STATISTICAL MECHANICS

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BASICS

- $du = f(\mathrm{T}, \mathrm{S}, \mathrm{P}, \mathrm{V})$
- Helmholtz Free Energy
- Enthalpy
- Gibbs Potential

Prove that: $du = f(T, S, P, V)$

$dQ = du + Pdv$……….(1st law)

$dQ = Tds$ ……………(2nd law)

From above two equations we get,

$$du + Pdv = Tds$$

$$du = Tds - Pdv$$

$$du = f(T, S, P, V)$$

$\boldsymbol{Helmholtz\ Free\ Energy}$: $\boldsymbol{F = U - TS}$

Enthalpy: $\boldsymbol{H = U + PV}$

Gibbs Potential: $\boldsymbol{G = H - TS}$

Partition Function: $\boldsymbol{Z = \frac{V}{\hbar^3}(2m\pi kT)^{\frac{3}{2}}}$

PARTITION FUNCTION

An assembly of Molecules Obey Classical Statistics that is they obey Maxwell Boltzman Distribution law .

$$n_i = g_i \; e^{-\alpha} \; e^{-\epsilon_i \beta}$$

where n_i = Number of particles.
g_i = Number of states.
ϵ_i = Energy @ a state.

$$n_i = g_i \ e^{-\alpha} \ e^{-\epsilon i\beta} \qquad (1)$$

Let's put ; $e^{-\propto} = \mathrm{A}$

$$n_i = \mathrm{A} \ g_i \ e^{\frac{-\in i}{KT}} \qquad (2)$$

Where $\beta = \frac{1}{KT}$

Taking summation on both the sides…..

$$\sum_i n_i = \mathrm{A} \ \sum_i gi \ e^{\frac{-\in i}{KT}} \qquad (3)$$

$$\sum_i n_i = \mathrm{N}$$

$$\text{so, N} = \mathrm{A} \sum_i \boldsymbol{gi} \;\; \boldsymbol{e}^{\frac{\boldsymbol{-\in i}}{\boldsymbol{KT}}}$$

$$\frac{N}{A} = \sum_i \boldsymbol{gi} \;\; \boldsymbol{e}^{\frac{\boldsymbol{-\in i}}{\boldsymbol{KT}}}$$

$$\mathrm{Z} = \sum_i \boldsymbol{gi} \;\; \boldsymbol{e}^{\frac{\boldsymbol{-\in i}}{\boldsymbol{KT}}} \qquad (4)$$

where , Z is called "**Partition Function**"

$$\mathrm{Z} = \int_0^\infty g(E)dE \;\; \boldsymbol{e}^{\frac{\boldsymbol{-E}}{\boldsymbol{KT}}}$$

for a momentum we know;

$$g(p)\,dp = \frac{V4\pi p^2}{h^3}\,dp \ldots\ldots\ldots\ldots\ldots\ldots(5)$$

where g(p) is a density of state

Further , we know, for a free particle

$$E = \frac{p^2}{2m}$$

$$p^2 = 2mE \qquad \ldots\ldots\ldots\ldots\ldots\ldots(a)$$

$$p = \sqrt{2m}\ E^{\frac{1}{2}}$$

$$dp = \sqrt{2m}\,\frac{1}{2}\,E^{\frac{-1}{2}}\ dE \ \ldots\ldots\ldots\ldots.(b)$$

Let’s substitute equation (a) & (b) in equation (5)

$$g(E)\,dE = \frac{V4\pi(2mE)}{h^3}\frac{\sqrt{2m}}{2\sqrt{E}}\,dE$$

$$g(E)\,dE = \frac{V2\pi(2mE)}{h^3}\frac{\sqrt{2m}}{\sqrt{E}}\,dE$$

$$g(E)\,dE = \frac{V2\pi\,(2m)^{\frac{3}{2}}\,E^{\frac{1}{2}}}{h^3}\,dE \qquad (6)$$

Now Let’s substitute this expression in equation (4)

$$\text{i.e } Z = \sum_i \boldsymbol{g(E)\,dE}\;\; \boldsymbol{e^{\frac{-\in i}{KT}}}$$

$$Z = \int_0^{\infty} g(E)dE \;\; \boldsymbol{e}^{\frac{-E}{KT}}$$

$$Z = \int_0^{\infty} \frac{V 2\pi\,(2m)^{\frac{3}{2}} \;\; E^{\frac{1}{2}}}{h^3} \; \boldsymbol{e}^{\frac{-E}{KT}} \;\; \mathrm{dE}$$

$$Z = \frac{V 2\pi\,(2m)^{\frac{3}{2}}}{h^3} \int_0^{\infty} E^{\frac{1}{2}} \;\; \boldsymbol{e}^{\frac{-E}{KT}} \;\; \mathrm{dE} \qquad (7)$$

Now solving this Integration in above eqn. we get

$$\int_0^{\infty} E^{\frac{1}{2}} \;\; \boldsymbol{e}^{\frac{-E}{KT}} \;\; \mathrm{dE} = \sqrt{\frac{\pi}{2}} \;\; (KT)^{\frac{3}{2}}$$

$$\boxed{Z = \frac{V}{h^3} \, (2\pi m KT)^{3/2}} \qquad (8)$$

Partition Function & Determination of other Parameters:

Now the entropy of the system

$$S = K \log \Omega_{max} \qquad (1)$$

for a classical system

$$\boldsymbol{\Omega} = N! \quad \frac{{g_i}^{n_i}}{n_i!}$$

Taking log on both the sides

$$\log \Omega = \log N! + \textstyle\sum_i (n_i \log g_i - \log n_i!)$$

Applying sterling approximation ($\log n_i$ = n log n – n)

$$\log \Omega = N \log N - N + \textstyle\sum_i n_i \log g_i - ni \log n_i + n_i$$

M.B.D for the most probable

$$n_i = g_i \; e^{-\alpha} \; e^{-\beta \in_i} \qquad (3)$$

but we know

$$N = \sum_i n_i \qquad (4)$$

$$\log \Omega = N \log N - N + \sum_i \left[n_i \log gi - n_i log(g_i \; e^{-\alpha} \; e^{-\beta \in_i}) + n_i \right]$$

$$= N \log N - N + \sum_i n_i \log g_i - \sum_i n_i \log g_i + \sum_i n_i \alpha + \sum_i n_i \beta \in_i + \sum_i n_i$$

$$= N \log N - \cancel{N} + \cancel{\sum_i n_i \log g_i} - \cancel{\sum_i n_i \log g_i} + \sum_i n_i \alpha + \sum_i n_i \beta \in_i + \cancel{\sum_i n_i}$$

$\log \Omega_{max}$ = N log N + αN + $\beta \sum_i n_i \in_i$ (5)

But E = $\sum_i n_i \in_i$

$\log \Omega_{max}$ = N log N + αN + β E (6)

let. A = $e^{-\alpha}$

taking log on both side

- log A = α (7)

put eqn. (7) in (6)

$\log \Omega_{max}$ = N log N - N log A + β E

$$= N \log \frac{N}{A} + \beta E$$

$$\log \Omega_{max} = N \log Z + \beta E \qquad (8)$$

$Z = \frac{N}{A}$ is exactly partition function

But $\beta = \frac{1}{KT}$

now equation (8) become

$$\log \Omega_{max} = N \log Z + \frac{E}{KT} \qquad (9)$$

let substitute this equation in (1)

$$S = K \log \Omega_{max}$$

$$S = K \left(N \log Z + \frac{E}{KT} \right)$$

$$S = K N \log Z + \frac{\cancel{K}E}{\cancel{K}T}$$

$$S = KN \log Z + \frac{E}{T}$$

for an ideal gas

$E = \frac{3}{2}$ NKT it is energy of three degree of freedom

$$\boxed{S = N K \log Z + \frac{3}{2} NK} \qquad (10)$$

This is the equation for the entropy of the assembly of Ideal gas molecules .

Other Thermodynamic Functions

- Helmholtz Free Energy , F

$$F = E - TS$$

$$F = E - T\left(NK \log Z + \frac{E}{T}\right)$$

$$F = E - NKT \log Z - T\frac{E}{T}$$

$$F = -NKT \log Z \longrightarrow \text{(a)}$$

- Total Energy E : If $\overline{\in}$ = Average Energy

$$\overline{\in} = \frac{E}{N} = \frac{\sum_i n_i \in_i}{\sum_i n_i}$$

$$= \frac{\sum_i g_i \; e^{-\alpha} \; e^{-\beta \in_{i \in_i}}}{\sum_i n_i}$$

$$\overline{\in} = \frac{\sum_i g_i \; \cancel{e^{-}}\alpha \;\; e^{\frac{-\in_i}{KT}} \in_i}{\sum_i g_i \; \cancel{e^{-}}\alpha \; e^{\frac{-\in_i}{KT}}}$$

$$\overline{\in} = \frac{\sum_i g_i \; e^{\frac{-\in_i}{KT}} \; \in_i}{Z} \qquad \text{(b)}$$

where

$$Z = \sum_i \; g_i \; e^{-\frac{\in_i}{KT}}$$

$$\left(\frac{\partial Z}{\partial T} \right)_V = \sum_i \; g_i \in_i \frac{1}{KT^2} \; e^{-\frac{\in_i}{KT}}$$

for Isothermal – Isochoric Transformation

$$\sum_i \; g_i \; e^{-\frac{\epsilon_i}{KT}} \epsilon_i = KT^2 \left(\frac{\partial Z}{\partial T} \right)_V$$

now put this eqn. in eqn. (b) therefore

$$\overline{\epsilon} = \frac{KT^2}{Z} \left(\frac{\partial Z}{\partial T} \right)_V$$

$$= KT^2 \left(\frac{\partial \log Z}{\partial T} \right)_V \qquad (c)$$

we know

$$\overline{\in} = \frac{E}{N}$$

$$E = N\,\overline{\in} \qquad \text{(d)}$$

now substitute (c) in (d)

$$E_{total} = NKT^2\left(\frac{\partial(logZ)}{\partial T}\right)_V \longrightarrow \text{(e)}$$

This is exp. for total Energy of an ensemble in term of partition function

- Enthalpy H :

$$H = E + PV$$

where $PV = RT$ for one mole

$$H = NKT^2 \left(\frac{dlogZ}{dT}\right)_V + RT \xrightarrow{\qquad} (f)$$

- Gibbs Potential G :

$$G = H - TS$$

$$G = NKT^2 \left(\frac{dlogZ}{dT}\right) v + RT - T\left(N\,K\log Z + \frac{3}{2}NK\right)$$

$$G = NKT^2 \left(\frac{dlogZ}{dT}\right) v + RT - N\,KT\log Z - \frac{3}{2}NKT$$

$$\xrightarrow{\qquad} (g)$$

- Pressure of the gas P:

$$P = -\left(\frac{\partial E}{\partial V}\right)_T = NKT\left(\frac{\partial(\log Z)}{\partial V}\right)_T \qquad \text{(h)}$$

HELMHOLTZ FREE ENERGY FOR AN IDEAL GAS

$$F = E - TS$$

As we know S= $Nk\log Z + \frac{E}{T}$

$$\therefore F = E - T\left[\boldsymbol{Nk\log Z + \frac{E}{T}}\right]$$

$\therefore$ $\mathbf{F = -NkT\log Z}$

…(**for free energy** in terms of partition **function eq'n**)

TOTAL ENERGY

$$\overline{E} = \frac{E}{N} = \frac{\sum_i n_i \in_i}{\sum_i n_i} \qquad (\overline{E} \ = mean\ Energy)$$

$$= \frac{\sum_i g_i e^{-\propto} e^{-\frac{\in_i}{kT}} \in_i}{\sum_i g_i e^{-\propto} e^{-\frac{\in_i}{kT}}} \ \ldots\ldots(\text{from } \ n_i = g_i e^{-\propto} e^{-\frac{\in_i}{kT}})$$

$$= \frac{\boldsymbol{e^{-\propto} \sum_i g_i e^{-\frac{\in_i}{kT}} \in_i}}{\boldsymbol{e^{-\propto} \sum_i g_i e^{-\frac{\in_i}{kT}}}}$$

$$\bar{E} = \frac{\sum_i \epsilon_i g_i e^{-\frac{\epsilon_i}{kT}}}{Z}$$ ....(since Z = $\sum_i g_i e^{\frac{\epsilon_i}{kT}}$)... (1)

Let us consider $\left(\frac{dZ}{dT}\right)_v$

$$\left(\frac{dZ}{dT}\right)_v = \sum_i g_i \frac{1}{kT^2} \epsilon_i\ e^{-\frac{\epsilon_i}{kT}}$$

$$\left(\frac{dZ}{dT}\right)_v = \frac{1}{kT^2} \sum_i g_i\ \epsilon_i\ e^{-\frac{\epsilon_i}{kT}}$$

$$\sum_i g_i\ \epsilon_i\ e^{-\frac{\epsilon_i}{kT}} = \mathrm{k}T^2 \left(\frac{dZ}{dT}\right)_v$$

Substituting the above expression in equation (1) we get

$$\bar{E} = \frac{kT^2}{Z} \left(\frac{dZ}{dT}\right)_v$$

$$\bar{E} = \mathrm{k}T^2 \left(\frac{d(logZ)}{dt}\right)_v$$

$$\text{E}= N\bar{E} = \text{Nk}T^2\left(\frac{d(logZ)}{dt}\right)_v \text{..............(2)}$$

Expression for total energy @ Partition Function

GIBBS POTENTIAL

$$H = E + PV$$

$H = E + RT$ …..(since PV =RT)

$$\therefore H = \text{Nk}T^2\left(\frac{d(logZ)}{dt}\right)_v + \text{RT} \quad \text{......(3)}$$

Enthalpy @ Partition Function

$$G = H - TS \;\ldots\ldots \text{(Gibbs potential)}$$

From $\mathrm{S = NklogZ} + \frac{3}{2}Nk$ and eq'n (3) we get,

$$G = \mathrm{Nk}T^2\left(\frac{d(logZ)}{dt}\right)_v + \mathrm{RT} - T\left(\mathrm{NklogZ} + \frac{3}{2}Nk\right)$$

Gibbs potential @ Partition Function

STATISTICAL MECHANICS CH II

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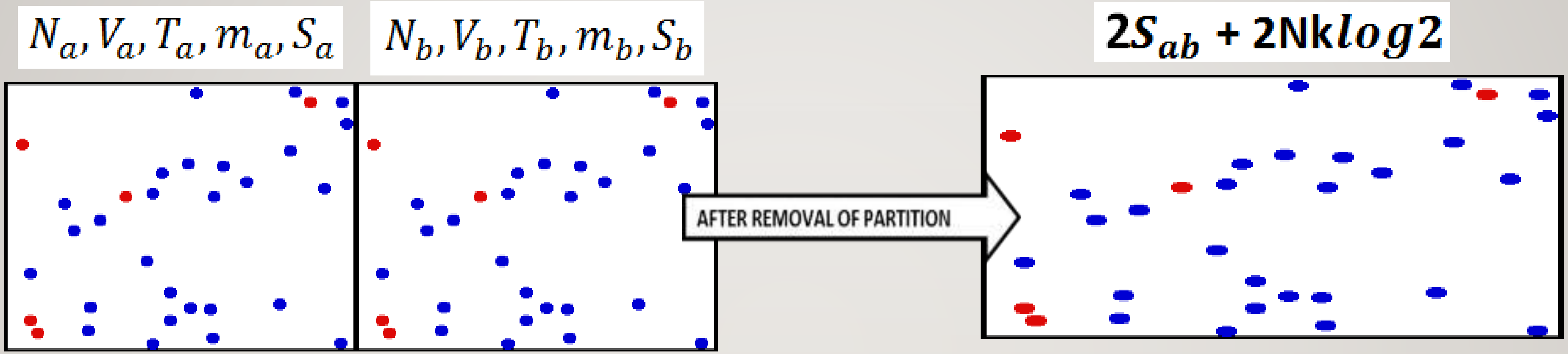
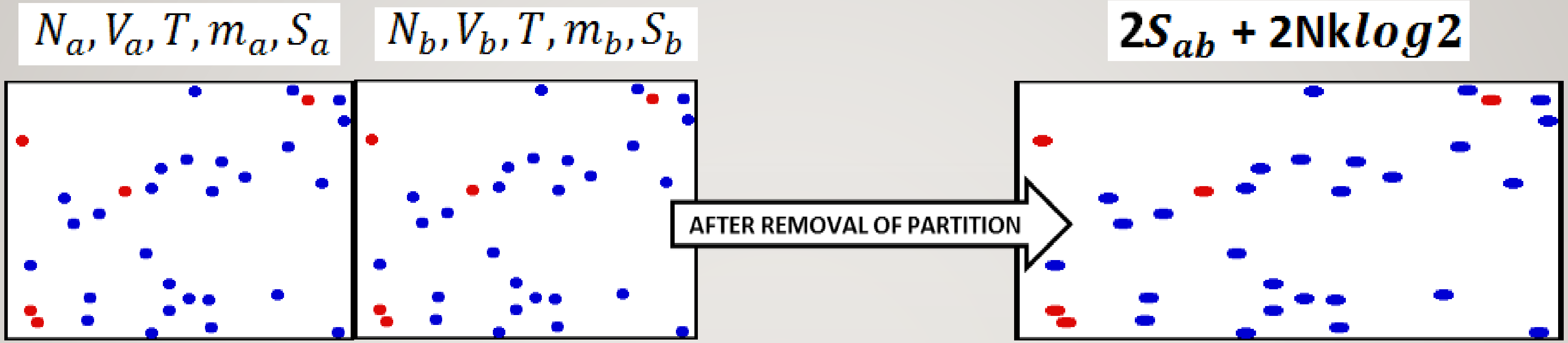
Gibbs Paradox

GIBBS PARADOX



GIBBS PARADOX BASICALLY DEALS WITH THE ENTROPY (RANDOMNESS) OF THE SYSTEM BEFORE AND AFTER THE REMOVAL OF THE PARTITION. AS WE ALL KNOW THAT ENTROPY IS AN ADDITIVE PROPERTY ($S_{ab} = S_a + S_b$), HOWEVER WE DEAL WITH A SYSTEM HAVING 2 SUBSYSTEMS 'A' & 'B'. AFTER THE REMOVAL OF THE PARTITION, WE OBSERVED THAT THE TOTAL ENTROPY WAS OBSERVED AS $2S_{ab}$ + 2NK$log2$, RATHER THAN S_{ab}, WHICH IS KNOWN AS GIBBS PARADOX

GIBBS PARADOX & RESOLUTION



N_a, V_a, T, m_a, S_a

N_b, V_b, T, m_b, S_b

AFTER REMOVAL OF PARTITION

$2S_{ab} + 2Nk\,log2$

LET THE SYSTEM BE IN THERMAL EQUILIBRIUM CONDITION , $T_a = T_b =$ T

AS WE KNOW THAT THE PARTITION FUNCTION OF A PERFECT GAS IS GIVEN AS,

$$Z = \frac{V}{h^3}(2\pi mkT)^{\frac{3}{2}} \text{……………………}(1)$$

THE ENTROPY IS GIVEN AS, S = NK$logZ$ + $\frac{3}{2}$ NK ……..(2)

Substituting eq'n (1) in (2) we get,

$$S = NK\, log[\frac{V}{h^3}(2\pi mkT)^{\frac{3}{2}}] + \frac{3}{2}NK$$

$$S = NK\,[logV + \frac{3}{2}log\, m + \frac{3}{2}logT + C] \text{ ……..(3)}$$

$$\text{where, } \left(C = log\frac{2\pi k}{h^3} + 3/2\right)$$

Equation(3) can be written for system 'A' & 'B'

$$S_a = N_aK\,[logV_a + \frac{3}{2}log\, m_a + \frac{3}{2}logT + C] \text{ ………..(A)}$$

$$S_b = N_bK\,[logV_b + \frac{3}{2}log\, m_b + \frac{3}{2}logT + C] \text{ ……….(B)}$$

- **Entropy is an extensive property , it must satisfy an additive property, i.e., the total entropy must given as ,**

$$S_{ab} = S_a + S_b \quad \ldots\ldots\ldots(4)$$

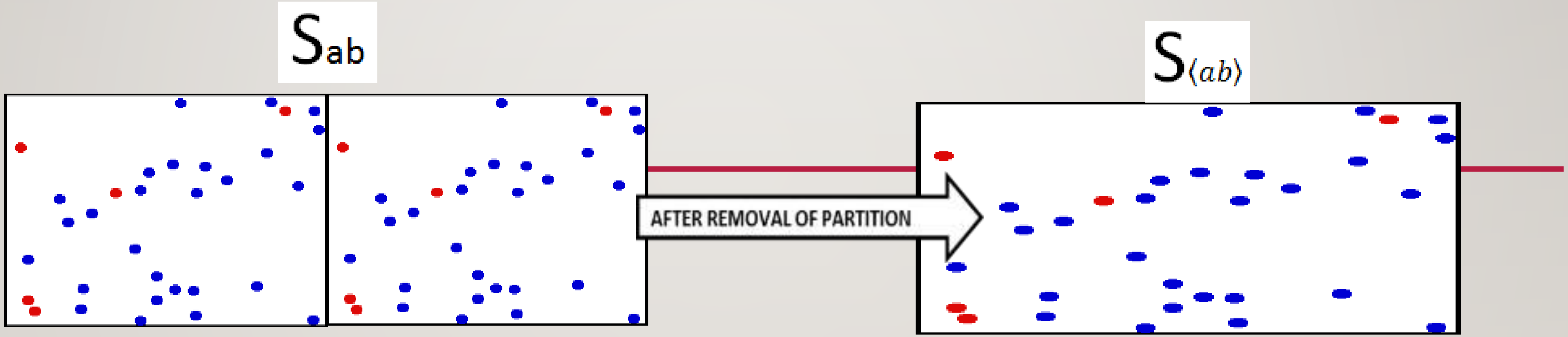
- **Put eq'n (A) and (B) in eq'n (4)**

- $S_{ab} = N_a K[\log V_a + \frac{3}{2}\log m_a + \frac{3}{2}\log T + C] + N_b K\,[\log V_b + \frac{3}{2}\log m_b + \frac{3}{2}\log T + C]$

$$let,\ \ V_a = V_b = \mathrm{V}\ \&\ N_a = N_b = \mathrm{N},$$

$$S_{ab} = 2\mathrm{NK}[\ \mathrm{LOGV} + \frac{3}{2} \log m + \frac{3}{2} \log T + C]\ \ldots.(5)$$

NOW AFTER THE REMOVAL OF THE PARTITION



- After the removal of the partition, Entropy 'Sab' become 'S$\langle ab \rangle$' & volume 'V' becomes '2V' then the equation becomes
- $S_{\langle ab \rangle} = 2NK[\log 2V + \frac{3}{2} \log m + \frac{3}{2} \log T + C]$

$$S\langle ab\rangle = 2NK[\log 2 + \log V + \frac{3}{2}\log m + \frac{3}{2}\log T + C]$$

$$S\langle ab\rangle = 2NK[\log V + \frac{3}{2}\log m + \frac{3}{2}\log T + C] + 2NK\log 2 \;\ldots.(6)$$

from eq'n (4) and (5), we can conclude that

$$S\langle ab\rangle = SA + SB + 2NK\log 2$$

implies that, $S\langle ab\rangle \neq SAB$

$$S\langle ab\rangle \neq SA + SB$$

$S\langle ab\rangle > SA + SB$ by a factor of $2NK\log 2$

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this extra factor **$2NK\log 2$** is unaccountable and it is called as **GIBBS PARADOX**

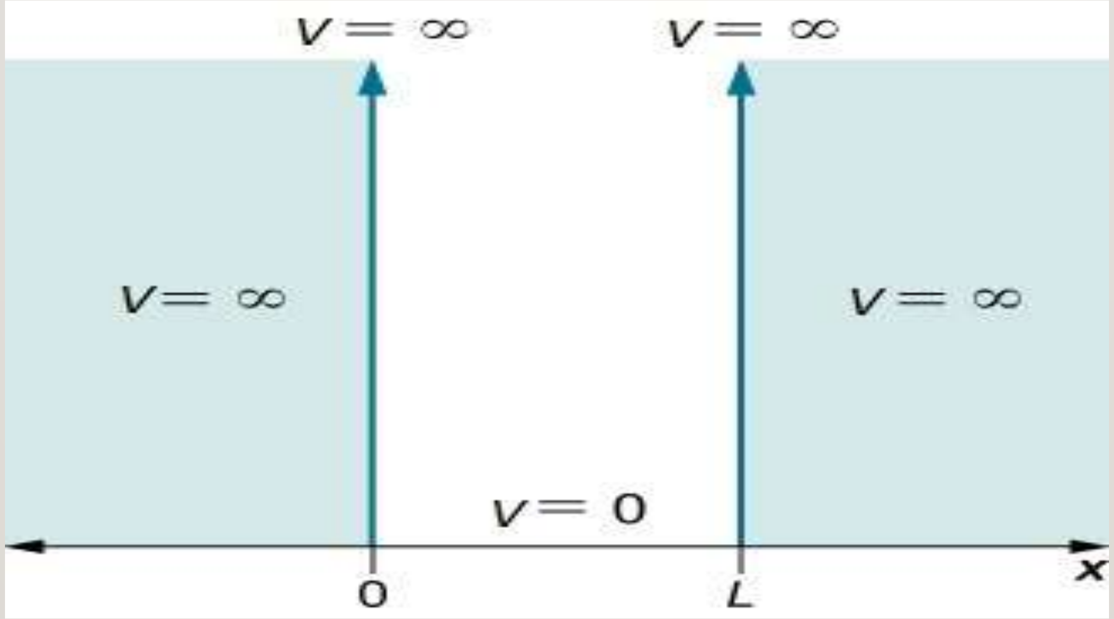
PARTICLE IN A BOX

The *particle in the box,* is the simplest non-trivial application of the Schrödinger equation, but illustrates many of the fundamental concepts of quantum mechanics.

For a particle moving in one dimension (again along the x- axis), the Schrödinger equation can be written as

$$(-\hbar^2/2m)\psi''(x)+V(x)\psi(x)=E\,\psi(x) \qquad (1)$$

PARTICLE IN A BOX



PARTICLE IN A BOX

Assume that the particle can move freely between two end points $x=0$ and $x=L$, but cannot penetrate past either end. This is equivalent to a potential energy dependent on *x* with

$$V(x)= 0, \infty \quad 0\leq x \leq L;\ x<0\ \&\ x>L \tag{2}$$

The infinite potential energy constitutes an impenetrable barrier since the particle would have an infinite potential energy if found there, which is clearly impossible.

PARTICLE IN A BOX

The particle is thus bound to a "*potential well*" since the particle cannot penetrate beyond $x=0$ or $x=L$

- $\psi(x) = 0$ for $x < 0$ & $x > L$ (3)

For the wave function be continuous, it must be that

- $\psi(0) = 0$ & $\psi(L) = 0$ (4)

PARTICLE IN A BOX

Which constitutes a pair of boundary condition. Inside the box, $V(x)=0$, so the Schrödinger Equation reduces to the free-particle form

$$[-\hbar^2/2m]\psi''(x)=E\,\psi(x) \qquad \text{with } 0 \le x \le L \quad 0 \le x \le L. \tag{5}$$

The differential equation can be expressed as

$$\psi''(x)+k^2\psi(x) = 0 \tag{6}$$

$$k^2 = 2mE/\hbar^2 \tag{7}$$

The general solution of the DE is expressed as

$$\psi(x) = A\sin kx+B\cos kx \tag{8}$$

PARTICLE IN A BOX

Where A and B are constants to be determined by the boundary conditions. By the first condition, we find

$$\psi(0) = A \sin 0 + B \cos 0; \text{ implies } B = 0 \qquad (9)$$

$$\psi(L) = A \sin kL = 0 \qquad (10)$$

For existence of the solution ; $A \neq 0$,

implies; $\sin kL = 0$

$$kL = n\pi \qquad (11)$$

PARTICLE IN A BOX

where n is a integer, positive, negative or zero. The case n = 0 must be excluded, for then k=0; again ψ(x) would vanish everywhere.

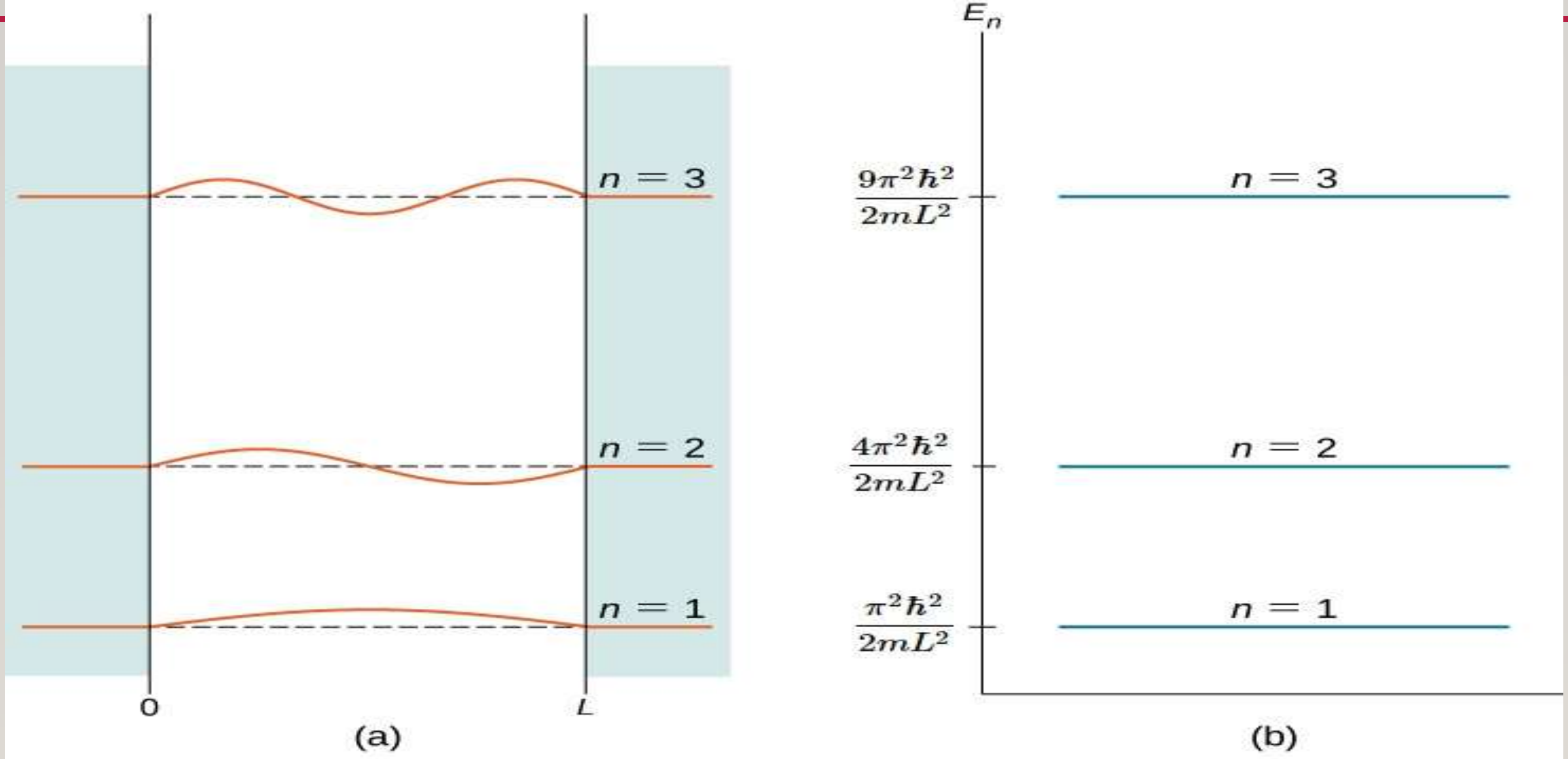
Eliminating k, between Equation 7 & 11, we get;

$$E_n = n^2 \hbar^2 \pi^2 / 2mL^2 \quad \text{with } n=1,2,3.... (12)$$

PARTICLE IN A BOX

- These are the only values of the energy which allows solutions of the Schrödinger Equation.
- The integer n, called a *quantum number*, is appended as a subscript on E to label the allowed energy levels.
- Negative values of n add nothing new because the energy depends on n^2.

PARTICLE IN A BOX



(a)

(b)

PARTICLE IN A BOX

- Figure shows part of the energy-level diagram for the particle in a box. The occurrence of discrete or quantized energy levels is characteristic of a bound system, that is, one confined to a finite region in space.
- The particle in a box assumes its lowest possible energy when n=1, namely

$$E1=h^28/mL^2 \qquad (13)$$

PARTICLE IN A BOX

- The state of lowest energy for a quantum system is termed its *ground state*.
- The particle-in-a-box eigenfunctions are given by with B=0 and $k=n\pi/L$, in accordance with Equation 11
- $\psi_n(x)=A\sin(n\pi x/L)$ (15)
- With $n=1,2,3\ldots$ (16)
- $n=1,2,3\ldots$like the energies, can be labeled by the quantum number n. The constant A, thus far arbitrary, can be adjusted so that $\psi_n(x)$ is normalized. The normalization condition is, in this case,
- $\int_0^L [\psi_n(x)]^2 dx = 1$ (17)

PARTICLE IN A BOX

- The integration running over the domain of the particle $0 \leq x \leq L$.

- $A^2\int_0^L \sin^2(n\pi x/L)dx = A^2L/2 = 1$ (18)
- We have made the substitution $\theta = n\pi x/L$

  $\sin^2(n\pi x/L) = \frac{1}{2}\,[1 - \cos(2n\pi x/L)]$
- General normalization constant
- $A = \sqrt{(2/L)}$ (19)

PARTICLE IN A BOX

- For all values of n. Finally we can write the normalized eigen functions:
- $$\Psi_n(x) = \sqrt{2/L}\,\sin(n\pi x/L) \qquad (20)$$

  With n=1,2,3..
- The first few eigen functions and the corresponding probability distributions are plotted.
- There is a close analogy between the states of this quantum system and the modes of vibration of a violin string.
- The patterns of standing waves on the string are, in fact, identical in form with the wave functions in Equation 20.

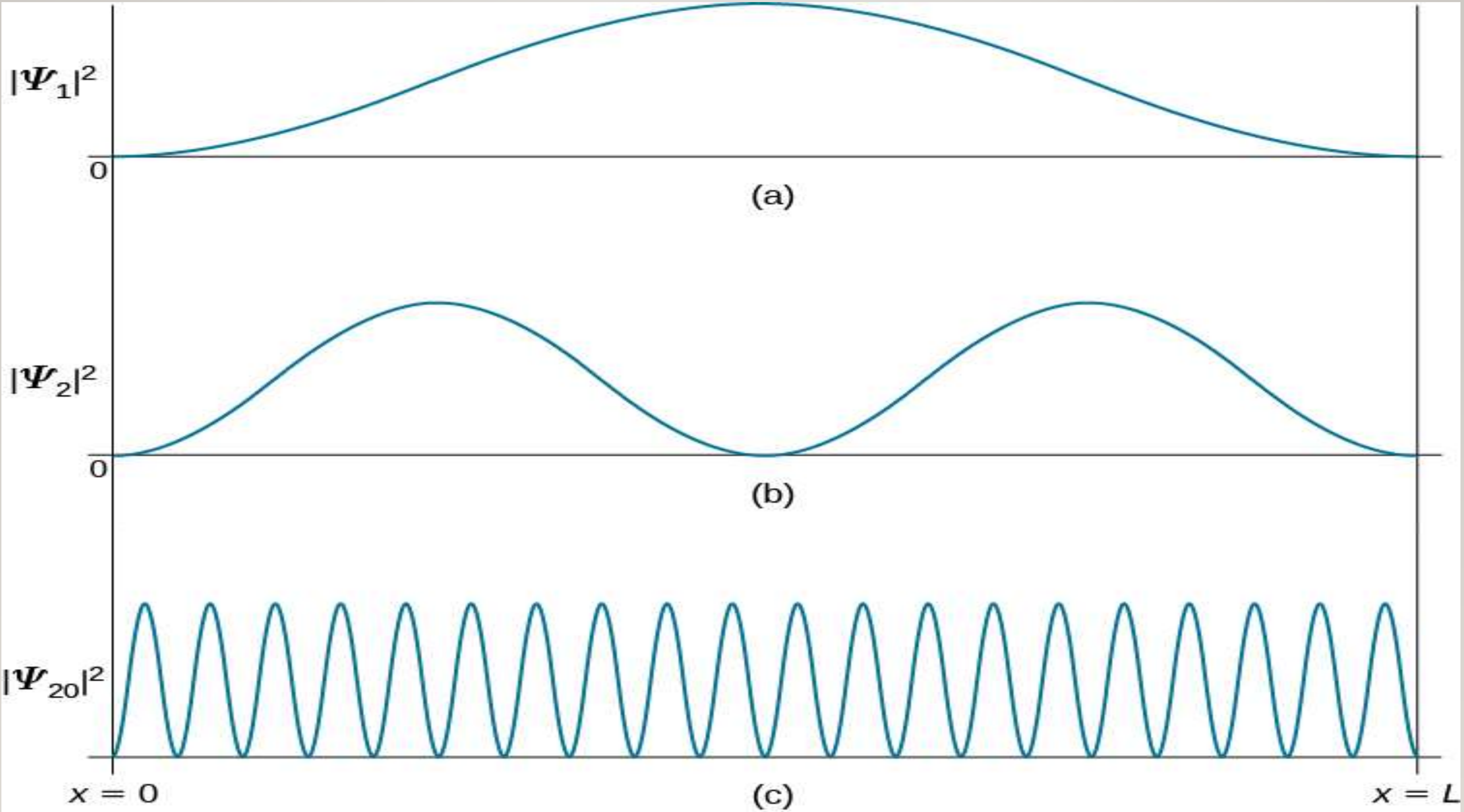
PARTICLE IN A BOX

The Probability Density Distribution:

(a) The ground state, n=1;

(b) The first excited state, n=2;

And so on………..



$|\Psi_1|^2$
0
(a)
$|\Psi_2|^2$
0
(b)
$|\Psi_{20}|^2$
$x = 0$
(c)
$x = L$

In a Gaseous System

Why C_p & C_v ?

Why $C_p > C_v$?

SPECIFICHEAT

It is defined as the quantity of heat required to raise the temperature of unit mass of a substance through 1 $°C$

Relation between **CV & CP of a Gaseous System**

C_p – C_v = R …..(Mayer's eq'n)

$\gamma = \frac{C_p}{C_v}$….(Heat Capacity Ratio)

Using 1st law of thermodynamics

$$(dQ) \quad = du + pdv$$

As we know that at constant volume ($dv=0$) , hence there is no work done by the system, therefore the total amount of heat supplied is only used to increase the internal energy of the system hence the above eq'n becomes as, $(dQ)_v = du$ & at constant pressure, $(dQ)_p = du + pdv$.

At constant pressure, here volume changes, work is done by the system, heat supplied is used in two parts i.e to increase the internal energy and some energy is used as work done by the system, hence more energy is required to rise the same temperature, therefore,

$$\mathbf{Cp > Cv}$$

Entropy of a perfect gas can be expressed by,

$$\text{s} = \text{NKlog}\left[\frac{V}{h^3}(2\pi mkT)^{\frac{3}{2}}\right] + \frac{3}{2}\ \text{NK} \quad \text{.....(1)}$$

Energy for the classical ideal gas is given as

$$\text{E} = \frac{3}{2}N\text{KT}$$

$$\text{KT} = \frac{2E}{3N} \quad \text{......(2)}$$

Substituting eq'n (2) in (1) we get,

$$\text{S} = \text{NKL}og\left[V\left(\frac{4\pi mE}{3Nh^2}\right)^{\frac{3}{2}}\right] + \frac{3}{2}\text{NK} \text{ ....(3)}$$

Dividing eq’n (2) by $\frac{3}{2}Nk, we\ get$

$$\frac{2S}{3Nk} = \frac{Nk}{\frac{3}{2}Nk} log\left[V\left(\frac{4\pi mE}{3Nh^2}\right)^{\frac{3}{2}}\right] + 1$$

$$\frac{2S}{3Nk} -1 = \frac{2}{3} log\left[V\left(\frac{4\pi mE}{3Nh^2}\right)^{\frac{3}{2}}\right]$$

Taking exponential,

$$e^{\left(\frac{2S}{3Nk}-1\right)} = \left[V\left(\frac{4\pi mE}{3Nh^2}\right)^{\frac{3}{2}}\right]^{\frac{2}{3}}$$

$$E = \frac{3h^2N}{4\pi mV^{\frac{2}{3}}} e^{\left[\frac{2S}{3Nk}-1\right]} \text{…………………………….(4)}$$

Eq'n (4) can give the following deduction

A) $Cv = \frac{dE}{dT}$ **[N, V is constant]**

$$\frac{dE}{dT} = \frac{3}{2}Nk \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \left(since, E = \frac{3}{2}NkT\right)$$

multiplying & dividing the above eq'n by N_A

$$\frac{N_A}{N_A}\frac{3}{2}NK = \frac{3}{2}nR \quad \ldots\ldots\left[(\text{No. of moles})n = \frac{N}{N_A};\right.$$

$$\left.(\text{Gas constant})\ R = kN_A\right]$$

$$\therefore Cv = \frac{3}{2}nR \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

B) $\mathrm{Cp} = \frac{d(E+PV)}{dT}$

$= \frac{5}{2}nR$ ……………………………[Cp = Cv + R]

$\therefore \mathrm{Cp} = \frac{5}{2}nR$ …..(2)

C) Heat Capacity Ratio

$$\gamma = \frac{\mathrm{Cp}}{\mathrm{Cv}} = \frac{\frac{5}{2}nR}{\frac{3}{2}nR} = \frac{5}{3}$$

D) The entropy of an ideal gas is given as

$$S = \mathrm{NKlog}\left[\frac{V}{h^3}(2\pi mkT)^{\frac{3}{2}}\right] + \frac{3}{2}\mathrm{NK}$$

if the volume changes from Vi to Vf, then the above equation becomes,

$$S_f = \mathrm{NKL}og\left[\frac{V_f}{h^3}(2\pi mkT)^{\frac{3}{2}}\right] + \frac{3}{2}\mathrm{NK}$$

$$S_i = \mathrm{NKL}og\left[\frac{V_i}{h^3}(2\pi mkT)^{\frac{3}{2}}\right] + \frac{3}{2}\mathrm{NK}$$

$\triangle$S = $S_f - S_i$

$$=\{ \mathrm{NKL}og\left[\frac{V_f}{h^3}(2\pi mkT)^{\frac{3}{2}}\right] + \frac{3}{2}\mathrm{NK}\} -\{ \mathrm{NKL}og\left[\frac{V_i}{h^3}(2\pi mkT)^{\frac{3}{2}}\right] + \frac{3}{2}\mathrm{NK}\}$$

$$=\mathrm{NK}logV_f + \frac{3}{2}Nklog(2\pi mkT) - Nklogh^3 - NklogV_i - \frac{3}{2}NK\ \mathrm{LOG}(2m\pi kT) + Nklogh^3$$

$$= \mathrm{NK}logV_f - NKlogV_i$$

$\therefore$ **(Change in Entropy)** $\triangle$S = NK$log\frac{V_f}{V_i}$


Thank you!

STATISTICAL MECHANICS CH III

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Ideal Gas as Canonical Ensemble
&
Some Mathematical Formulae

BASICS

- $du = f(\mathrm{T}, \mathrm{S}, \mathrm{P}, \mathrm{V})$
- **Helmholtz Free Energy**
- **Enthalpy**
- **Gibbs Potential**

Prove that: $du = f(T, S, P, V)$

$dQ = du + Pdv$**……….(1st law)**

$dQ = Tds$ **…………….(2nd law)**

From above two equations we get,

$$du + Pdv = Tds$$

$$du = Tds - Pdv$$

$$du = f(T, S, P, V)$$

$\boldsymbol{Helmholtz\ Free\ Energy}$: $\boldsymbol{F = U - TS}$

Enthalpy: $\boldsymbol{H = U + PV}$

Gibbs Potential: $\boldsymbol{G = H - TS}$

Partition Function: $\boldsymbol{Z = \frac{V}{\hbar^3}(2m\pi kT)^{\frac{3}{2}}}$

Mathematical Formulae

(A)If $dA = -SdT - PdV + \mu dN$........(1)

and $A = \varphi[T,V,N]$

where;A=Helmoltz free energy

μ=chemical potential

then $-\left(\frac{\partial A}{\partial T}\right)_{N,V} = S$........(2)

$-\left(\frac{\partial A}{\partial V}\right)_{T,N} = P$........(3)

$\left(\frac{\partial A}{\partial N}\right)_{T,V} = \mu$........(4)

$U = A + TS$........(5)

Prove that:$U = A - T\left(\frac{\partial A}{\partial N}\right)_{T,V} = -T^2\left[\frac{\partial}{\partial T}\left(\frac{A}{T}\right)\right]_{N,V}$

Using eq.^{n} (2) and (5),$U = A - T\left(\frac{\partial A}{\partial N}\right)_{T,V}$

$= T^2\left[A\left(\frac{-1}{T^2}\right) + \frac{1}{T}\left(\frac{\partial A}{\partial T}\right)\right]$

$= -T^2\left[\frac{\partial}{\partial T}\left(\frac{A}{T}\right)\right]_{N,V}$.......($R_1$)

(B)If $Q_N(V,T)=\frac{1}{N!}[\frac{V}{h^3}(2\pi mKT)^{3/2}]^N$

where; Q_N=Partition Function

$A(N,V,T)=-KTlogQ_N(V,T)$

<u>Prove That:</u>

$$A(N,V,T)=NKT[log\frac{N}{V}(\frac{h}{2\pi mKT})^{3/2}-1]$$

Consider, $A(N,V,T)=-KTlogQ_N(V,T)$

$$=-KTlog\left\{\frac{1}{N!}\left[\frac{V}{h^3}(2\pi mKT)^{3/2}\right]^N\right\}$$

$$=-KT\left[N\log\frac{V}{h^3}(2\pi mKT)^{3/2}-\log N!\right]$$

$$=-KT\left[N\log\frac{V}{h^3}(2\pi mKT)^{3/2}-N\log N+N\right]$$

$$=NKT\left[-\log\frac{V}{h^3}(2\pi mKT)^{3/2}+\log N-1\right]$$

$$=NKT\left[\log\frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2}-1\right]$$

Hence, proved.

(C)If $Q_N(V,T)=\frac{1}{N!}\left[\frac{V}{h^3}(2\pi mKT)^{3/2}\right]^N$

and $A(N,V,T)=-KTlogQ_N$

Prove That: $\mu=\left(\frac{\partial A}{\partial N}\right)_{V,T}=KTlog\left[\frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2}\right]$

Consider, $\mu=\left(\frac{\partial A}{\partial N}\right)$

$$=\frac{\partial}{\partial N}\left\{NKT\left[log\,\frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2}-1\right]\right\}$$

$$=KT\left\{\log\left[\frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2}\right]-1\right\}+NKT\left[\frac{\frac{1}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2}}{\frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2}}\right]$$

$$=KT\left\{\log\left[\frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2}-1+1\right]\right\}$$

$$=KT\left\{\log\left[\frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2}\right]\right\}$$

(D)If A=$NKT\left\{\log\left[\frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2}\right]-1\right\}$

Prove that: P=$-\left(\frac{\partial A}{\partial V}\right)_{N,T}=\frac{NKT}{V}$

Consider, P=$-\left(\frac{\partial A}{\partial V}\right)_{N,T}$

$$=-NKT\,\frac{\partial}{\partial V}\left\{\log\left[\frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2}\right]-1\right\}$$

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

$$=\frac{NKT}{V}$$

(E)If A=$NKT\left\{\log\left[\frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2}\right]-1\right\}$

Prove that:

$$S=-\left(\frac{\partial A}{\partial T}\right)_{N,V}=NK\left\{\log\left[\frac{V}{N}\left(\frac{h^2}{2\pi mKT}\right)^{3/2}+\frac{5}{2}\right]\right\}$$

Consider, S=$-\left(\frac{\partial A}{\partial T}\right)_{N,V}$

$$=-\frac{\partial}{\partial T}\left\{\mathrm{NKTlog}\left[\frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2}\right]-NKT\right\}$$

$$=-NK\left\{\log\left[\frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2}\right]\right\}+NKT\times\frac{\frac{N}{V}\left(\frac{h^2}{2\pi mK}\right)\times\frac{-3}{2}T^{-5/2}}{\frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2}}-NK$$

$$=-NK\left\{\log\left[\frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2}\right]-\frac{3}{2}-1\right\}$$

$$=NK\left\{\log\left[\frac{V}{N}\left(\frac{2\pi mKT}{h^2}\right)^{3/2}\right]+\frac{5}{2}\right\}$$

(F)Prove that $\log[\sum_r e^{-\beta E_r}] = \frac{-A}{KT}$

Consider, U=A+TS $= -T^2\left[\frac{\partial}{\partial T}\left(\frac{A}{T}\right)\right]_{N,V}$

$$=\left[\frac{\partial\left(\frac{A}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right]$$

and U=$-\frac{\partial}{\partial\beta}\log(\sum_r e^{-\beta E_r})$

$$\therefore -T^2\left[\frac{\partial}{\partial T}\left(\frac{A}{T}\right)\right] = \frac{-\partial}{\partial\beta}\log(\sum_r e^{-\beta E_r})$$

$$\therefore \frac{-\partial}{\partial\beta}\log(\sum_r e^{-\beta E_r}) = \left[\frac{\partial\left(\frac{A}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right]$$

$$\therefore \partial\left(\frac{A}{T}\right) = -\,\partial\left(\frac{1}{T}\right)\frac{\partial}{\partial\beta}\log(\sum_r e^{-\beta E_r})$$

$$\therefore \partial\left(\frac{A}{T}\right) = -\,\partial\left(\frac{KT}{T}\right)\log(\sum_r e^{-\beta E_r})$$

$$\therefore \frac{-A}{KT} = \log(\sum_r e^{-\beta E_r})$$