# Statistical Thermodynamics

Statistic ⇒ probability distribution

Thermodynamic probability = '$\Omega$' = No. of accessible microstates to a macrostate

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

Equilibrium ⇒ Maximum $\Omega$ ⇒ Maximum S.

S : additive ; $\Omega$ : 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 | Quantum statistics |
|---|---|
| eg: M-B. statistics (1875) | eg : Bose-Einstein (1926) |
| | FD. (1928) |
| - Energy emitted/absorbed : continuous | - energy is quantized taking discrete values. |
| - distinguishable particles | - Indistinguishable |
| - spin not the criteria | - spin is |
| | ↳ full integral - BE |
| | half " - FD |
| ↓ No. of particles / cell | ↓ No. of particles / cell |
| ↳ no restriction | → 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. distn fn. @ eqm Temp.

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

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

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

$E_i$ — fun.

In MB :

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

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

∴ $n_i = g_i A e^{-E_i/kT}$ $(\beta = 1/kT)$.

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In BE:

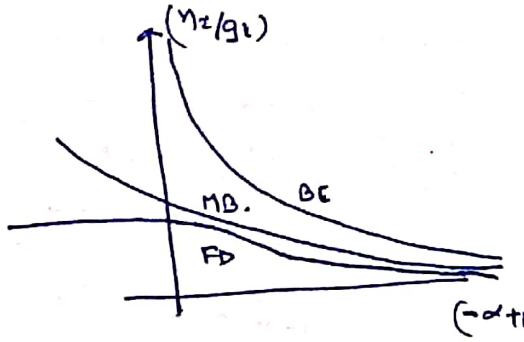
$$f(\epsilon_i) = \frac{1}{e^{(\alpha+\beta\epsilon_i)} - 1}$$ $\beta = 1/kT$ , $\alpha = -\mu/kT$ $\mu$: chemical potential

In FD:

$$f(\epsilon_i) = \frac{1}{e^{(\alpha+\beta\epsilon_i)}+1}$$ : $\alpha = -\frac{\epsilon_F}{k_B T}$ where $\epsilon_F$: fermi energy of fermions

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

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




$\Rightarrow$ indistinguishable becomes distinguishable.

CM $\rightarrow$ distinguishable particles
QM $\rightarrow$ 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.

$$\text{or } P_s = C e^{-\beta E_s}$$

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

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

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

$$\text{If } \epsilon_s = E_s/n$$

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

## The occupation number

$$\bar{n} = \sum P_s n$$
$$= \frac{\sum n e^{-\beta n(\epsilon_s - \mu)}}{\sum e^{-\beta n(\epsilon - \mu)}}.$$
$$= \frac{\sum n e^{-xn}}{\sum e^{-xn}}.$$

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

lower $n \equiv 0$

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 FD statistics

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

∴ 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 $\infty$.

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

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

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

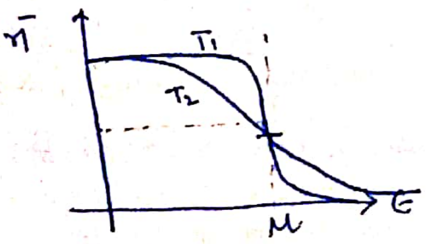
∴ In general we can write:

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

where $k = +1$ → ferm.
$-1$ → Bos
$0$ → MB.

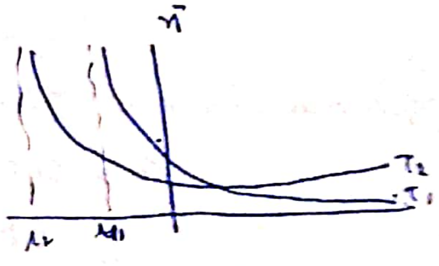
At two temp., $T_1$ & $T_2$ s.t $T_2 > T_1$:

Fermions




$$\frac{1}{e^{\frac{1}{kT}(E-\mu)}+k}.$$

Bosons




## Alternative method for $\bar{n}$

$\Omega$ → no. of ways in which we can distribute particles in the available energy states.

Then the most probable distribution can be calculated by maximising $\ln\Omega$ subject to following constraints:

1. total no. of particles conserved.
2. " energy " " system " " "
3. Maximum entropy ie $d(\ln\Omega) = 0$
4) A priori prob: all states are equally probable to be occupied by the particles

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Let available energy levels be $\epsilon_1, \epsilon_2, \epsilon_3 \cdots \epsilon_n$ & no. of particles in each level be $n_1, n_2, n_3 \cdots$. Moreover, each energy level be divided into several sublevels. Let $g_1, g_2, g_3 \cdots$ be sublevels corresponding to energies $\epsilon_1, \epsilon_2, \epsilon_3 \cdots$

Let us consider $i^{th}$ sublevel. The probability that a particular ~~ith~~ sub level is occupied is $\frac{1}{g_i}$. Hence, the average no. of particles in that state will be $n_i/g_i$ which is occupation no. of ~~that~~ with ith state

## Classical Mech:

We focus on the particle and determine the no. of ways in which total no. of particles $N$ can be grouped into levels having respectively $n_1, n_2, n_3 \cdots$ no. of particles

No. of ways it can be done

$$W = \frac{N}{n_1!\, n_2! \cdots} = \frac{N}{\prod n_i!}$$

Now, ~~this is~~ we need to find out the no. of ways in which these can occupy severale sublevels:

① $\Omega_{cl}$:

→ we calculate the no. of ways in which $n_i$ particles can be distributed among $g_i$ sublevels when there is no restriction on no. of particles occupying a sublevel. The classical particles are distinguishable. So, the total no. of ways in which $n_i$ particles can $g_i$ sublevels is $g_i^{n_i}$.

∴ no. of ways in which $g_i$ particles occupy $g_i$ level and so on will be given by:

$$P_{cl} = g_1^{n_1} g_2^{n_2} \cdots g_n^{n} \cdots = \prod_i g_i^{n_i}$$

$$\therefore \boxed{\Omega_{cl} = \frac{N_i}{\prod n_i!} \times \prod_i g_i^{n_i}}$$

② $\Omega_{FD}$:

Fermions are governed by PE Principle, so no two particle can occupy same sublevel ⇒ $g_i$ must be greater than $n_i$.

No. of ways in which $n_i$ can be occupied in $g_i$ levels is given by:

$${}^{g_i}C_{n_i}$$

∴ for all the sublevels:

$$\Omega_{FD} = \prod_i \frac{g_i!}{n_i!\,(g_i - n_i)!}$$

③ $\Omega_{BE}$: No restriction on no. of ways in which $n_i$ bosons can occupy $g_i$ levels.

$$\therefore \Omega_{BE} = \prod_i \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!}$$

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## Most probable distribution

↳ can be attained by maximising $\ln(\Omega)$ i.e.

$\boxed{d(\ln\Omega) = 0}$ (∵ entropy is max)

Subject to $\sum n_i = \text{Const}$ or $\sum \delta n_i = 0$

$\sum \epsilon_i n_i = \text{const}$ $\quad \sum \epsilon_i \delta n_i = 0$

## MB distribⁿ

$$\Omega = \prod_i \frac{N!}{n_i!}(g_i)^{n_i}$$

$$\ln\Omega = \sum_i (\ln N! - \ln n_i! - n_i \ln g_i)$$

$$d(\ln\Omega) = -d\left(\sum_i (n_i \ln n_i - n_i) - n_i \ln g_i\right)$$

Stirling's approx: $\boxed{\ln n! = n\ln n - n}$

$$= -\sum(\delta n_i \ln n_i + \delta n_i - \delta n_i - \delta n_i \ln g_i) = 0$$

$$\text{or} \quad \sum \ln\left(\frac{g_i}{n_i}\right)\delta n_i = 0$$

Also $\sum dn_i =$

$\sum \epsilon_i \delta n_i = 0$

Using Lagrange's method of undetermined multipliers:

$$\sum\left(\ln\left(g_i/n_i\right) + \alpha - \beta\epsilon_i\right) dn_i = 0.$$

If holds for all i if:

$$\ln(g_i/n_i) + \alpha - \beta\epsilon = 0$$

$$\text{or} \quad n_i/g_i = e^{+(\alpha - \beta\epsilon_i)}$$

$$\text{or} \quad n_i = g_i e^{\alpha - \beta\epsilon_i}$$

$$\text{or} \quad \boxed{n_i = g_i A e^{-\beta\epsilon_i}} \qquad A = e^{-\alpha}.$$

now, $\sum n_i = N$.

$$\therefore A = \frac{N}{\sum g_i e^{-\beta\epsilon_i}} \rightarrow Z \text{ i partition fn.}$$

$$\therefore \boxed{n_i = \frac{N}{Z} g_i e^{-\beta\epsilon_i}}$$

$P_i$: prob. of occupancy of $\epsilon_i$ energy levels.

$$\boxed{P(\epsilon_i) = \frac{n_i}{N} = \frac{g_i e^{-\beta\epsilon_i}}{\sum g_i e^{-\beta\epsilon_i}}}$$

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To determine $\beta$:

$$S = k\ln(\Omega)$$

$$dS = k\,d(\ln\Omega)$$

$$T\,dS = kT\,d(\ln\Omega)$$

$$\text{or } dE = T\,dS = \sum \varepsilon_i\,dn_i = kT\,d\ln(\Omega).$$

$$\text{or } \quad \sum \varepsilon_i\,dn_i = kT\sum_i -(\alpha-\beta\varepsilon_i)\,dn_i$$

$$= -kT\sum_i (\alpha-\beta\varepsilon_i)\,dn_i$$

$$\text{or } \sum \varepsilon_i\,dn_i = -kT\cancelto{0}{\sum\alpha} + kT\sum \beta\,\varepsilon_i\,dn_i$$

$$\Rightarrow \quad \boxed{\beta = \frac{1}{kT}}$$

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