Macroscopic States | Microscopic States | Postulates of equal a priori probabilities | Entropy $\boxed{S = k \ln \Omega}$ (3rd law) | $\boxed{\beta = \frac{1}{kT}}$ ① → 0th law (thermal eqm)

LEC-1

Quantum Mechanics & Statistical Mechanics

$\boxed{\eta = \frac{P}{kT}}$ Mech. eq. | $\boxed{\xi = -\frac{\mu}{kT}}$ Chemical eq.

A

UNIT-1 & 2

Boltzmann Const. $k = 1.38 \times 10^{-23}\ JK^{-1}$

Macroscopic and the Microscopic states :-

Suppose a Physical system

Composed of N identical particles confined to a space of volume V.

$N \rightarrow$ extremely large $\rightarrow 10^{23}$

Thermodynamic limit,

$N \rightarrow \infty, \quad V \rightarrow \infty$

$\rho = \frac{N}{V} = \text{finite} \rightarrow$ particle density (n)

In this limit, the extensive properties of system become directly proportional to the size of the system (i.e. $\propto N$ or $\propto V$),

while intensive properties become independent thereof;

The particle density, of course, remains an important parameters for all physical properties of the system.

Total energy

$$E = \sum_i n_i \epsilon_i \rightarrow ①$$

Where

$$N = \sum_i n_i \rightarrow ②$$

(If the particles comprising the system is noninteracting, the total energy E would be equal to the sum of energies of individual

According to Quantum Mechanics

↓

the single particle energies are discrete

↓ If $V \to$ large

Spacing of energy levels become so small.

↓ Continuous

This is done even if the particles were mutually interacting ; in that case the total energy E cannot be written in the form (1).

$\boxed{\text{A Macrostate is specified by parameters } (N, V, E)}$

↓

molecular level

$E \to$ A large number of different ways in which the macrostate of a system can be realized'

↓

A large number of different ways in which the total energy E of the system can be distributed among the N particles consisting it.

↓

Each of these (different) ways specifies a microstate, or complexion of the given system.

$$H\psi = E\psi$$

Various microstate of a given system can be identify with the independent solns $\psi(r_1, \ldots r_N)$ of the Schrödinger eqn.

Postulate of "equal a priori probabilities" ②

2nd Postulate
ensemble average = time average
Average behavior of any system ↓ ensemble

↓ For all microstates consistent with a given macrostate.

For a given macrostate of the system there does in general correspond to a large number of microstates and it seems natural to assume, when there are no other constraints, that at any time t the system is equally likely to be in any one of these microstates.

Actual Number of all Possible microstates $\Omega(N, V, E)$

Here $V \rightarrow$ The dependence on V comes in because the possible values ϵ_i of the single-particle energy ϵ are themselves a function of this parameter.

$\Omega(N,V,E)$ = No. of all microstates that give rise to the macrostate (extensive) parameters N, V, E, ---

"All microstates satisfying the macrostate parameters are equally likely to occur."

→ Extensive properties of the system directly proportional to the size of the system (i.e. $\propto N$, $\propto V$), while the intensive properties (bulk) become independent. → (not depend on size) T, P, n

additive for subsystem

Ⓝ A macrostate is specified by parameters (N, V, E, -)

The Symbol $\Omega(N,V,E) \rightarrow$ # The actual number of of all microstates that give rise to the macrostate (extensive) parameters N, V, E - - -

Ⓝ → Extensive properties ↓ Energy E; Enthalpy, H; Entropy, S; Gibbs energy, G; Heat energy, Cp; Internal energy, U, Mass, volume

Contact between Statics and thermodynamics: physical significance of the number $\Omega(N,V,E)$:-

(or Defn of entropy from microstates)

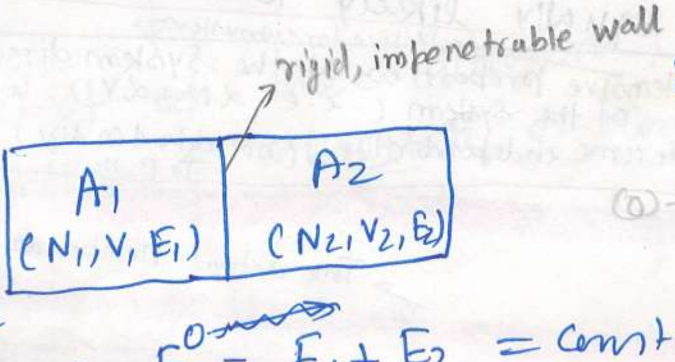
Two physical systems, A_1 & A_2 which are separately in equilibrium.

A_1 $\downarrow$ macrostate of A_1 be represented by the parameters N_1, V_1 & E_1 $\downarrow$ It has $\Omega_1(N_1, V_1, E_1)$ possible microstates

A_2 $\downarrow$ $N_2\ V_2,\ E_2$ $\downarrow$ possible microstates $\Omega_2(N_2, V_2, E_2)$

All thermodynamic properties of the systems A_1 and A_2 can be derived from the functions $\Omega_1(N_1, V_1, E_1)$ and $\Omega_2(N_2, V_2, E_2)$, respectively

Now bring the two systems into thermal contact with each other,
$\downarrow$
Allowing the possible exchange of energy between these two (However, V_1 & V_2, N_1 & N_2 remain fixed.)



(0) → denotes properties of the composite system

E_1 & E_2 become variable $\longrightarrow$ but

$$E^{0} = E_1 + E_2 = \text{Const.} \longrightarrow (1)$$

$\downarrow$ This is energy of composite system $A^0 (\equiv A_1 + A_2)$ (Energy of interaction between A_1 & A_2 neglected)

At any time t, the subsystem A_1 is equally likely ③
to be in any of the $\Omega_1(E_1)$ microstates,
while A_2 is equally likely to be in any one of
the $\Omega_2(E_2)$ microstates;

Therefore the composite system $A^{(0)}$ is equally likely
to be in any of the

$$\Omega_1(E_1)\,\Omega_2(E_2) = \Omega_1(E_1)\,\Omega_2(E^{(0)} - E_1)$$
$$= \Omega^0(E^0, E_1) \longrightarrow ②$$

microstates

Here the number $\Omega^{(0)}$ itself varies with E_1.

{ E_1 and E_2; or E^0 & E_1

Question: At what value of E_1 will the composite system is in equilibrium?

In other words, how far will the energy exchange go in order to bring the subsystems A_1 and A_2 into mutual equilibrium?

A macrostate ~~that~~ with a larger number of microstates as a more probable stable.

This will happen at that value of E_1 which maximizes the number $\Omega^0(E^{(0)}, E_1)$

The most probable state of a system is the macrostate in which the system spends an "overwhelmingly" large fraction of its time.

It is then natural to identify this state with the equilibrium state of the system.

$$\Omega^{0}(E^{(0)}) = \Omega_1(E_1)\,\Omega_2(E_2)\Big|_{E^{(0)}=E_1+E_2}$$

Equilibrium is achieved if E_1 (with $E_2 = E^{(0)} - E_1$) maximizes $\Omega^{(0)}$:

$$\frac{\partial \Omega^{(0)}}{\partial E_1} = 0 = \frac{\partial \Omega_1(E_1)}{\partial E_1}\Omega_2(E_2) - \Omega_1(E_1)\frac{\partial \Omega_2(E_2)}{\partial E_2}$$

$E_1+E_2=\text{Con}$

$\frac{\partial E_2}{\partial E_1} = -1$

$$\Rightarrow \frac{\partial \Omega_1(E_1)}{\partial E_1}\Omega_2(E_2) - \Omega_1(E_1)\frac{\partial \Omega_2(E_2)}{\partial E_2} = 0 \qquad \Big|\ \because \frac{\partial \Omega_2(E_2)}{\partial E_1} = -\frac{\partial \Omega_2(E_2)}{\partial E_2}$$

$$\downarrow$$

$$\Rightarrow \frac{1}{\Omega_1(E_1)}\frac{\partial \Omega_1(E_1)}{\partial E_1} = \frac{1}{\Omega_2(E_2)}\frac{\partial \Omega_2(E_2)}{\partial E_2}$$

$$\downarrow$$

$$\Rightarrow \frac{\partial \ln \Omega_1(E_1)}{\partial E_1} = \frac{\partial \ln \Omega_2(E_2)}{\partial E_2}$$

Let $\boxed{\beta = \frac{\partial \ln \Omega(E)}{\partial E}}$ $\Rightarrow$ two systems are in thermal equilibrium if they have the same β.

Denoting the equilibrium value of E_1 by $\bar{E}_1$ (and that of E_2 by $\bar{E}_2$), we obtain on maximizing $\Omega^{(0)}$,

$$\left(\frac{\partial \Omega_1(E_1)}{\partial E_1}\right)_{E_1=\bar{E}_1} \Omega_2(\bar{E}_2) + \Omega_1(\bar{E}_1)\left(\frac{\partial \Omega_2(E_2)}{\partial E_2}\right)_{E_2=\bar{E}_2} \cdot \frac{\partial E_2}{\partial E_1} = 0$$

Since $\frac{\partial E_2}{\partial E_1} = -1$, (from eq^n 1),

The above condition can be written as

$$\left(\frac{\partial \ln \Omega_1(E_1)}{\partial E_1}\right)_{E=\bar{E}_1} = \left(\frac{\partial \ln \Omega_2(E_2)}{\partial E_2}\right)_{E_2=\bar{E}_2}$$

Thus, our condition for equilibrium reduces to the equality of parameters β_1 and β_2 of the subsystems A_1 and A_2, respectively, where β is defined as

$$\beta \equiv \left(\frac{\partial \ln \Omega(N,V,E)}{\partial E}\right)_{N,V,E=\bar{E}} \rightarrow (3)$$

We thus find that when two physical systems are brought into thermal contact, which allows an exchange of energy between them, this exchange continuous until the equilibrium value of $\bar{E}_1$ and $\bar{E}_2$ of variables E_1 and E_2 are reached.

$\downarrow$

Once equilibrium is reached, now there is no exchange of energy

$\downarrow$

thermal equilibrium.

$$\beta_1 = \beta_2$$

It is then natural to expect that the parameter β is somehow related to the thermodynamic temperature T of a given system.

$ds = \frac{\partial S}{\partial E} dE$

$dQ = T ds$

$\left(\frac{\partial S}{\partial E}\right) = \frac{1}{T}$

We know thermodynamic formula

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T} \quad \rightarrow (4) \quad S \rightarrow \text{Entropy}$$

From (3) & (4)

$$\frac{\partial S}{\partial (\ln \Omega)} = \frac{1}{\beta T} = \text{Const}(k) \rightarrow (5)$$

$\partial E = \frac{\partial \ln \Omega}{\beta}$

from (5) & (6)

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

$\downarrow$ 0th law (thermal eqm.)

$$\boxed{S = k \ln \Omega} \rightarrow (6) \leftarrow \text{Given by Plank}$$

$\rightarrow$ Third law of thermodynamic

$S \downarrow$ ~~Thermal~~ Thermodynamical quantity (entropy)

$\Omega \downarrow$ Statistical quantity (microstates)

$k \rightarrow$ Boltzmann Const.

Thermodynamic Probability $\downarrow$ $\Omega = \frac{LN}{Ln_1 Ln_2 Ln_3}$

If entropy is zero

$\ln \Omega = 0$

$\Omega = 1$ (one microstate is accessible)

$\downarrow$

"unique configuration"

$\downarrow$

Statistical approach that provides a theoretical basis for the third law of thermodynamics

Eq^n (6), is of fundamental importance in physics; it provides a bridge between the microscopic and macroscopic.

"How disorder (S) arises microscopically" — eq^n (6) tells us

From eq^n (5) and (6) $\boxed{\beta = \frac{1}{kT}}$

$k \rightarrow$ Boltzmann Const

$k \rightarrow R/N$ (R → gas, N → Av. No.)

$R = k N_A$