vec{n}^2 = \frac{h^2}{2mL^2}\,\vec{n}^2} \quad \text{(discretised)}$$

Important: $\sum_{\vec{n}} \approx \sum_{\vec{k}} \overset{L\to\infty}{\approx} \int d\vec{k} \approx \int d|\vec{k}| \approx \int d\epsilon$

$\sum_{\vec{n}}$: properly discretised; $\sum_{\vec{k}}$: properly discretised; $d\vec{k}$: spherical coordinates; $\epsilon = \epsilon(|\vec{k}|)$

In order to evaluate a sum over microstates $|r\rangle$ we will take the "Thermodynamics limit"

$$L \to \infty \;, \quad N \to \infty \qquad \text{with} \qquad \frac{N}{V} \equiv \text{cte}$$

Then, for an arbitrary function $g(\epsilon_r)$ of a discrete variable ϵ_r, one has

$$\sum_r g(\epsilon_r) = \frac{1}{\underbrace{\Delta K_x}_{\frac{2\pi}{L}} \underbrace{\Delta K_y}_{\frac{2\pi}{L}} \underbrace{\Delta K_z}_{\frac{2\pi}{L}}} \sum_{\vec{k}} \Delta K_x \, \Delta K_y \, \Delta K_z \, g(\vec{k})$$

($\vec{k}$: discrete)

Continuum limit ($L \to \infty$):

$$= \frac{V}{(2\pi)^3} \int_{-\infty}^{\infty} d\vec{k} \; g(\vec{k}) = \frac{V}{(2\pi)^3} (4\pi) \int_0^{\infty} d|\vec{k}| \, |\vec{k}|^2 \, g(|\vec{k}|)$$

($\vec{k}$: continuous; $g(\vec{k}) = g(|\vec{k}|)$)

$\epsilon = \epsilon(|\vec{k}|)$:

$$= \int_0^{\infty} d\epsilon \; \underbrace{\omega(\epsilon)} \; g(\epsilon)$$

"density of states" $\equiv$> It depends on $\left\{ \begin{matrix} \Delta\vec{k} \\ \epsilon = \epsilon(|\vec{k}|) \end{matrix} \right.$

Ex: Non-relativistic free particle

- $\epsilon(|\vec{k}|) = \frac{\hbar^2 |\vec{k}|^2}{2m} \Rightarrow |\vec{k}| = \frac{\sqrt{2m\epsilon}}{\hbar} = \sqrt{\frac{2m}{\hbar^2}}\, \epsilon^{\frac{1}{2}}$

- $d\epsilon = \frac{\hbar^2}{m} |\vec{k}|\, d|\vec{k}| = \underbrace{\frac{\hbar^2}{m} \frac{\sqrt{2m\epsilon}}{\hbar}}_{\sqrt{\frac{2\hbar^2}{m}}\sqrt{\epsilon}} d|\vec{k}| \Rightarrow d|\vec{k}| = \sqrt{\frac{m}{2\hbar^2}}\, \epsilon^{-\frac{1}{2}}\, d\epsilon$

Then

$$\sum_r g(\epsilon_r) = \frac{V}{(2\pi)^3} (4\pi) \int_0^\infty d|\vec{k}|\, |\vec{k}|^2\, g(|\vec{k}|)$$

$$= \underbrace{\frac{V}{(2\pi)^3} (4\pi) \sqrt{\frac{m}{2\hbar^2}} \left(\frac{2m}{\hbar^2}\right)}_{\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}} \int_0^\infty d\epsilon\, \underbrace{\epsilon^{-\frac{1}{2}}}_{\epsilon^{\frac{1}{2}}} \epsilon\, g(\epsilon)$$

$$= \int_0^\infty d\epsilon \left[\frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \epsilon^{\frac{1}{2}}\right] g(\epsilon)$$

$$\Rightarrow \boxed{\omega(\epsilon) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \epsilon^{\frac{1}{2}}\, \underbrace{g_s}}$$

spin s degeneration: $g_s = 2s+1$

Let's go back to our original question: how to evaluate the sum i)

$$N = \sum_r \bar{n}_r = \sum_r \frac{1}{e^{\beta(\epsilon_r - \mu)} \pm 1} = \sum_r g(\epsilon_r)$$

Using $\omega(\epsilon)$ for non-relativistic particles one has

$$N = \int_0^\infty \frac{\omega(\epsilon)}{e^{\beta(\epsilon-\mu)} \pm 1}\, d\epsilon = \frac{V}{4\pi^2} g_s \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \int_0^\infty \frac{\epsilon^{\frac{1}{2}}}{e^{\beta(\epsilon-\mu)} \pm 1}\, d\epsilon$$

$$\Rightarrow \boxed{\frac{N}{V} = \underbrace{\frac{g_s}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}}_{C} \int_0^\infty \frac{\epsilon^{\frac{1}{2}}}{e^{\beta(\epsilon-\mu)} \pm 1}\, d\epsilon \overset{t=\beta\epsilon}{=} C\beta^{-\frac{3}{2}} \underbrace{\int_0^\infty \frac{t^{\frac{1}{2}}}{\frac{e^t}{z} \pm 1}\, dt}}$$

Remark: $I(z)$ does not count particles in the ground state ($\epsilon_0 = 0$)

$$I(z) = \pm \underbrace{\Gamma\left(\tfrac{3}{2}\right)}_{\frac{1}{2}\Gamma\left(\frac{1}{2}\right) = \frac{\sqrt{\pi}}{2}} Li_{3/2}(\pm z)$$

Important: We see that, when cooling down a quantum gas to $T \to 0$ ($\beta \to \infty$) while keeping $\frac{N}{V} = \text{constant}$ there is a relation:

↳ effective consequence of the Remark above

Particles missing? ($\beta \to \infty$) ↳ $\frac{N}{V} = C\beta^{-\frac{3}{2}} I(z) \Rightarrow \boxed{z = z(\beta)}$

NOTE: Polilogarithm function $Li_{3/2}(z)$ is real-valued in $z \in [0, 1]$

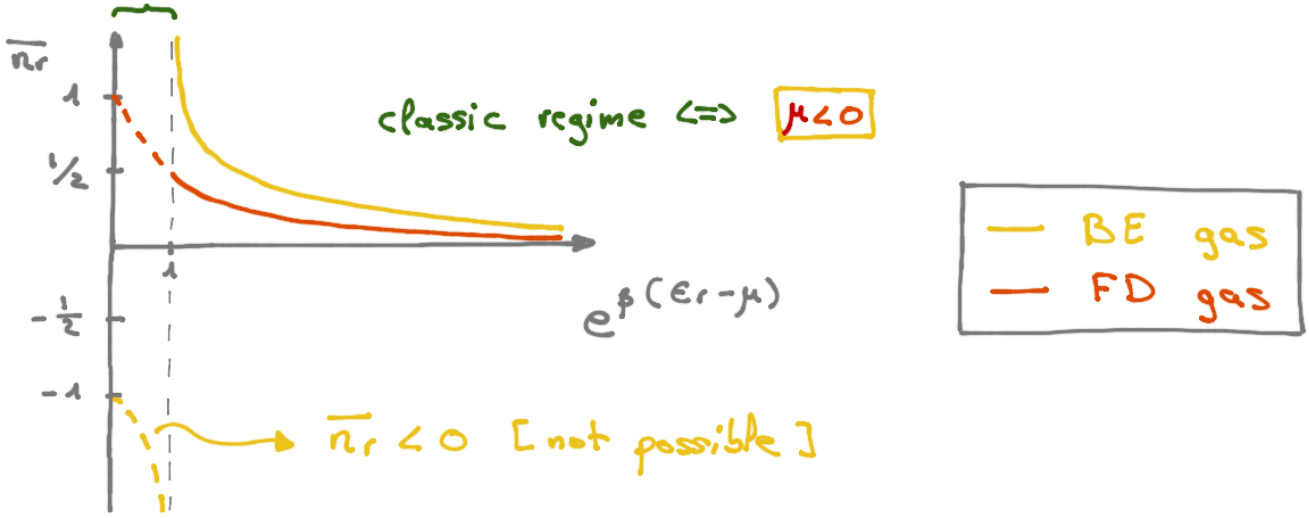
$$Li_{3/2}(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^{3/2}} \quad \text{so} \quad \begin{cases} Li_{3/2}(0) = 0 \\ Li_{3/2}(1) = \zeta(3/2) \approx 2.612 \end{cases}$$

Taylor around $z=0$

Let's try to understand the curve $\mu(\beta)$:

- High-temperature ($\beta \to 0$): Classic regime $\Leftrightarrow \mu < 0$
- Low-temperature ($\beta \to \infty$): Quantum regime $\Leftrightarrow \mu \geq \epsilon_F \geq 0$

Quantum regime $\Leftrightarrow \epsilon_r - \mu \leq 0 \Leftrightarrow \boxed{\mu \geq \epsilon_r \geq 0}$



classic regime $\Leftrightarrow \boxed{\mu < 0}$

Classic to Quantum $\Leftrightarrow$ $\mu < 0$ ($\beta \to 0$, $T \to \infty$) to $\mu \geq \epsilon_r \geq 0$ ($\beta \to \infty$, $T \to 0$)

Bose - Einstein condensate (1.924)

* Let us focus on the ground state $\Rightarrow \epsilon_0 = 0$

$$\bar{n}_0 = \frac{1}{e^{-\beta\mu} - 1} = \frac{1}{z^{-1} - 1} \quad \text{with} \quad z = e^{\beta\mu} \in (0, \infty) \quad (\mu \in (-\infty, \infty))$$

Then

$$\mu > 0 \Rightarrow z > 1 \Rightarrow \bar{n}_0 < 0 \text{ (not possible)} \Rightarrow z \in [0, 1] \Rightarrow \mu \leq 0$$

(classic ← → quantum)

i) μ can never grow beyond $\mu = 0$ otherwise $\bar{n}_0 < 0$ (non sense)

ii) when $\mu = 0$ then, at very low T, one has

$$\bar{n}_r = \frac{1}{e^{\beta\epsilon_r} - 1} \Big|_{\beta \to \infty} \approx 0 \quad [|r\rangle \neq |0\rangle]$$

"Bose - Einstein condensation"

Q: At which temperature T_c does the condensation happen?

$$I(z=1) = C^{-1}\,\beta_c^{\frac{3}{2}}\,\frac{N}{V} \quad \Rightarrow \quad \beta_c = \left[C\,\frac{V}{N}\,\Gamma(3/2)\,\zeta(\tfrac{3}{2})\right]^{\frac{2}{3}}$$

$$[g_s = 1] \quad \Rightarrow \quad \boxed{T_c = \frac{1}{k_B}\,\frac{2\pi\hbar^2}{m}\left[\frac{N}{V}\,\frac{1}{\zeta(\frac{3}{2})}\right]^{\frac{2}{3}}}$$

"Critical temperature"

[Nobel prize 2001]
(Cornell, Wieman, Ketterle)

Fermi sphere [1.978, experimentally]

* Fermions cannot all go to the ground state [Pauli]

* Let us focus on a one-particle state $|r\rangle$ at low T

$$\overline{n_r} = \left.\frac{1}{e^{\beta(\epsilon_r-\mu)}+1}\right|_{\beta\to\infty} \approx \begin{cases} 1 & \text{for } \epsilon_r < \mu \\ 0 & \text{for } \epsilon_r > \mu \end{cases}$$

Important: States with $\epsilon_r < \mu$ are filled while states with $\epsilon_r > \mu$ are empty

Important: Given the value $\mu(T=0) \equiv \epsilon_F$ "Fermi energy" states with $\epsilon < \epsilon_F$ are filled. In momentum space this defines the "Fermi sphere"

$$\epsilon_F = \frac{p_F^2}{2m} = \frac{\hbar^2 k_F^2}{2m} \quad \Rightarrow \quad k_F = \frac{\sqrt{2m\epsilon_F}}{\hbar} \equiv \text{"Fermi surface"}$$

Q: How do we determine $\epsilon_F = \mu(T=0) \equiv k_B T_F$

↳ "Fermi temperature"

$$\frac{N}{V} = \underbrace{\frac{g_s}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}}_{C} \int_0^\infty \frac{\epsilon^{\frac{1}{2}}}{e^{\beta(\epsilon-\epsilon_F)}+1}\, d\epsilon$$

$$\overset{\beta\to\infty}{\approx} C \int_0^{\epsilon_F} \epsilon^{\frac{1}{2}}\, d\epsilon = C\left[\frac{2}{3}\epsilon^{\frac{3}{2}}\right]_0^{\epsilon_F}$$

$$= \frac{2}{3} C\, \epsilon_F^{\frac{3}{2}} \Rightarrow \boxed{\epsilon_F = \left[\frac{3}{2} C^{-1} \frac{N}{V}\right]^{\frac{2}{3}} > 0}$$

$$\Rightarrow \mu(T=0) = \epsilon_F > 0$$

NOTE: While cooling down the Fermi gas, the chemical potential μ grows till reaching a maximal permitted value

$$\mu(T=0) = \epsilon_F = \left[\frac{6\pi^2}{g_s}\frac{N}{V}\right]^{\frac{2}{3}} \frac{\hbar^2}{2m} > 0$$

Application: Modelling of metals as free electron gases.

VII. Black body radiation (thermal electromagnetic radiation)

Let us focus on the photon statistics and study the black body radiation. This is a gas of photons inside a cavity at temperature T. According to Planck distribution

$$\overline{n_r} = \frac{1}{e^{\beta\epsilon_r} - 1}$$

* **Reminder about electromagnetism :** Let us start from the electromagnetic wave equation in vacuum

$$\nabla^2 \vec{E} = \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \vec{E}$$

which has solutions of the form

$$\vec{E} = \underbrace{\vec{A}}_{\text{cte}} \cdot e^{i(\vec{k}\cdot\vec{r} - \omega t)}$$

provided $(i\vec{k})^2 = \frac{1}{c^2}(-i\omega)^2 \Rightarrow |\vec{k}| = \frac{\omega}{c}$

In a relativistic framework one has that

$$p_\mu = (p_0, \vec{p}) = (\epsilon, \vec{p}) = \hbar(\omega, \vec{k}) \quad \text{with} \quad |\vec{k}| = \frac{\omega}{c}$$

and one of the Maxwell equations reads

$$\vec{\nabla}\cdot\vec{E} = (i\vec{k})\cdot\vec{A}\cdot e^{i(\vec{k}\cdot\vec{r} - \omega t)} = i\vec{k}\cdot\vec{E} = 0$$

$$\Rightarrow \underbrace{\vec{k}\cdot\vec{E} = 0}$$

$\vec{E}$ is transverse to the direction of propagation $\vec{k}$

$\Rightarrow$ 2 d.o.f [polarisations]

Let us define

- $f(\vec{k})\, d^3\vec{k} \equiv$ Mean number of photons per unit volume with one specified polarisation whose wave vector lies between $\vec{k}$ and $\vec{k} + d\vec{k}$

Then one has that (this comes from $\sum_{\vec{n}} \to \frac{V}{(2\pi)^3} \sum_{\vec{k}}$)

$$f(\vec{k})\, d^3\vec{k} = \frac{1}{e^{\beta\hbar\omega} - 1} \frac{1}{(2\pi)^3} d^3\vec{k}$$

$$= \frac{1}{e^{\beta\hbar\omega} - 1} \frac{1}{2\pi^2} |\vec{k}|^2 \, d|\vec{k}| \qquad \left(d^3\vec{k} = 4\pi |\vec{k}|^2 d|\vec{k}|\right)$$

$$= \frac{1}{e^{\beta\hbar\omega} - 1} \frac{4\pi}{(2\pi c)^3} \omega^2 \, d\omega \qquad \left(|\vec{k}| = \frac{\omega}{c}\right)$$

Keeping in mind that there are two independent polarisations we arrive at

$$2 \, f(\vec{k})\, d^3\vec{k} = 2 \, f(|\vec{k}|)\, 4\pi |\vec{k}|^2 \, d|\vec{k}|$$

(2 ↓ polarisations)

$$= f(|\vec{k}|) \frac{8\pi}{c^3} \omega^2 \, d\omega \qquad \left(|\vec{k}| = \frac{\omega}{c}\right)$$

$$= \frac{1}{e^{\beta\hbar\omega} - 1} \frac{8\pi}{(2\pi c)^3} \omega^2 \, d\omega$$

Finally we define

- $\bar{u}(\omega;T)\,d\omega \equiv$ Mean energy per unit volume of photons of both directions of polarisation with frequency between ω and $\omega + d\omega$

Then one has that

$$\bar{u}(\omega;T)\,d\omega = 2\,f(|\vec{k}|)\,4\pi\,|\vec{k}|^2\,d|\vec{k}| \times \underbrace{(\hbar\omega)}_{\text{energy per photon}}$$

$$= \frac{\hbar}{e^{\beta\hbar\omega}-1}\,\frac{8\pi}{(2\pi c)^3}\,\omega^3\,d\omega$$

$$= \frac{\hbar}{\pi^2 c^3}\,\frac{\omega^3}{e^{\beta\hbar\omega}-1}\,d\omega$$

Introducing $\eta \equiv \beta\hbar\omega = \frac{\hbar\omega}{kT}$ then

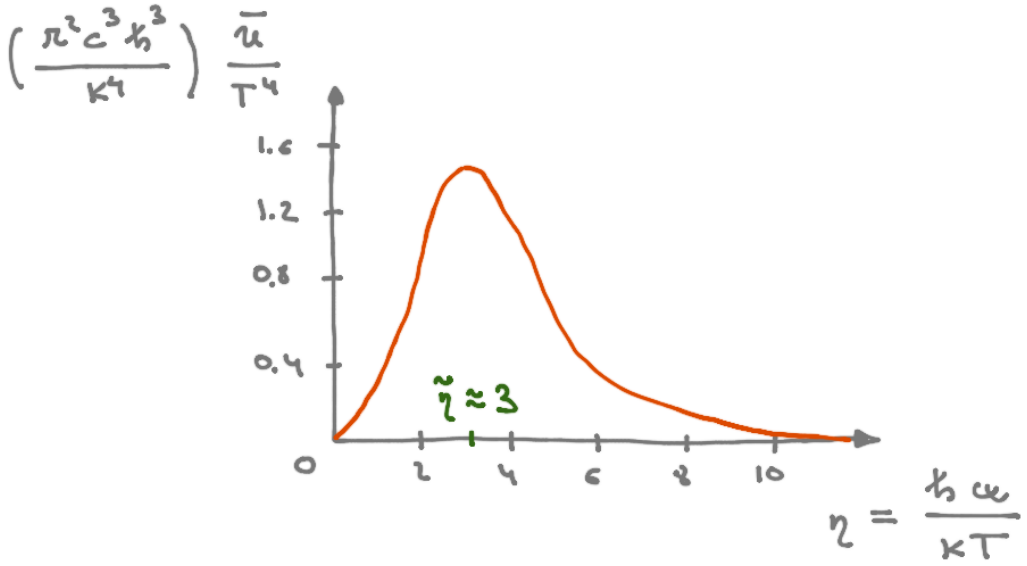
$$\bar{u}(\eta,T)\,d\eta = \frac{\hbar}{\pi^2 c^3}\left(\frac{kT}{\hbar}\right)^4 \frac{\eta^3}{e^{\eta}-1}\,d\eta$$

The mean total energy is then given by

$$\bar{u}_0(T) = \frac{\hbar}{\pi^2 c^3}\left(\frac{kT}{\hbar}\right)^4 \underbrace{\int_0^\infty \frac{\eta^3}{e^{\eta}-1}\,d\eta}_{\frac{\pi^4}{15}} = \frac{\pi^2}{15}\,\frac{(kT)^4}{(\hbar c)^3} \propto T^4$$

"Stefan-Boltzmann law" (1879, 1884)

Lastly it is instructive to discuss the following plot



$\Rightarrow$ Maximum at

$$\tilde{\eta} = 3 \quad \approx > \quad \underbrace{\frac{\hbar\tilde{\omega}_1}{\kappa T_1} = \frac{\hbar\tilde{\omega}_2}{\kappa T_2}}_{\text{Scaling behaviour}} = \tilde{\eta}$$

$$\frac{\tilde{\omega}_1}{T_1} = \frac{\tilde{\omega}_2}{T_2}$$ "Wien's displacement law (1893)"

$\Rightarrow$ Universality of black body radiation !!

Examples :

- Black bodies (absorbing all incident elektromagnetic radiation, although they can also emit radiation)
- Cosmic Microwave Background (CMB)
- Stars and planets (to a good approximation)
- Black holes