Statistical Thermodynamics

Statistic ⇒ probability distribution

Thermodynamic probability = 'Ω' = No. of accessible microstates to a macrostate

Entropy : $S = k \ln \Omega$ (bridge b/w statistics and thermodynamics)

Equilibrium ⇒ Maximum Ω ⇒ Maximum S.

S : additive ; Ω : multiplicative

$S = S_1 + S_2$; $\Omega = \Omega_1 \Omega_2$

→ we chose,

$S \propto \ln \Omega$

$$\boxed{S = k \ln \Omega}$$ k : Boltzmann const.

- Whether particles are distinguishable / indistinguishable, a specification of the no. of particles n_i in each energy level is said to define a macrostate of the assembly.
- In thermodynamics, we encounter two types of distributions :

Statistical distributions

Classical statistics

eg: M-B. statistics (1875)

- Energy emitted/absorbed : continuous
- distinguishable particles
- spin not the criteria

↓ No. of particles / cell

↳ no restriction

Quantum statistics

eg : Bose-Einstein (1926)

FD. (1928)

- energy is quantized taking discrete values.
- Indistinguishable
- spin is

↳ full integral — BE

half " — FD

↓ No. of particles / cell

→ No restriction on BE

→ Restriction by Pauli's exclusion principle.

* cell : level of degeneracy corresponding to a given energy level E.

Occupation index / No. of particles per cell of Energy E_i at eqm temp. or Prob. distb. fn. @ eqm Temp.

$n(E_i)$ = no. of particles with energy level E_i

$g(E_i)$ = " " cells " " " E_i

$$\frac{n(E_i)}{g(E_i)} = \frac{n_i}{g_i} = f(E_i).$$ ↳ occupation index.

E_i — cells.

In MB :

$f(E_i) = Ae^{-\beta E_i}$

$\Rightarrow f(E_i) = e^{-(\alpha + \beta E_i)}$ where $e^{-\alpha} = A$.

$\Rightarrow f(E_i) = e^{-E_i/kT}$ ($\beta = 1/kT$).

$\therefore n_i = g_i A e^{-E_i/kT}$

In BE:

$$f(\epsilon_i) = \frac{1}{e^{\alpha+\beta\epsilon_i} - 1} \qquad \beta = 1/kT, \ \alpha = -\mu/kT \qquad \mu: \text{chemical potential}$$

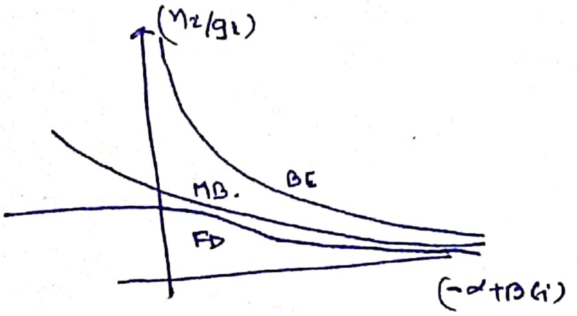
In FD:

$$f(\epsilon_i) = \frac{1}{e^{\alpha+\beta\epsilon_i} + 1} \ : \ \alpha = -\frac{E_F}{kT}$$

where E_F: fermi energy of fermions

$e^{\alpha+\beta\epsilon_i}$:	MB	BE	FD
	(g_i/n_i)	$(g_i/n_i)+1$	$(g_i/n_i)-1$

- If $(g_i/n_i) \approx e^{\alpha+\beta\epsilon_i}$ is large, Both BE and FD will approach MB i.e. indistinguishable particles become distinguishable, when no. of cells are much more than the particles that have to be placed in the cell [Concept of uniqueness no.]



⇒ indistinguishable becomes distinguishable.

CM → distinguishable particles
QM → indistinguishable "

$$\left[P = C_0 e^{-\beta(\Delta E + p\Delta V - \mu\Delta N)} \right]$$

The probability that a microscopic system is in state of energy E, is given by

$$P_s = C_0 e^{-\beta(E_s - E_0)}$$

where E_0 : energy corresponding to the reference level.

$$\text{or} \quad P_s = Ce^{-\beta E_s}$$

$$\because \sum P_s = 1 \Rightarrow \boxed{P_s = \frac{e^{-\beta E_s}}{\sum e^{-\beta E_s}}}$$

In quantum statistics, $p\Delta V = 0$ but $\mu\Delta N \neq 0$.

$$\therefore P_s = C_0 e^{-\beta(\Delta E - \mu\Delta N)}$$

$$= Ce^{-\beta(E_s - \mu n)}$$

If $\epsilon_s = E_s/n$

$$P_s = C e^{-\beta n(\epsilon_s - \mu)} \quad \text{const} \quad C = \left(\sum_n e^{-\beta n'(\epsilon_s - \mu)}\right)^{-1}$$

The occupation number

$$\bar{n} = \sum P_s n$$

$$= \frac{\sum n e^{-\beta n(\epsilon_s - \mu)}}{\sum e^{-\beta n(\epsilon_s - \mu)}}$$

$$= \frac{\sum n e^{-xn}}{\sum e^{-xn}}$$

or $\bar{n} = \frac{-\frac{\partial}{\partial x} \sum e^{-nx}}{\sum e^{-nx}} = -\frac{\partial}{\partial x} \ln\left(\sum e^{-nx}\right)$

lower $n = 0$

upper $n =$ max. no. of particles occupying a single quantum state

⎿ ① Particles obeying Pauli exclusion principle: a given state can't have more than 1 particle. ⇒ fermions obeying F D statistics

② No restriction on the no. of particle occupying a state. → bosons following BE stat.

$\therefore$ ① ⇒ $n = 0$ or 1.

$\therefore \sum_{n=0}^{1} e^{-nx} = 1 + e^{-x}$ $\quad \therefore \bar{n}_{FD} = \frac{e^{-x}}{1+e^{-x}} = \boxed{\frac{1}{e^{x}+1} = \bar{n}_{FD}}$

② ⇒ $n = 0$ to ∞.

$$\sum_{n=0}^{\infty} e^{-nx} = 1 + e^{-x} + e^{-2x} + \cdots = \frac{1}{1-e^{-x}}.$$

$$\therefore \bar{n}_{BE} = -\frac{\partial}{\partial x}\left[\ln(1-e^{-x})^{-1}\right] = \frac{e^{-x}}{1-e^{-x}}.$$

$$\therefore \boxed{\bar{n}_{BE} = \frac{1}{e^{x}-1}}$$

$\therefore$ In general we can write:

$$\boxed{\bar{n} = \frac{1}{e^{+\beta(E-\mu)} + K}.}$$

where $K = +1 \longrightarrow$ ferm.

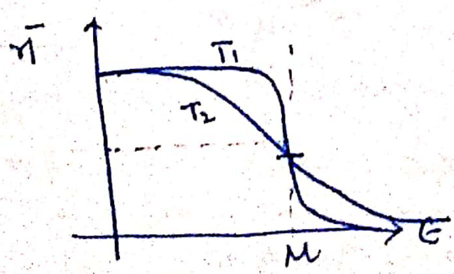
$ -1 \longrightarrow$ Bos

$ 0 \longrightarrow$ MB.

At two temp., T_1 & T_2 s.t. $T_2 > T_1$:

Fermions

$$\frac{1}{e^{\frac{1}{K_0 T}(E-\mu)} + K}.$$



Bosons