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 $\underbrace{Q}_{\text{orbital + spin}}$) in state $|r\rangle$

- whole gas :

$$\Psi_{\{r_1, r_2, \dots, r_N\}}(Q_1, Q_2, \dots, Q_N) = \underbrace{\psi_{r_1}(Q_1) \cdots \psi_{r_N}(Q_N)}_{\text{Restricted to specific symmetry requirements when two identical particles are exchanged}}$$

* 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)

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

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

9 possible states for the whole gas

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

$\|1\rangle$	$\|2\rangle$	$\|3\rangle$	$\|R\rangle$
••			1)
	••		2)
		••	3)
•	•		4)
•		•	5)
	•	•	6)

6 possible states for the whole gas

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

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

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

$\|1\rangle$	$\|2\rangle$	$\|3\rangle$	$\|R\rangle$
•	•		1)
•		•	2)
	•	•	3)

3 possible states for the whole gas

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

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

It is interesting to look at the following quantity :

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

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

* 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

additivity

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

with

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

The partition function is then given by

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

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

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

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

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

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

$\oplus$ possible permutations of particles in $\underbrace{\text{different}}_{|r\rangle_{AB} \,=\, |r\rangle_{BA}}$ states $|r\rangle$ [distinguishable]

b) BE statistics : $n_r = 0, 1, 2, 3, \ldots$ with $\underbrace{\sum_r n_r = N}$

This condition can be relaxed if particles can be emitted - 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 $\overbrace{\frac{N!}{n_1!\, n_2! \cdots}}^{N \text{ balls in boxes } |r\rangle\text{'s}}$ possible ways of distributing N distinguishable particles. Therefore

$$Z = \sum_R e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)} = \sum_{\substack{n_1, n_2, \dots \\ \Downarrow \\ n_r = 0, 1, 2, 3, \dots}} \underbrace{\frac{N!}{n_1!\, n_2! \cdots}}_{\text{multiplicity}} e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots)}$$

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

$$\underset{\sum_r n_r = N}{\downarrow} = \left[e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2} + \dots \right]^N = \Big[\underbrace{\sum_r e^{-\beta\epsilon_r}}_{Z_{1\text{-particle canonical}}} \Big]^N$$

Multinomial theorem (restriction on n_r)

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

$$\Rightarrow \quad \overline{n_r} = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \epsilon_r} = N \frac{e^{-\beta\epsilon_r}}{\sum_s e^{-\beta\epsilon_s}}$$

$\equiv$ "Maxwell-Boltzmann distribution"

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

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

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

$\Downarrow$

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

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

[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

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

and therefore

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

$$(n_r \text{ unrestricted}) = \underbrace{\left(\sum_{n_1=0}^{\infty} e^{-\beta n_1 \epsilon_1} \right)}_{\text{geometric series}: \; 1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon} + \ldots = \frac{1}{1-e^{-\beta\epsilon}}} \cdot \left(\sum_{n_2=0}^{\infty} e^{-\beta n_2 \epsilon_2} \right) \ldots$$

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

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

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

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

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

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

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

$$= \frac{e^{\beta\epsilon_r}-1+1}{(e^{\beta\epsilon_r}-1)^2} = \underbrace{\frac{1}{e^{\beta\epsilon_r}-1}}_{\overline{n_r}} + \underbrace{\frac{1}{(e^{\beta\epsilon_r}-1)^2}}_{\overline{n_r}^2}$$

$$= \overline{n_r}\,(1+\overline{n_r})$$

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

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

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.

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

each $|r\rangle$ has its α

$\hookrightarrow$ n_r unrestricted but $\alpha[\epsilon_r] \equiv$ Lagrange multiplier

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

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

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

$$= \underbrace{\sum_{n_1=0}^{\infty} e^{-(\alpha+\beta\epsilon_1)n_1}}_{\text{geometric series}} \cdot \sum_{n_2=0}^{\infty} e^{-(\alpha+\beta\epsilon_2)n_2} \ldots$$

[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 $\quad \frac{\partial}{\partial \alpha}(\ln \mathcal{Z} + \alpha N) = \frac{\partial \ln \mathcal{Z}}{\partial \alpha} = 0$

$$\overline{n_r} = -\frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial \epsilon_r} = -\frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial \epsilon_r} - \frac{1}{\beta}\overbrace{\left(\frac{\partial \ln \mathcal{Z}}{\partial \alpha} + N\right)}\frac{\partial \alpha}{\partial \epsilon_r}$$

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

Since the partition function $\mathcal{Z}$ of the whole gas has factorised one has

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

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

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

$$(ii) \quad \sum_r \overline{n_r} = N = \sum_r \frac{1}{e^{\alpha+\beta\epsilon_r} - 1} \quad \Rightarrow \quad \text{Conservation of particles [unlike photon gas]}$$

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

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

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

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

$$\frac{e^{\alpha+\beta\epsilon_r}-1+1}{(e^{\alpha+\beta\epsilon_r}-1)^2} = \underbrace{\frac{1}{e^{\alpha+\beta\epsilon_r}-1}}_{\overline{n_r}} + \underbrace{\frac{1}{(e^{\alpha+\beta\epsilon_r}-1)^2}}_{\overline{n_r}^2}$$

$$= \overline{n_r}\,(1+\overline{n_r})$$

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

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

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

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

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

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

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

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

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

=> 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

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

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

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

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

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

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

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

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

$$\overline{n_r} = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \epsilon_r} = -\frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial \epsilon_r} - \frac{1}{\beta}\underbrace{\left(\frac{\partial \ln \mathcal{Z}}{\partial \alpha} + N\right)}\frac{\partial \alpha}{\partial \epsilon_r}$$

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

Since the partition function $\mathcal{Z}$ has factorised one again has

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

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

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

$$(ii) \qquad \sum_r \overline{n_r} = N = \sum_r \frac{1}{e^{\alpha+\beta\epsilon_r}+1} \equiv> \text{Conservation of particles}$$

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

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

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

$$\frac{e^{\alpha+\beta\epsilon_r}+1-1}{(e^{\alpha+\beta\epsilon_r}+1)^2} = \underbrace{\frac{1}{e^{\alpha+\beta\epsilon_r}+1}}_{\overline{n_r}} - \underbrace{\frac{1}{(e^{\alpha+\beta\epsilon_r}+1)^2}}_{\overline{n_r}^2}$$

$$= \overline{n_r}\,(1-\overline{n_r})$$

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

$$\Rightarrow \frac{\overline{(\Delta n_r)^2}}{\overline{n_r}^2} = \left(\frac{1}{\overline{n_r}}-1\right)\left[1+\underbrace{\frac{1}{\beta}\frac{\partial\alpha}{\partial\epsilon_r}}_{\text{Correction due to } \alpha\neq 0}\right]$$

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

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

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

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

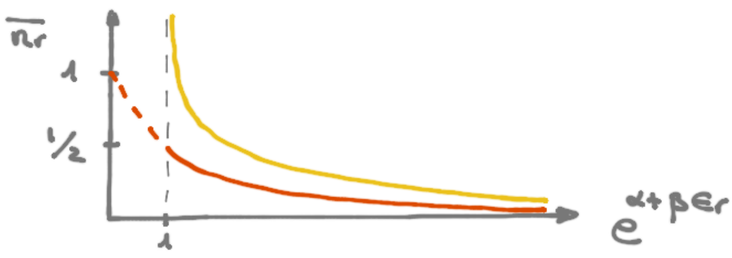
$$\Rightarrow \quad \frac{\overline{(\Delta n_r)^2}}{\bar{n}_r^2} = \left(\frac{1}{\bar{n}_r} - 1\right)\left[1 - \frac{\bar{n}_r(1-\bar{n}_r)}{\sum_s \bar{n}_s(1-\bar{n}_s)}\right]$$

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 $\underset{\text{fugacity}}{\underline{z}} = e^{-\alpha} = e^{\beta\mu}$

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

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

Therefore

$$\text{Classical limit} \iff \overbrace{e^{\alpha+\beta\epsilon_r}}^{\frac{1}{z}e^{\beta\epsilon_r}} \gg 1 \iff \bar{n}_r \ll 1$$

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

↳ see quantum regime !!

$z = z(\beta)$

In this limit both BE and FD reduce to

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

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

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

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: $\ln(1 \pm x) \approx \pm x - \frac{x^2}{2} \pm \frac{x^3}{3} - \ldots$ $\quad |x| < 1$

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

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

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

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

- 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

$$\overline{n_r} = \frac{1}{e^{\alpha + \beta \varepsilon_r} \pm 1} = \frac{1}{e^{\beta(\varepsilon_r - \mu)} \pm 1}$$

so that

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

$\underline{\underline{Q}}$: How do we evaluate this sum (i) ??

- $\underset{\sim\sim\sim}{\text{Density of states } \omega(\epsilon)}$: 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

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

so that

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

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

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

Important:

$$\underbrace{\sum_{\vec{n}}}_{\text{properly discretised}} \approx > \underbrace{\sum_{\vec{k}}}_{\text{properly discretised}} \overset{L\to\infty}{\approx >} \int d\vec{k} \approx > \underbrace{\int d|\vec{k}|}_{\downarrow \text{ spherical coordinates}} \approx > \underbrace{\int d\epsilon}_{\downarrow\ \epsilon = \epsilon(|\vec{k}|)}$$

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

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

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

$$\sum_r g(\epsilon_r) = \frac{1}{\underbrace{\Delta k_x}_{\frac{2\pi}{L}} \underbrace{\Delta k_y}_{\frac{2\pi}{L}} \underbrace{\Delta k_z}_{\frac{2\pi}{L}}} \sum_{\vec{k}} \Delta k_x \Delta k_y \Delta k_z \overbrace{g(\vec{k})}^{\text{discrete } \vec{k}}$$

Continuum limit $L\to\infty$

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

$$g(\vec{k}) = g(|\vec{k}|)$$

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

$$= \int_0^{\infty} d\epsilon\ \underbrace{\omega(\epsilon)}_{\text{"density of states"}} g(\epsilon)$$

"density of states" $\approx >$ It depends on $\begin{cases} \Delta\vec{k} \\ \epsilon = \epsilon(|\vec{k}|) \end{cases}$

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

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

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

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

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

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

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

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

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

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

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

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 $z \in [0,1]$

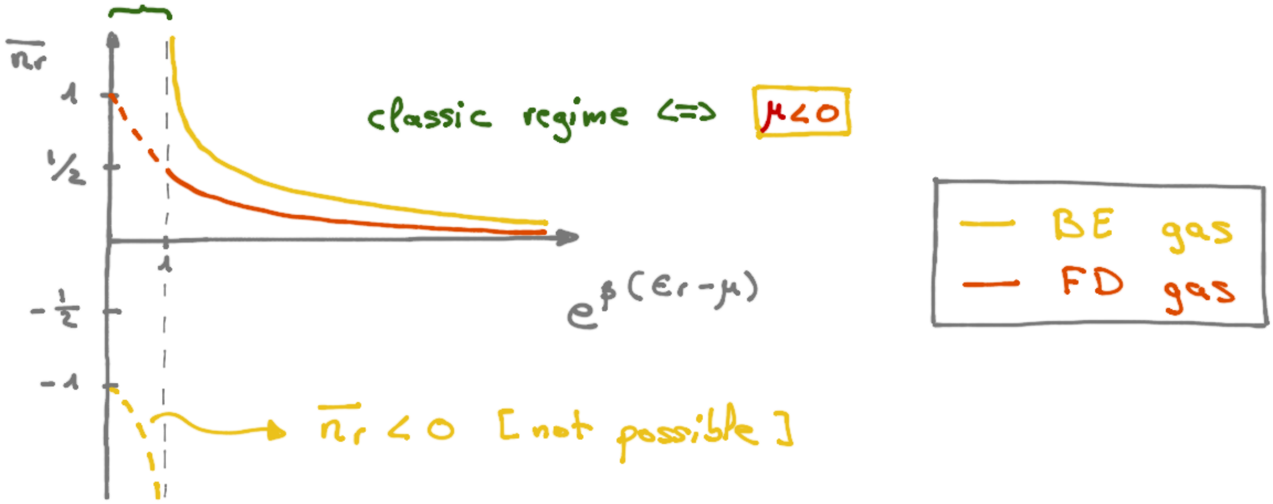
$$Li_{3/2}(z) = \sum_{k=1}^\infty \frac{z^k}{k^{3/2}} \quad \text{so} \quad \begin{cases} Li_{3/2}(0) = 0 \\ Li_{3/2}(1) = \zeta(3/2) \approx 2.612 \end{cases}$$

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 $\Leftrightarrow$ $\mu \geq \epsilon_r \geq 0$

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



Classic to Quantum $\Leftrightarrow$ $\mu < 0$ to $\mu \geq \epsilon_r \geq 0$

$(\beta \to 0)$ $(\beta \to \infty)$

Bose - Einstein condensate (1.924)

$(T \to \infty)$ $(T \to 0)$

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

$$\overline{n_0} = \frac{1}{e^{-\beta\mu} - 1} = \frac{1}{z^{-1} - 1} \quad \text{with} \quad z = e^{\beta\mu} \in (0, \infty)$$

$\mu \in (-\infty, \infty)$

Then

classic ← → quantum

$\mu > 0 \Rightarrow z > 1 \Rightarrow \overline{n_0} < 0$ (not possible) $\Rightarrow z \in (0, 1] \Rightarrow \mu \leq 0$

i) μ can never grow beyond $\mu = 0$ otherwise $\overline{n_0} < 0$ (non sense)

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

$$\overline{n_r} = \frac{1}{e^{\beta\epsilon_r} - 1} \Bigg|_{\beta \to \infty} \approx 0 \qquad [\,|r\rangle \neq |0\rangle\,]$$

"Bose - Einstein condensation"

Q: At which temperature T_c does the condensation happen?

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

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

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

Fermi sphere [1978, experimentally]

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

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

$$\bar{n}_r = \frac{1}{e^{\beta(\epsilon_r - \mu)} + 1} \Bigg|_{\beta \to \infty} \simeq \begin{cases} 1 & \text{for } \epsilon_r < \mu \\ 0 & \text{for } \epsilon_r > \mu \end{cases}$$

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"

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

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

↳ "Fermi temperature"

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

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

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

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

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 $\quad \underbrace{\text{This}}$ comes from $\sum_{\vec{k}} \to \frac{V}{(2\pi)^3} \sum_{\vec{k}}$

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

$d^3\vec{k} = 4\pi |\vec{k}|^2 d|\vec{k}|$

$$= \frac{1}{e^{\beta\hbar\omega}-1} \frac{1}{2\pi^2} |\vec{k}|^2 d|\vec{k}|$$

$$= \frac{1}{e^{\beta\hbar\omega}-1} \frac{4\pi}{(2\pi c)^3} \omega^2 d\omega$$

$|\vec{k}| = \frac{\omega}{c}$

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

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

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

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

Finally we define

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

Then one has that

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

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

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

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

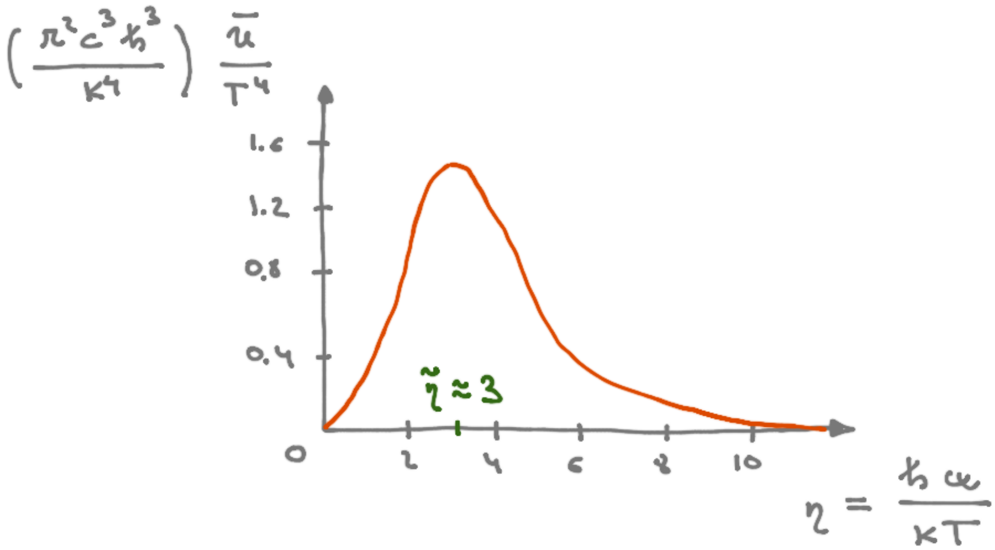
$$\overline{u}(\eta,T)\,d\eta = \frac{\hbar}{\pi^2 c^3}\left(\frac{kT}{\hbar}\right)^4 \frac{\eta^3}{e^\eta - 1}\, d\eta$$

The mean total energy is then given by

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

"Stefan-Boltzmann law" (1879, 1884)

Lastly it is instructive to discuss the following plot



$\Rightarrow$ Maximum at

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

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

$\Rightarrow$ Universality of black body radiation !!

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