

Chapter 5

Introduction to Statistical Mechanics

Thermodynamics limit :

If $N \rightarrow \infty$ $V \rightarrow \infty$

Particle density $n = \frac{N}{V}$ is fixed at a preassigned value.

Extensive property : In the thermodynamic limit the properties that become directly proportional to the size of the system (or proportional to the extensive parameters A, N, V, S, E) i.e $N \rightarrow \alpha N$, $V \rightarrow \alpha V$ $S \rightarrow \alpha S$ then such properties are called extensive properties. They have an additive nature.

Intensive property: In the thermodynamic limit the properties that become independent of the size of the system.

Example: T, P, μ (chemical potential)

Accessible microstate : The microstate which are permitted under the constraints imposed upon the system are called accessible microstate.

Thermodynamic Probability : For a given macrostate the total number of microstate is called thermodynamic Probability of that microstate.

$$S = k_B \log \omega \quad \text{or} \quad S = k_B \log \Omega$$

where ω or $\Omega \rightarrow$ Total no. of microstate for a given macrostate
(thermodynamic Probability)

Fundamental Postulate of statistical mechanics :

(equal a priori probability) :

For a system in equilibrium all accessible microstate corresponding to a given macrostate are equally probable i.e. probability of finding the system in all microstate for a given macrostate are equal

$$S = k_B \log \Omega \rightarrow \text{Boltzman entropy probability relation}$$

This eqn. shows the relation between macroscopic & microscopic properties or relation between thermodynamics and statistical mechanics

Random Walk: Let n_1 denote the number of steps to the right and n_2 the corresponding number of steps to the left.

Total number of steps $N = n_1 + n_2$

Net displacement $m = n_1 - n_2 = n_1 - (N - n_1) = 2n_1 - N$ (towards right)

If P = Probability that the step is to the right, $q = 1 - p$ = Probability that step is to the left.

Probability $W_N(n_1)$ of taking (in a total of N steps) n_1 steps to the right and n_2 steps to the left is given

$$\text{by } W_N(n_1) = \frac{N!}{n_1! n_2!} p^{n_1} q^{n_2} .$$

Mean Free Path: Mean free path λ is the average distance traversed by molecule between collisions. Mean free path of a molecule is related to its size, larger its size, shorter its mean free path.

$$\lambda = \frac{1}{\sqrt{2} \pi N d^2}$$

where d = diameter of the gas molecule, N = Number of molecules per unit volume.

Q. 54. A system of N particles has only two allowed state A and B. The probability for A is P and for B is $1 - P$? What is the probability for the system to be in macrostate defined by the distribution of $(r, N - r)$?

Ans. The probability of finding r particle in state A = P^r
 The probability of finding $N - r$ particle in state B = $(1 - P)^{N-r}$

The Total no. of ways in which r particle can be choosen from $N -$ particle is ${}^N C_r = \frac{N!}{r!(N-r)!}$

The probability in which r particle are in state A and $N - r$ particle in state B is = $\frac{N!}{r!(N-r)!} P^r (1 - P)^{N-r}$

Q. 55. A one dimensional random walker takes step to left or right with equal probability. The probability that the random walker starting from origin is back to origin after N even number of step, is

(i) $\frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!} \left(\frac{1}{2}\right)^N$ (ii) $\frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!}$ (iii) $2N! \left(\frac{1}{2}\right)^{2N}$ (iv) $N! \left(\frac{1}{2}\right)^N$

Ans. Probability $P = \frac{N!}{r!(N-r)!} P^r (1 - P)^{N-r}$

$$= \frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!} \left(\frac{1}{2}\right)^{\frac{N}{2}} \left(1 - \frac{1}{2}\right)^{N - \frac{N}{2}} = \frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!} \left(\frac{1}{2}\right)^N$$

(i) is correct

Q. 56. Calculate the no. of microstates for a configuration of a system of N distinguishable particles in which there are n_1 particles in a particle state 1 & n_2 particle in state 2, n_3 particle..... n_i particle in the i th state.

Ans. Total No. of particle = N

No. of microstate for state -1 = ${}^N C_{n_1}$

No. of microstate for state -2 = ${}^{N - n_1} C_{n_2}$

No. of microstate for state i^{th} = ${}^{N - n_1 - n_2 - \dots - n_{i-1}} C_{n_i}$

So total number of microstate is

$${}^N C_{n_1} \times {}^{N - n_1} C_{n_2} \times {}^{N - n_1 - n_2} C_{n_3} \times \dots \times {}^{N - n_1 - n_2 - n_3 - \dots - n_{i-1}} C_{n_i}$$

$$= \frac{N!}{n_1!(N - n_1)!} \times \frac{(N - n_1)!}{n_2!(N - n_1 - n_2)!} \times \dots \times \frac{(N - n_1 - n_2 - \dots - n_{i-1})!}{n_i!(N - n_1 - n_2 - \dots - n_i)!}$$

$$= \frac{N!}{n_i!(N - n_1 - n_2 - \dots - n_i)!} \quad \text{-- For distinguishable particle}$$

$$= \frac{1}{n_i!(N - n_1 - n_2 - \dots - n_i)!} \rightarrow \text{For indistinguishable particle}$$

Q. 57. Four distinguishable coins are tossed a large no. of time write down the different microstate which may be observed & the macrostate into which they would fall. Give the probability of the most probable macrostate.

| Macrostate | Microstate coins having head up | Microstate coins having tail up | No. of microstate | Pr obability |
|--------------------|----------------------------------|----------------------------------|-------------------|----------------|
| $n_1 = 4, n_2 = 0$ | a b c d | – | 1 | $\frac{1}{16}$ |
| $n_1 = 3, n_2 = 1$ | abc bcd cda dab | d a b c | 4 | $\frac{4}{16}$ |
| $n_1 = 2, n_2 = 3$ | ab ac ad bc bd cd | cd bd bc ad ac ab | 6 | $\frac{6}{16}$ |
| $n_1 = 1, n_2 = 3$ | a b c d | bcd acd abd abc | 4 | $\frac{4}{16}$ |
| $n_1 = 0, n_2 = 1$ | – | abcd | 1 | $\frac{1}{16}$ |

Total no. of microstate = 16

The probability of most probable state = $\frac{6}{16}$

Q. 58. An isolated system consist of two non-interacting Spin $-\frac{1}{2}$ particles a & b fixed in space & kept in magnetic field B. Find out the total no. of microstates allowed to the system.

| System state or macrostate | Particle state or Microstate | Magnetic moment | energy | no. of microstate |
|----------------------------|------------------------------|-----------------|---------------|-------------------|
| 1 | U U | $2\mu_0$ | $-2\mu_0B$ | 1 |
| 2 | U D D U | 0 0 | 0 0 | }2 |
| 3 | D D | $-2\mu_0$ | $+ - 2\mu_0B$ | 1 |

Total no. of microstate = 4 for Spin $-\frac{1}{2}$ two particle system no. of accessible microstate corresponding to energy

E = 0 is 2.



The no. of microstate for N no. of Spin S particle

$$(2S + 1)^N$$

The probability of getting a macrostate in which there are r particle out of N Spin 1/2 particle in spin up state

$$N_{C_r} \times \frac{1}{2^N}$$

CONTACT BETWEEN STATISTICS & THERMODYNAMICS

Now we consider two physical systems A₁ and A₂ which are separately in equilibrium. Let the macrostate of E₁ be

| | |
|--|--|
| A ₁ | A ₂ |
| N ₁ , V ₁ , E ₁ | N ₂ , V ₂ , E ₂ |

represented by parameter N₁, V₁, E₁ so that it has possible microstate Ω₁(N₁, V₁, E₁)

Similarly system A₂ by " " " " N₂, V₂, E₂ " " " " Ω₂(N₂, V₂, E₂)

Now bring the two system into contact with each other through a wall (conducting, rigid & impenetrable) such that N₁, N₂ and V₁, V₂ remain fixed but energies E₁ and E₂ become variable such that

$$E_1 + E_2 = E^{(0)} = \text{constant.}$$

The no. of microstate at any time t of the composite system is represented by

$$\Omega(E_1, E_2) = \Omega_1(E_1) \Omega_2(E_2) = \Omega_1(E_1) \Omega_2(E^0 - E_1) = \Omega(E^0, E_1)$$

The microstate of composite system is also represented by

$$\begin{aligned} \Omega^0(E_1, E_2) &= \Omega_1(E_1) \Omega_2(E_2) \\ &= \Omega_1(E^0 - E_2) \Omega_2(\bar{E}_2) \end{aligned}$$

For maximum Number of microstate $\frac{d\Omega}{dE_1} = 0$ $\left\{ \begin{array}{l} \frac{d\Omega}{dE_1} = \Omega_2 \frac{\partial \Omega_1}{\partial E_1} + \Omega_1 \frac{\partial \Omega_2}{\partial E_2} \frac{\partial E_2}{\partial E_1} \\ 0 = \Omega_2 \frac{d\Omega_1}{dE_1} - \Omega_1 \frac{d\Omega_2}{dE_2} \end{array} \right. \left\{ \begin{array}{l} \therefore E_2 = E^0 - E_1 \\ \therefore \frac{dE_2}{dE_1} = -1 \end{array} \right.$

$$\frac{1}{\Omega_1} \left(\frac{\partial \Omega_1}{\partial E_1} \right)_{N_1, V_1, E_1 = \bar{E}_1} = \frac{1}{\Omega_2} \left(\frac{\partial \Omega_2}{\partial E_2} \right)_{N_2, V_2, E_2 = \bar{E}_2} \quad (\because \text{at equilibrium } E_1 \text{ and } E_2 \rightarrow \bar{E})$$

Let $\beta = \left(\frac{\partial \ln \Omega}{\partial E} \right)_{N_1, V_1, E_1 = \bar{E}_1}$

Under equilibrium β₁ = β₂

$$\frac{1}{k_B} \left(\frac{\partial S}{\partial E} \right)_{N, V} = \frac{1}{k_B T} \quad \text{so} \quad \frac{1}{k_B T_1} = \frac{1}{k_B T_2} \Rightarrow \boxed{T_1 = T_2} \quad \dots (1)$$

This is the condition for thermal equilibrium

If the wall is movable and conducting

$$\eta = \frac{1}{k_B} \left(\frac{\partial S}{\partial V} \right) = \frac{1}{k_B} \left(\frac{P}{T} \right)$$

under equilibrium $\eta_1 = \eta_2 \Rightarrow \frac{P_1}{k_B T_1} = \frac{P_2}{k_B T_2}$

for conducting medium $T_1 = T_2 \Rightarrow \boxed{P_1 = P_2}$... (2)

Eqn (2) is the condition for mechanical equilibrium and thermal equilibrium.

If the wall is conducting, non-rigid, movable and penetrable

$$V_1 + V_2 = V^0 \quad E_1 + E_2 = E^0, \quad N_1 + N_2 = N^0 \text{ (fixed)}$$

$$\beta_1 = \beta_2 \quad \Rightarrow \quad T_1 = T_2$$

$$\eta_1 = \eta_2 \quad \Rightarrow \quad P_1 = P_2$$

Now, let $\xi = \left(\frac{\partial}{\partial N} \ln \Omega \right)_{E,V}$

$$\frac{1}{k_B} \left(\frac{\partial S}{\partial N} \right)_{E_1} = - \frac{\mu}{k_B T}$$

$$\xi_1 = \xi_2 \quad \Rightarrow \quad \boxed{\mu_1 = \mu_2} \quad \dots (3)$$

$\mu_1 = \mu_2 \rightarrow$ system is in chemical equilibrium

If $T_1 = T_2$, $P_1 = P_2$ and $\mu_1 = \mu_2$ then system is thermodynamic equilibrium.

Classical ideal gas : Now we discuss the thermodynamical properties of a classical ideal gas composed of N monoatomic (non-interacting) molecule, by statistical method the total no. of ways in which the N - particle can be distributed in the system will be simply equal to the product of the no. of ways in which the individual particles can be distributed in the same space independently of one another volume of phase space

$$d\tau = \int d^3x d^3P = \int dx dy dz \int d^3P = V \times \frac{4}{3} \pi P^3 \quad (6D \text{ phase space } \because 3D \text{ position and } 3D \text{ momentum})$$

Volume of each phase cell = h^3 (\because particle have 3 degree of freedom)

$$\Omega = \text{No of microstate} = \frac{\text{Volume of phase space}}{\text{Volume of phase cell}} = \frac{V}{h^3} \frac{4}{3} \pi P^3$$

$$\text{So } \Omega = \frac{V}{h^3} \frac{\pi P^3}{\frac{3}{4}} = \frac{V}{h^3} \frac{\sqrt{\pi} \pi P^3}{\frac{3}{2}!} \quad \left| \quad \sqrt{\frac{5}{2}} = \frac{3}{2}! = \frac{3}{2} \times \frac{1}{2} \sqrt{\pi} \right.$$

$$\Omega = \frac{V}{h^3} \frac{(2\pi ME)^{3/2}}{\left(\frac{3}{2}\right)!}$$

No. of microstate composed of N identical particle

$$\Omega(E) = \left(\frac{V}{h^3} \right)^N \left[\frac{(2\pi ME)^{3N/2}}{\left(\frac{3N}{2}\right)!} \right] \rightarrow \text{for sharp energy}$$

If the energy lies between E and $E + dE$ number of microstate

$$\Omega(E + \Delta E) = \Omega(E) + \frac{\partial \Omega}{\partial E} \Delta E \text{ higher terms neglected}$$

$$= \left(\frac{V}{h^3}\right)^N \frac{(2\pi ME)^{3N/2}}{\left(\frac{3N}{2}\right)!} \frac{3N}{2} E^{\frac{3N}{2}-1} dE$$

Now entropy $S = k_B \log \Omega = k_B \left[\ln \left(\frac{V}{h^3}\right)^N \frac{(2\pi ME)^{3N/2}}{\left(\frac{3N}{2}\right)!} \right]$

$$S = k_B \left[\ln \left(\frac{V}{h^3}\right)^N (2\pi ME)^{3N/2} - \ln \left(\frac{3N}{2}\right)! \right]$$

$$= k_B \left[\ln \left(\frac{V}{h^3}\right)^N (2\pi ME)^{3N/2} - \left\{ \frac{3N}{2} \ln \frac{3N}{2} - \frac{3N}{2} \right\} \right]$$

(log n! = n log n - n) = Stirling relation

$$S = k_B \left[\ln \left(\frac{V}{h^3}\right)^N (2\pi ME)^{3N/2} - \frac{3N}{2} \ln \frac{3N}{2} + \frac{3N}{2} \right] = k_B \left[\ln \left(\frac{V}{h^3}\right)^N (2\pi ME)^{3N/2} - \ln \left(\frac{3N}{2}\right)^{3N/2} + \frac{3N}{2} \right]$$

$$= k_B \left[\ln \left[\left(\frac{V}{h^3}\right)^N \left(\frac{(2\pi ME)^{3N/2}}{\left(\frac{3N}{2}\right)^{3N/2}}\right) \right] + \frac{3N}{2} \right]$$

$$S = N k_B \ln \left(\frac{V}{h^3}\right) \left(\frac{(4\pi ME)}{3N}\right)^{3/2} + \frac{3}{2} N k_B \dots (1)$$

Equation (1) can also be written as

$$S = N k_B \ln \frac{V}{h^3} + N k_B \ln \left(\frac{4\pi ME}{3N}\right)^{3/2} + \frac{3}{2} N k_B$$

$$N k_B \ln \frac{V}{h^3} + \frac{3}{2} N k_B [1 + \ln (2\pi M k_B T)] \quad \left(\because E = \frac{3}{2} N k_B T \right)$$

$$N k_B \ln V - N k_B \ln (h^2)^{3/2} + \frac{3}{2} N k_B [1 + \ln (2\pi M k_B T)]$$

$$N k_B \ln V - \frac{3}{2} N k_B \ln h^2 + \frac{3}{2} N k_B [1 + \ln (2\pi M k_B T)]$$

$$S = N k_B \ln V + \frac{3}{2} N k_B \left[1 + \ln \frac{2\pi M k_B T}{h^2} \right] \dots (2)$$

From equation (1)

$$E(N, V, S) = \frac{3h^2 N}{4\pi m V^{2/3}} \exp \left[\frac{2S}{3Nk_B} - 1 \right]$$

$$dQ = TdS = dU + PdV - \mu dN \quad (U = E = \text{internal energy} \because P.E = 0)$$

$$T = \left(\frac{\partial E}{\partial S} \right)_{N, V} = \frac{3h^2 N}{4\pi m V^{2/3}} \exp \left[\frac{2S}{3Nk_B} - 1 \right] \frac{2}{3Nk_B}$$

$$T = E \times \frac{2}{3Nk_B}$$

$$E = \frac{3}{2} Nk_B T = \frac{3}{2} RT$$

Internal energy of an classical ideal gas $U = \frac{3}{2} k_B T$ specific heat

$$\text{Specification } C_V = \left(\frac{\partial Q}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{3}{2} Nk_B$$

$$\text{Pressure: } TdS = dE + PdV - \mu dN$$

$$P = - \left(\frac{\partial E}{\partial V} \right)_{N, S} = \frac{2}{3} \frac{E}{V} \quad \text{So } \boxed{PV = \frac{2}{3} E}$$

$$PV = \frac{2}{3} \times \frac{3}{2} Nk_B T = Nk_B T \quad \boxed{PV = Nk_B T = RT} \rightarrow (\text{Ideal gas equation})$$

$$C_P = \left(\frac{\partial E + PdV}{\partial T} \right)_P = \left(\frac{\partial E + PdV + VdP}{\partial T} \right)_P \quad [\because P = \text{constant } dP = 0 \text{ so we can add}]$$

$\therefore dP = 0$

$$C_P = \left[\frac{\partial}{\partial T} (E + PV) \right]_P = \left(\frac{\partial H}{\partial T} \right)_P \quad \boxed{C_P = \left(\frac{\partial H}{\partial T} \right)_P}$$

$$C_P = \left[\frac{\partial}{\partial T} \left(\frac{3}{2} Nk_B T + Nk_B T \right) \right]_P = \frac{\partial}{\partial T} \frac{5}{2} Nk_B T = \frac{5}{2} Nk_B \quad \left[\begin{array}{l} \because E = \frac{3}{2} Nk_B T \\ PV = Nk_B T \text{ from} \end{array} \right]$$

$$C_P = \frac{5}{2} Nk_B$$

$$\text{Now, } \gamma = \frac{C_P}{C_V} = \frac{\frac{5}{2} Nk_B}{\frac{3}{2} Nk_B} = \frac{5}{3} \Rightarrow \boxed{\gamma = \frac{5}{3}}$$

For adiabatic process $PV^\gamma = \text{constant}$

$$\boxed{PV^{5/3} = \text{const}}$$

$$\boxed{TV^{\gamma-1} = TV^{2/3} = \text{const}}$$

$$P = \frac{2}{3} \frac{E}{V} \quad \frac{E}{V} = \text{energy density} \quad dQ = dE + PdV$$

For adiabatic process $dQ = 0$

$$0 = dE + PdV = d\left(\frac{3}{2}PV\right) + PdV, \quad 0 = \frac{3}{2}PdV + \frac{3}{2}VdP + PdV$$

$$-\frac{3}{2}VdP = \frac{5}{2}PdV, \quad \frac{dP}{P} = -\frac{5}{3} \frac{dV}{V}$$

Integrating both side

$$\ln P = -\frac{5}{3} \ln V + c = -\ln V^{5/3} + c$$

$$\ln P + \ln V^{5/3} = c, \quad \ln PV^{5/3} = c$$

$$PV^{5/3} = \text{constant}$$

$$(dE)_{\text{adiabatic}} = -PdV \quad (\because dQ = 0)$$

$$= -\frac{2}{3} \frac{E}{V} dV \quad S = Nk_B \ln \left[\frac{V}{h^3} \left(\frac{4\pi ME}{3N} \right)^{3/2} \right] + \frac{3}{2} Nk_B$$

Replace $N = \alpha N$, $V = \alpha V$ and $E = \alpha E$ and if $S = \alpha S$

Then S is an extensive property

$$= (\alpha N) k_B \ln \left[\frac{\alpha V}{h^3} \left(\frac{4\pi M \alpha E}{3N k_B} \right)^{3/2} \right] + \frac{3}{2} N \alpha k_B \neq \alpha S$$

Since entropy doesn't satisfy the extensive property

(additive). So we have to modify

Entropy of mixing : The entropy of mixing is defined as

$$\Delta S = S_T - \sum_{i=1}^N S_i, \quad S_T = \text{Entropy after mixing}, \quad S_i = \text{Entropy before mixing of individual system}$$

The entropy of an ideal gas given by

$$S = Nk_B \ln V + \frac{3}{2} Nk_B \left[1 + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right]$$

Entropy is not an extensive quantity of the system i.e if we increase the extensive parameter by a factor α , keeping the intensive variable unchanged then the entropy of the system which should also increase by same factor α doesn't increase. The entropy of an ideal gas is not extensive due to the term $\ln V$. This means that entropy of the system is different from the sum of the entropies of its parts. This is called **Gibbs paradox**. Gibbs visualised the mixing of two ideal gas (1) and (2) both being initially at the same temperature T . The temperature remain same after mixing and before mixing

$$\begin{aligned} & \sum_{i=1}^2 N_i k_B \ln V_i + \frac{3}{2} N_i k_B \left[1 + \ln \left(\frac{2\pi m_i k_B T}{h^2} \right) \right] \\ &= N_1 k_B \ln V_1 + \frac{3}{2} N_1 k_B \left[1 + \ln \left(\frac{2\pi m_1 k_B T}{h^2} \right) \right] + N_2 k_B \ln V_2 + \frac{3}{2} N_2 k_B \left[1 + \ln \left(\frac{2\pi m_2 k_B T}{h^2} \right) \right] \end{aligned}$$

Entropy after mixing $\rightarrow N = N_1 + N_2$ $V = V_1 + V_2$

$$S_T = (N_1 + N_2) k_B \ln (V_1 + V_2) + \frac{3}{2} (N_1 + N_2) k_B \left[1 + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right]$$

Here $m_1 = m_2 = m$

Entropy of mixing

$$\Delta S = S_T - \sum_{i=1}^2 S_i = (N_1 + N_2) k_B \ln (V_1 + V_2) + \frac{3}{2} (N_1 + N_2) k_B \left[1 + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right]$$

$$- N_1 k_B \ln V_1 - \frac{3}{2} N_1 k_B \left[1 + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right] - N_2 k_B \ln V_2 - \frac{3}{2} N_2 k_B \left[1 + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right]$$

$$= (N_1 + N_2) k_B \ln (V_1 + V_2) - N_1 k_B \ln V_1 - N_2 k_B \ln V_2$$

$$= \left[N_1 k_B \ln (V_1 + V_2) - N_1 k_B \ln V_1 \right] + \left[N_2 k_B \ln (V_1 + V_2) - N_2 k_B \ln V_2 \right]$$

$$\Delta S = N_1 k_B \ln \frac{V_1 + V_2}{V_1} + N_2 k_B \ln \frac{V_1 + V_2}{V_2}$$

Since $\frac{V_1 + V_2}{V_1} > 1$ or $\frac{V_1 + V_2}{V_2} > 1$

So $\Delta S > 0$

If, initial density = density of mixture i.e. $\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N_1 + N_2}{V_1 + V_2}$

$$\Delta S = k_B \left[N_1 \ln \frac{N_1 + N_2}{N_1} + N_2 \ln \frac{N_1 + N_2}{N_2} \right]$$

$\Delta S = > 0$

If we consider the mixing of two same gas with a common initial temperature T and a common initial particle density n (reversible process) we get

$$\Delta S = > 0$$

But for reversible process $\Delta S = > 0$

Thus once again we are led to believe that there is something basically wrong with that expression. To avoid the paradoxical situation Gibbs diminished entropy (S) by an another term $k_B \ln N!$, S_1 by $k_B \ln N_1!$ and S_2 by $k_B \ln N_2!$

$$S = N k_B \ln V + \frac{3}{2} N k_B \left[1 + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right] - k_B \ln N!$$

$$= N k_B \ln V + \frac{3}{2} N k_B \left[1 + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right] - N k_B \ln N + N k_B$$

$$S = N k_B \ln \frac{V}{N} + \frac{3}{2} N k_B \left[\frac{5}{2} + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right] \rightarrow \text{Sackur Tetrode eqn.}$$

By replacing E by αE , V by αV and N by αN we get αS instead of S . So, S is an extensity property

Chemical Potential :

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{V,S} = E \left[\frac{S}{3N} - \frac{2S}{3N^2 k_B} \right] = k_B T \ln \left(\frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} \right)$$

Gibb's free energy :

$$G = \mu N = N k_B T \ln \left[\frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} \right] \quad G = E + PV - TS, \quad A = E - TS = G - PV$$

Helmholtz free energy :

$$\text{So } A = N k_B T \left[\ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} \right\} - 1 \right]$$

A is an extensive property while μ is an intensive property of the system.

Q. 59. We have equal amount of two identical ideal gases at the same temperature T but at different pressure P_1 and P_2 in two containers of volume V_1 and V_2 respectively. The containers are connected. Find the change in entropy (The temperature after mixing also remains same)

Ans.

$$S = N k_B \ln \left(\frac{V}{N} \right) + \frac{3}{2} N k_B \left[\frac{5}{3} + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right]$$

$$\sum_{i=1}^2 S_i = N_1 k_B \ln \frac{V_1}{N} + \frac{3}{2} N_1 k_B \left[\frac{5}{3} + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right]$$

$$= N k_B \ln \frac{V_1}{N} + \frac{3}{2} N k_B \left[\frac{5}{3} + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right] +$$

$$= N k_B \ln \frac{V_2}{N} + \frac{3}{2} N k_B \left[\frac{5}{3} + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right]$$

$$\left\{ \begin{array}{l} P_1 V_1 = N k_B T \Rightarrow \frac{V_1}{N} = \frac{k_B T}{P_1} \\ P_2 V_2 = N k_B T \Rightarrow \frac{V_2}{N} = \frac{k_B T}{P_2} \end{array} \right.$$

$$\sum_{i=1}^2 S_i = N k_B \ln \frac{k_B T}{P_1} + \frac{3}{2} N k_B \left[\frac{5}{3} + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right] +$$

$$N k_B \ln \frac{k_B T}{P_2} + \frac{3}{2} N k_B \left[\frac{5}{3} + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right]$$

Total entropy :

$$S_T = 2N k_B \ln \frac{V_1 + V_2}{2N} + \frac{3}{2} \times 2N k_B \left[\frac{5}{3} + \ln \left(\frac{2\pi m k_B T}{h^2} \right) \right]$$

Change in entropy

$$\Delta S = S_T - \sum_{i=1}^2 S_i = 2N k_B \ln \frac{V_1 + V_2}{2N} - N k_B \ln \frac{k_B T}{P_1} - N k_B \ln \frac{k_B T}{P_2}$$

Let after mixing pressure = P and after mixing total No of particle = N + N = 2N

$$P(V_1 + V_2) = 2N k_B T$$

$$P(V_1 + V_2) = 2N k_B T$$

$$\frac{(V_1 + V_2)}{2N} = \frac{k_B T}{P}$$

$$\Delta S = 2Nk_B \ln \frac{k_B T}{P} - Nk_B \ln \frac{k_B T}{P_1} - Nk_B \ln \frac{k_B T}{P_2}$$

$$= Nk_B \ln \left(\frac{k_B T}{P} \right)^2 - Nk_B \ln \frac{k_B T}{P_1} - Nk_B \ln \frac{k_B T}{P_2}$$

$$= Nk_B \ln \frac{\left(\frac{k_B T}{P} \right)^2}{\left(\frac{k_B T}{P_1} \right) \left(\frac{k_B T}{P_2} \right)}$$

$$= Nk_B \ln \left[\frac{(k_B T)^2 (P_1 + P_2)^2}{(2 P_1 P_2)^2} \times \frac{P_1 P_2}{(k_B T)^2} \right]$$

$$\Delta S = Nk_B \ln \frac{(P_1 + P_2)^2}{4 P_1 P_2}$$

$$\Delta S = Nk_B \ln \frac{(P_1 + P_2)^2}{4 P_1 P_2}$$

Here we get $\Delta S > 0$

(We are considering identical particle. So it is a reversible case only when the particle density is same otherwise for identical gas also we will get $\Delta S > 0$).

PHASE SPACE

Phase Space:

$$\begin{aligned} d\tau &= dx \, dy \, dz \, dP_x \, dP_y \, dP_z \\ &= dx \, dP_x \, dy \, dP_y \, dz \, dP_z = h \cdot h \cdot h = h^3 \end{aligned}$$

Volume of phase cell = $h^{3N} = h^f$

Dimension of phase space = $2f$ (f degree of freedom). If f is the degree of freedom of a single particle and N is the total no. of particle, then dimension of phase space is = $2Nf$

$$\text{No. of microstate in phase space} = \frac{\text{Total Volume of Phase Space allowed to the system}}{\text{Volume of phase Cell } (h^3)}$$

Q. 60. Calculate the number of microstate for a free particle in 3-dimension that have momentum p .

Ans. $d\tau = dx \, dy \, dz \, dp_x \, dp_y \, dp_z$

$$\text{Allowed Phase Space Volume} = \int d\tau = \int dx \, dy \, dz \int dp_x \, dp_y \, dp_z$$

$$= V \int p^2 \, dp \int_0^\pi \sin \theta \, d\theta \int_0^{2\pi} d\phi = V \frac{4}{3} \pi p^3$$

$$\text{No. of microstate} = \frac{V}{h^3} \times \frac{4}{3} \pi p^3$$

Note : for 2. dimension.

$$\int dx = \int dx \int dy \int dp_x \int dp_x$$

$$= \int d^2q \cdot d^2p = A \cdot \pi p^2 \quad \{\text{where } A = \text{area}\}$$

Since wave polarize in 2 dimension

$$\int dr = 2A\pi p^2$$

If momentum lies between p and $p + dp$

$$\therefore \text{No. of microstate} = \frac{2A}{h^2} 2\pi p dp = \frac{4A\pi}{h^2} p dp$$

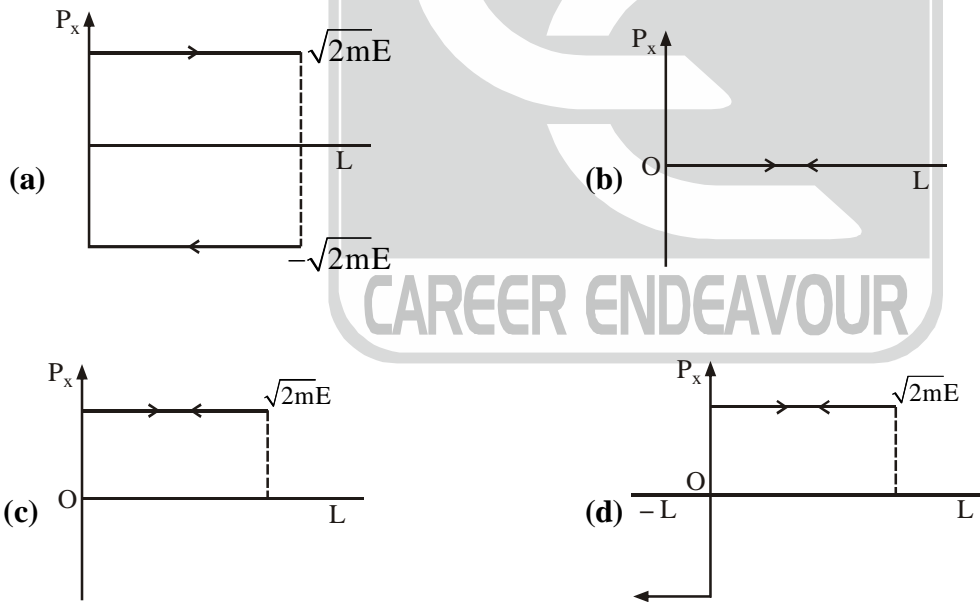
If momentum lies between p and $p + dp$ then no. of microstate = $\frac{V}{h^3} 4\pi p^2 dp$

$$\text{Density of state} = \frac{\text{no. of state}}{\text{Volume}} \quad \text{or} \quad \frac{\text{no. of state}}{\text{energy interval}}$$

PHASE – SPACE DIAGRAM

Problems that appeared in GATE from this section :

G-1. The phase diagram of a free particle of mass M and K.E, E moving in one-dimensional box with perfectly elastic walls at $x = 0$ and $x = L$ is given by [GATE-2006]



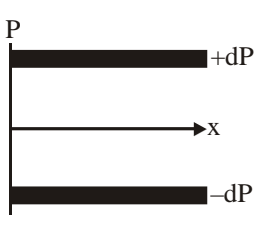
Soln. For free particle momentum P_x is doubly degenerate. For each energy E

$$\frac{P^2}{2M} = E \Rightarrow P = \pm \sqrt{2mE}$$

Which is independent of x but x can only be +ve between 0 to L .

Hence correct option is (a).

- If there would be some range for E from E to $E + dE$ instead of sharp values.

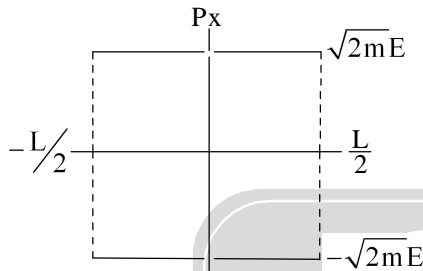


$$E = \frac{P^2}{2m} \Rightarrow P^2 = 2mE \Rightarrow P = \sqrt{2mE}$$

$$dP = \frac{1}{2\sqrt{2mE}} 2m dE$$

$$dP = \frac{m dE}{\sqrt{2mE}}$$

- If the origin of phase space is the origin of box



For the above problem we now calculate the no. of phase cell or accessible microstate. If \bar{E} lies between E and $E + dE$

As it is 1 dimension case the area of phase cell in phase space is

$$\delta x \delta P_x = h$$

$$2L dP_x \rightarrow \text{this is area of region accessible to free space}$$

$$2L d(\sqrt{2mE}) = 2L \times \frac{1}{\sqrt{2mE}} 2m dE = \sqrt{2m} L \bar{E}^{-1/2} dE$$

Density of state $g(E) =$ number of states per unit energy range

$$= \frac{L(2M)^{1/2} \bar{E}^{-1/2}}{h}$$

G-2. The dimension of phase space of ten rigid diatomic molecules is:

- (a) 5 (b) 10 (c) 50 (d) 100

[GATE-2004]

Soln. A rigid diatomic molecule \Rightarrow degree of function = 5 so, each molecule will require total 5 coordinate variables and 5 momentum variables for their complete description (3-translational, 2-rotational). Hence, each molecule requires 10 phase space dimensions.

\therefore Total dimension of 10 such molecules in the phase space = $10 \times 10 = 100$.

Hence correct option is (d).

(5 degree of freedom for a rigid diatomic molecule can also be understood by the fact that there are 2 particles each with 3 degree of function but there is one constraint that being rigid, the distance between them is fixed, therefore, total degree of function = $3 + 3 - 1 = 5$).

PHASE SPACE DIAGRAM OF AN OSCILLATOR

Energy of a one dimensional harmonic oscillator whose position co-ordinate is x and momentum co-ordinate is P_x is given by

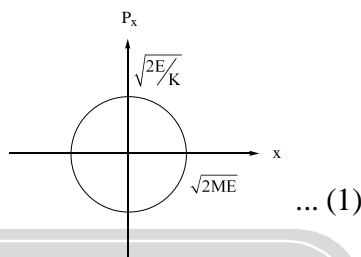
$$E = \frac{P_x^2}{2m} + \frac{1}{2} Kx^2 \quad K = m\omega^2 \quad \omega = \text{angular frequency}$$

Where the 1st term is the K.E and the 2nd term is P.E. What is the trajectory of oscillator in phase space?

Q. 61. Find the accessible region & the no. of accessible microstate of oscillator?

Ans. $E = \frac{P_x^2}{2m} + \frac{1}{2} Kx^2$ or $\frac{P_x^2}{2mE} + \frac{Kx^2}{2E} = 1$

$$\frac{P_x^2}{(\sqrt{2mE})^2} + \frac{x^2}{\left(\sqrt{\frac{2E}{K}}\right)^2} = 1$$



For constant energy E eqn.(1) describes an ellipse in phase space i.e. $x - p_x$ plane

The phase points are those lying on the elliptical path having a semimajor axis $\sqrt{2mE}$ and semiminor axis $\sqrt{\frac{2E}{K}}$

At any particular instant the phase space of the oscillator is represented by some point on the ellipse.

The area of the ellipse in phase space is πab where a is the semimajor axis and b is the semiminor axis.

$$A = \pi ab = \pi \sqrt{2mE} \sqrt{\frac{2E}{K}} = 2\pi E \sqrt{\frac{m}{K}} = \frac{2\pi E}{\omega}$$

It represents the phase space available to the oscillator having energy between 0 & E or this is the accessible region.

$$\begin{aligned} \text{Now the accessible no. of microstates} &= \frac{\text{Area of accessible region}}{\text{Area of a point in phase space (i.e.cell)}} \\ &= \frac{2\pi E}{\omega h} = \frac{E}{\omega \hbar} \end{aligned}$$

The phase space available to the oscillator having energy between E and $E + dE$ is

$$dA = 2\pi \sqrt{\frac{m}{K}} dE = \frac{2\pi}{\omega} dE$$

Q. 62. Calculate the number of microstates accessible to the photon having frequency between ν and $\nu + d\nu$ confined to a 3 dimensional cavity of volume V .

Ans. No. of microstate in frequency range 0 to ν

$$\Omega = \frac{V}{h^3} \frac{4}{3} \pi (2mE)^{3/2} \quad E = \frac{P^2}{2m} \Rightarrow P = \sqrt{2mE}$$

$$= \frac{V}{h^3} \frac{4}{3} \pi (P^2)^{3/2} \quad P = \frac{E}{C} = \frac{h\nu}{C}$$

$$\Omega = \frac{V}{h^3} \frac{4}{3} \pi P^3 = \frac{V}{h^3} \frac{4}{3} \pi \left(\frac{h\nu}{c} \right)^3 = \frac{4}{3} \frac{\pi V \nu^3}{c^3}$$

No. of microstates in the frequency range ν and $\nu + d\nu$ is

$$d\Omega = \frac{4}{3} \frac{\pi V}{c^3} 3\nu^2 d\nu = \frac{4\pi V}{c^3} \nu^2 d\nu$$

Density of state

$g(E)$ = no. of states per unit energy range

we have
$$\Omega = \frac{V}{h^3} \frac{4}{3} \pi (2mE)^{3/2}$$

$$\begin{aligned} d\Omega &= \frac{V}{h^3} \frac{4}{3} \cdot \frac{3}{2} \pi (2mE)^{1/2} 2m dE \\ &= \frac{V}{h^3} \cdot 2\pi (2m)^{3/2} E^{1/2} dE \end{aligned}$$

$$\left[E = \frac{P^2}{2m} \Rightarrow 2m = \frac{P^2}{E} = \frac{E^2}{c^2 E} = \frac{E}{c^2} \right]$$

$$= \frac{V}{h^3} 2\pi \left(\frac{E}{c^2} \right)^{3/2} E^{1/2} dE$$

$$= \frac{V}{h^3} \frac{2\pi}{c^3} E^2 dE$$

$$g(E) = \frac{d\Omega}{dE} = \frac{2\pi V E^2}{h^3 c^3}$$

