Quantum Statistics

So far we have discussed statistical mechanics which can be applied to classical systems (or quantum systems with distinguishable entities.

To explain quantum-mechanical system with indistinguishable entities, it is advisable to set-up quantum ensemble theory in quantum-mechanics language i.e in terms of operators and wavefunctions. This may not give us new ideas but can help us in better understand quantum-mechanical systems.

Quantum Mechanical Ensemble Theory

Consider an ensemble of N identical systems, where $N \gg 1$. These systems are characterised by $\hat{H}$ (Hamiltonian Operator).

At time t, the physical state of various system in the ensemble is represented by $\psi(x_i, t)$ x_i = position coordinate.

Also, $\psi^k(x_i, t)$ is a normalized eigen wavefunction representing the physical state of the k^{th} system in which of ensemble is at time t. $[k = 1, 2 \ldots N)$

Now time variation of $\psi^k(t)$ can be written as

$$\hat{H}\psi^k(t) = i\hbar\dot{\psi}^k(t) \quad \text{——— (1)}$$

(the x_i coordinate is suppressed in ψ^k)

Now, we can write

$$\psi^k(t) = \sum_n a_n^k(t)\,\phi_n \quad \text{——— (2)}$$

where $a_n^k(t) = \int \phi_n^* \psi^k(t)\, d\tau$ ——— (3)

or we can write $\psi^k(t) = \int \phi_n^* \psi^k(t)\, \phi_n\, d\tau$

where ϕ_n = orthonormal function in eq. (3)

where, ϕ_n^* is complex conjugate of ϕ_n & $d\tau$ is the coordinate space of the given system.

multiplying by $i\hbar$ on b/s of eq. (2)

$$i\hbar\, \dot{a}_n^k(t) = i\hbar \int \phi_n^* \dot{\psi}^k(t)\, d\tau$$

$$= \int \phi_n^* \, i\hbar\, \dot{\psi}^k(t)\, d\tau$$

$$= \int \phi_n^* \hat{H} \psi^k(t)\, d\tau \quad \text{from eq. (1)}$$

$$= \int \phi_n^* \hat{H} \left[\sum_m a_m^k(t)\phi_m\right] d\tau \quad \text{from eq. (2)}$$

$$= \sum_m H_{nm}\, a_m^k(t) \quad \text{——— (4)}$$

where $H_{nm} = \int \phi_n^* \hat{H} \phi_m\, d\tau$ ——— (5)

from eq. (2) it is evident that $\sum_n |a_n^k(t)|^2$ is the probability for a system represented by $\psi^k(t)$ to be in state $\phi_n(t)$ at any time t.

So we can write $\sum_n |a_n^k(t)|^2 = 1$ for all k. — (6)

Now, we can define term called density operator $\hat{\rho}(t)$, represented by matrix elements.

$$\rho_{mn}(t) = \frac{1}{N}\sum_{k=1}^{N}\left\{a_m^k(t)\, a_n^{k*}(t)\right\} \quad \text{—— (7)}$$

from eq. (6) & (7) we can write

$$\sum_n \rho_{mn}(t) = 1 \quad \text{(8)}$$

, this represents the probability that a system, chosen at random from ensemble, at any time t, to be in its state ϕ_n.

Now to obtain eq. of motion for the density matrix $\rho_{mn}(t)$, we can write

$$\dot{\rho}_{mn}(t) = \frac{1}{N}\sum_{k=1}^{N}\left[\dot{a}_m^k(t)\, a_n^{k*}(t) + a_m^k(t)\, \dot{a}_n^{k*}(t)\right]$$

or

$$i\hbar\,\dot{\rho}_{mn}(t) = \frac{1}{N}\sum_{k=1}^{N}\left[i\hbar\left[\dot{a}_m^k(t)\, a_n^{k*}(t) + a_m^k(t)\, \dot{a}_n^{k*}(t)\right]\right]$$

$$= \frac{1}{N}\sum_{k=1}^{N}\left[\underline{i\hbar\,\dot{a}_m^k(t)}\, a_n^{k*}(t) + a_m^k(t)\, \underline{i\hbar\,\dot{a}_n^{k*}(t)}\right]$$

$$= \frac{1}{N}\sum_{k=1}^{N}\left[\left\{\underline{\sum_l H_{ml}\, a_l^k(t)}\right\} a_n^{k*}(t) - a_m^k(t)\left\{\underline{\sum_l H_{nl}^*\, a_l^{k*}(t)}\right\}\right]$$

$$= \sum_l \left\{ H_{ml} P_{ln}(t) - P_{ml}(t) H_{ln} \right\}$$

$i\hbar \dot{P}_{mn} = (\hat{H}\hat{P} - \hat{P}\hat{H})_{mn}$ ——— (9) where $H^*_{ml} = H_{lm}$

$\Rightarrow i\hbar \dot{\hat{\rho}} = [\hat{H}, \hat{\rho}]$ ——— (10), this is quantum-mechanical analog of the Classical Liouville thm.

Now for a system to be in equilibrium, the corresponding ensemble must be stationary. This can be achieved if (i) $\hat{\rho} = \hat{\rho}(\hat{H})$ i.e density operator $\hat{\rho}$ must be explicit fn of Hamiltonian operator $\hat{H}$.

(ii) $\frac{\partial \hat{H}}{\partial t} = 0$ i.e Hamiltonian must not depend explicitly on time.

Now if ϕ_n is eigen fn of $\hat{H}$, then matrices H & P would be diagonal

$$H_{mn} = E_n \delta_{mn}, \quad P_{mn} = P_n \delta_{mn} \text{ ——— (11)}$$

where $\hat{\rho} = \sum_n |\phi_n\rangle P_n \langle \phi_n|$ ——— (12)

The diagonal element P_n will depend naturally on the corresponding eigen value E_n of the Hamiltonian.

The density may or may not be diagonal but generally symmetric.

i.e $$P_{mn} = P_{nm} \quad \text{---(13)}$$

which means, in statistical equilibrium, the tendency of a physical system to switch from one state to another must be counterbalanced by an equally strong tendency to switch b/w the same states in the reverse direction.

This condition of detailed balancing is crucial for the maintenance of an equilibrium distribution within the ensemble.

Now expectation value of physical quantity G, expressed as $\hat{G}$, is given by

$$\langle G \rangle = \frac{1}{N} \sum_{K=1}^{N} \int \psi^{K*} \hat{G} \psi^{K} \, d\tau \quad \text{---(14)}$$

or

$$\langle G \rangle = \frac{1}{N} \sum_{K=1}^{N} \left[\sum_{m,n} a_n^{K*} a_m^{K} G_{nm} \right] \quad \text{---(15)}$$

where $$G_{nm} = \int \phi_n^* \hat{G} \phi_m \, d\tau \quad \text{---(16)}$$

we can also write eq. (15) as

$$\langle G \rangle = \sum_{m,n} P_{mn} G_{nm} = \sum_{m} (\hat{P}\hat{G})_{mm} = Tr(\hat{P}\hat{G}) \quad \text{---(17)}$$

if $\hat{C} = \hat{1}$ (identity matrix)

then $Tr(\hat{P}) = 1$ ——— (18)

if ψ^k is not normalized, $\langle \hat{C} \rangle = \frac{Tr(\hat{P}\hat{C})}{Tr(\hat{P})}$ ——— (19)

Statistics of Various Ensemble

The Micro Canonical Ensemble (MCE) :- In MCE, the members systems are characterized by N(fixed), V(fixed) & $E-\frac{1}{2}\Delta, E+\frac{1}{2}\Delta$ (energy range) where $\Delta << E$.

The total microstates accessible to a system is then denoted by Γ. or $\Gamma(N, V, E, \Delta)$

Also, any microstate is equal likely to occur as any other. (equal a-priori probability)

According to our representation of density matrix

$$\rho_{mn} = \rho_n \delta_{mn} \quad \text{①}$$ (this is a energy representation, which must be diagonal)

with $$\rho_n = \begin{cases} \frac{1}{\Gamma} & \text{for each accessible states} \\ 0 & \text{for all other states} \end{cases}$$ ——— (2)

to determine thermodynamics of the system, we know

$$S = k \ln \Gamma$$ ——— (3)

Q what happen to Gibb's Paradox in Quantum statistics?

Now, we have to consider two situations $\Gamma = 1$ or $\Gamma > 1$

for $\Gamma = 1$, means system has only one microstates (i.e all the masters are in one step) or we can say all the microscopic entities occupy single state.

Then entropy will vanish i.e $S = k \ln 1 = 0$

$\Gamma = 1$, is called pure state or pure case.

In this pure case, the density matrix (which is diagonal) will have only one non-zero element (equal to unity), while all other are zero.

$$\rho = \begin{pmatrix} 0 & 0 & 0 & \cdots \\ 0 & 1 & 0 & \cdots \\ 0 & 0 & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

$\rho = 1$

the density matrix, thus satisfy $\rho^2 = \rho$ ——— (4)

In other representation, the pure case can be represented as $\rho_{mn} = \frac{1}{N} \sum_{k=1}^{N} a_m^k a_n^{k*} = a_m a_n^*$ ——— (5)

only one element

Now, because all values of k are now literally equivalent, we can write $\rho_{mn}^2 = \sum_l \rho_{ml} \rho_{ln} = \sum_l a_m a_l^* a_l a_n^*$

$$= a_m a_n^* \qquad \text{because } \sum_l a_l^* a_l = 1$$

probability

$$\rho'_{mn} = \rho_{mn} \quad \text{—} \quad (6)$$

Thus relation (4) holds in other representations as well.

Now for $\Gamma > 1$, it called mixed case.

In energy representation, the density matrix will be of form (1) & (2).

In other representations, the density matrix generally remain same i.e

1) off-diagonal elements should be zero.
2) the diagonal elements should continue to be equal to one another. (equal a-priori probability)

To make off-diagonal elements zero in other representations of density matrix, we are invoking another postulate. i.e the postulate of random a-priori phases. for probability amplitude a_n^k. which means that wavefunction ψ^k, for all k, is an incoherent superposition of the basis $\{\phi_n\}$.

To invoke above mentioned two postulates, we can express density matrix in any representations

$$\rho_{mn} \equiv \frac{1}{N}\sum_{K=1}^{N} a_m^k a_n^{k*} = \frac{1}{N}\sum_{K=1}^{N} |a|^2 e^{i(\theta_m^k - \theta_n^k)} \quad (96)$$

$$= C\left\langle e^{i(\theta_m^k - \theta_n^k)} \right\rangle$$

$$\rho_{mn} = C\,\delta_{mn} \quad \text{——} \quad (7)$$

So, in quantum analog of MCE, we require in general two postulates. The other postulate (second) arises solely from quantum-mechanical introduce non-interference (or complete absence of correlations) among member systems i.e every system is isolated, as is required in MCE.

The Canonical Ensemble

In canonical ensemble, the system is defined by N, V, T (Energy is variable).

The probability that a system possess energy E_n at time t is determined by $\exp(-\beta E_n)$.

Now the diag. density matrix in energy representation is

$$\rho_{mn} = \rho_n \delta_{mn} \quad \text{——} \quad (8)$$

with $\rho_n = C\exp(-\beta E_n)$ —— (9) $n = 0, 1, 2 \cdots$

where $C = \frac{1}{\sum_n \exp(-\beta E_n)} = \frac{1}{Q_N(\beta)}$ ——— (10)

Now, the energy representation of density matrix can be written as

$$\hat{\rho} = \sum_n |\phi_n\rangle \frac{1}{Q_N(\beta)} e^{-\beta E_n} \langle \phi_n|$$

$$= \frac{1}{Q_N(\beta)} e^{-\beta E_n} \sum_n |\phi_n\rangle\langle\phi_n|$$

$$= \frac{1}{Q_N(\beta)} e^{-\beta \hat{H}} \sum_n |\phi_n\rangle\langle\phi_n|$$

$$= \frac{1}{Q_N(\beta)} e^{-\beta \hat{H}} = \frac{e^{-\beta \hat{H}}}{Tr(e^{-\beta \hat{H}})}$$

$\sum_n |\phi_n\rangle\langle\phi_n|$ is a unit operator

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{Tr(e^{-\beta \hat{H}})} \quad \text{——— (11)}$$

where operator $e^{-\beta \hat{H}}$ stands for $\sum_{j=0}^{\infty} (-1)^j \frac{(\beta \hat{H})^j}{j!}$ ——— (12)

Now, expectation value of physical quantity G, is

$$\langle G \rangle_N = Tr(\hat{\rho}\hat{G}) = \frac{1}{Q_N(\beta)} Tr(\hat{G} e^{-\beta \hat{H}})$$

$$\langle G \rangle_N = \frac{Tr(\hat{G} e^{-\beta \hat{H}})}{Tr(e^{-\beta \hat{H}})} \quad \text{——— (13)}$$

(N is fixed)

The Grand Canonical Ensemble

In this ensemble, the density operator must commute with Hamiltonian operator $\hat{H}$ as well as with number operator $\hat{n}$ whose eigenvalues are $0, 1, 2 \ldots$.

$$\hat{\rho} = \frac{1}{Q(\mu, V, T)} e^{-\beta(\hat{H} - \mu\hat{n})} \quad \text{---(14)}$$

where Grand partition fn $Q(\mu, V, T) = \sum_{r,s} e^{-\beta(E_r - \mu N_s)}$

$$= Tr\{e^{-\beta(\hat{H} - \mu\hat{n})}\} \quad \text{---(15)}$$

The ensemble average,

$$\langle G \rangle = \frac{1}{Q(\mu, V, T)} Tr\left(\hat{G} e^{-\beta(\hat{H} - \mu\hat{n})}\right)$$

$$= \frac{1}{Q(\mu, V, T)} Tr\left(\hat{G} e^{-\beta\hat{H}} \cdot e^{\beta\mu\hat{n}}\right)$$

$$= \frac{Tr\left(e^{\beta\mu\hat{n}} \cdot \hat{G} \cdot e^{-\beta\hat{H}}\right)}{Q(\mu, V, T)}$$

$$\langle G \rangle = \frac{\sum_{N=0}^{\infty} z^N \langle G \rangle_N Q_N(\beta)}{\sum_{N=0}^{\infty} z^N Q_N(\beta)} \quad \text{---(16)}$$

z = fugacity

$\langle G \rangle_N$ = Canonical ensemble average

SYSTEM COMPOSED OF INDISTINGUISHABLE PARTICLES.

Consider a system of N-identical non-interacting particles. The Hamiltonian of such a system could be represented as sum of single-particle Hamiltonians (Since particles are non-interacting)

$$\hat{H}(q,p) = \sum_{i=1}^{N} \hat{H}_i(q_i, p_i) \quad \text{---(1)}$$

where $\hat{H}_i (i = 1, 2 \cdots N)$

The time-independent Schrödinger eq. for the system is

$$\hat{H}\,\psi_E(q) = E\,\psi_E(q) \quad \text{---(2)}$$

E is eigenvalue & $\psi_E(q)$ is eigenfunction of Hamiltonian $\hat{H}$.

Now total wave function of the system in terms of single-particle wave functions can be written as

$$\psi_E(q) = \prod_{i=1}^{N} u_{Ei}(q_i) \quad \text{---(3)}$$

where $u_{Ei}(q_i)$ is the single-particle eigenfunction of single particle ~~wave~~ function Hamiltonian $\hat{H}_i(q_i, p_i)$ with eigen value ε_i.

i.e $\hat{H}_i\, u_{Ei}(q_i) = \varepsilon_i\, u_{Ei}(q_i) \quad \text{---(4)}$

Thus, a stationary state of a given system may be described by single-particle state of the constituent particles.

To do this, we are specifying set of numbers $\{n_i\}$ to represent particular state of the system.
i.e there are n_i particles in the eigenstate characterized by the energy value ε_i

So, $$\sum_i n_i = N \quad \text{——— (6)}$$

& $$\sum_i n_i \varepsilon_i = E \quad \text{——— (7)}$$

And wave function of this state will be

$$\psi_E(q) = \prod_{m=1}^{n_1} u_1(m) \prod_{m=n_1+1}^{n_1+n_2} u_2(m) \quad \text{——— (8)}$$

$u_i(m)$ stands for single-particle wave function $u_{\varepsilon_i}(q_m)$

Now, if we consider permutations among co-ordinates appearing in the above eq., then we can write

$$P\psi_E(q) = \prod_{m=1}^{n_1} u_1(Pm) \prod_{m=n_1+1}^{n_1+n_2} u_2(Pm) \quad \text{——— (9)}$$

Now, in case of distinguishable particles (Classical Statistics) these permutations, or rearrangements of $\{n_i\}$ can be expressed as

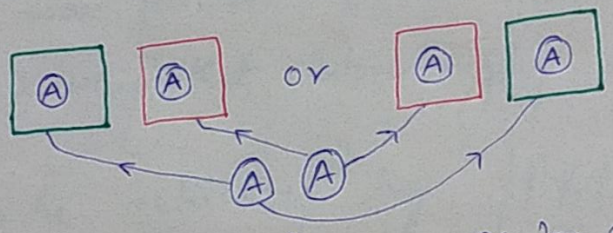
$$W\{n_i\} = \frac{N!}{n_1! n_2! \cdots} \quad \text{——— (10)}$$

if we include Gibb's Paradox then

$$W_c(n_i) = \frac{1}{n_1! n_2! \ldots} \quad \text{——— (11)}$$

Now, in quantum relm, switching (interchanging) identical particles, even if they are in different single-particle state, does not leads to new microstate.

i.e let us take two particles denoted as (A) & (A) Now



Above two scenarios are same, as for as particles are identical. Here, labelling them as 1 or 2 OR labelling seats as red or green is just for our convinence but not reality.

Hence, only description we have for a particular state is set of numbers $\{n_i\}$ which tells us how many particles are there in single particle states i.e

which particle is in which single particle state has no relevance.

Thus any permutation will generate identical microstate i.e the weight factor

$$W_Q(n_i) \equiv 1 \quad \text{(12)} \qquad \text{(As long as } \{n_i\} \text{ is allowed)}$$

if for some physical reason set $\{n_i\}$ is disallowed, W_Q should be identically equal to zero.

Now the wave function $\psi_\epsilon(q)$ must be modified in such a way that interchanging does not affect it.

This can be achieved by $|P\psi|^2 = |\psi|^2$ — (13)

or $\underline{P\psi = \psi}$ for all P — (14)

$\Rightarrow$ wavefunction is symmetric in all its arguments.

i.e $\underline{P\psi} = \begin{cases} +\psi & P \text{ is even permutation} \\ -\psi & P \text{ is odd } " \end{cases}$ — (15)

which means wavefunction is antisymmetric in its arguments.

$\delta P = +1$ For even P
$= -1$ For odd P

We call these wavefunctions as

Symmetric $\psi_S(q) = \text{Const.} \sum_P P\,\psi_{Boltz}(q)$ — (16)

Antisymmetric $\psi_A(q) = \text{Const.} \sum_P \delta_P\, P\,\psi_{Boltz}(q)$ — (17)

The antisymmetric wave function $\psi_A(q)$ can be written in the form of Slater determinant

$$\psi_A(q) = \text{const.} \begin{vmatrix} u_i(1) & u_i(2) & \cdots & u_i(N) \\ u_j(1) & u_j(2) & \cdots & u_j(N) \\ \vdots & \vdots & & \vdots \\ u_l(1) & u_l(2) & \cdots & u_l(N) \end{vmatrix} \quad (18)$$

Now, if we change (interchange) a pair of arguments i.e equivalent to interchanging the corresponding columns of the determinant, then the resultant wavefunction will be same with -ive sign.

Also, if two or more arguments made to be same, then corresponding rows will be identical & the wave function vanishes. (i.e ψ_A collapses) which is not possible.

Thus if we have system characterized by ~~non-int~~ indistinguishable particles characterized by ψ_A, then each particle must be all in different single-particle state (equivalent to Pauli's exclusion principle)

$\Rightarrow$ System characterized by ψ_A, must obey Pauli's exclusion principle or vice versa.

The statistics obeying the behavior of such particles is called Fermi-Dirac or Fermi Statistics

And the constituents particles are referred to as fermions.

$$W_{F.D}\{n_i\} = \begin{cases} 1 & \text{if } \sum_i n_i^2 = N \\ 0 & \text{if } \sum_i n_i^2 > N \end{cases}$$

No such problems arise for systems defined by symmetric wave functions, where no restriction on values of $\{n_i\}$ ~~exist~~ apply.

The statistics governing behaviour of such systems are called Bose-Einstein or Bose-statistics & Constituents particles are called bosons.

$$W_{B.E}\{n_i\} = 1 \qquad n_i = 0, 1, 2 \cdots$$

Particles with integral spins obey B.E statistics
Ex:- photons, phonons, gravitons, He^4-atoms, π-mesons.

Fermions have $\frac{1}{2}$-integer spins.
Ex:- e^-, protons, neutron, μ-mesons, He^3-atoms.

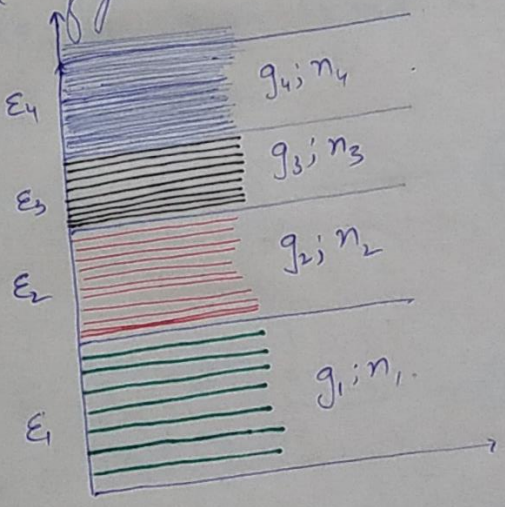
For interacting system, above discussions holds because the system depends on ψ_A, ψ_S not on single particle wave functions ~~$u_i(q_m)$~~ $u_i(q_m)$

An Ideal Gas In A Quantum-Mechanical Mode

Consider a gaseous system of N non-interacting, indistinguishable particles in volume V, energy E.

So, the no. of distinct microstate corresponding to macrostate (N, V, E) is represented as $\Omega(N, V, E)$.

In case of very large V, the single-particle energy levels in the system are very close to one another. So, it can be allowed to group energy levels into cells as showed in the fig.



Let ε_i be average energy of level, g_i be no. of levels in i^{th} cell ($g_i >> 1$.

Now, n_1 be particles in first cell, n_2 be particles in second cell and so on.

So we can write $\sum_i n_i = N$ ——— (1)

And $\sum_i n_i \varepsilon_i = E$ ——— (2)

Then, we can write

$$\Omega(N, V, E) = \sum_{(n_i)}{}' W(n_i) \quad \text{——— (3)}$$

where the primed summation goes over all distribution sets that conforms to condition (1)

Also $$W(n_i) = \prod_i w(i) \quad \text{——— (4)}$$

where, $w(i)$ is no. of distinct microstates associated with i^{th} cell of the system. And $\prod_i$ goes over all the cells.

Now, $w(i)$ represents no. of distinct ways in which n_i particles in i^{th} cells, can be arranged in g_i levels

In B-E case, $w(i)$ can be written as

$$w_{B\text{-}E}(i) = \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!} \quad \text{——— (5)}$$

So that

$$W_{B\text{-}E}(n_i) = \prod_i \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!} \quad \text{——— (6)}$$

In F-D case, no single level can accomodate more than one particle, so

$$w_{F\text{-}D}(i) = \frac{g_i!}{n_i!\,(g_i - n_i)!} \quad \text{——— (7)}$$

$$W_{F\text{-}D}(n_i) = \prod_i \frac{g_i!}{n_i!\,(g_i - n_i)!} \quad \text{——— (8)}$$

For, M-B case we know

$$W(n_i) = \frac{N!}{n_1! n_2! \cdots} \quad \text{——— (9)}$$

or $$W(n_i) = \frac{N!}{n_1! n_2! \cdots} = \frac{1}{n_1! n_2! \cdots}$$ (correction for Gibb's paradox)

In, M-B case, particles are distinguishable and any particle can occupy any level, independent of each other., generating no. of distinct ways of $(g_i)^{n_i}$

So $$W_{M\text{-}B}(n_i) = \prod_i \frac{(g_i)^{n_i}}{n_i!} \quad \text{——— (11)}$$

Now, entropy of the system would be given by

$$S(N,V,E) = k \ln \Omega(N,V,E) = k \ln \left[\sum_{n_i}{}' W(n_i) \right] \quad \text{——— (12)}$$

we can write eq. (12) as

$$S(V,N,E) \simeq k \ln W(n_i^*) \quad \text{(13)}$$

where n_i^* is the value of n_i for which W is maximum.

Condition to determine most probable distribution set $\{n_i^*\}$ is

$$\delta \ln W\{n_i\} - \left[\alpha \sum_i \delta n_i + \beta \sum_i \varepsilon_i \delta n_i \right] = 0 \quad \text{——— (14)}$$

$\sum n_i = N$ (constant) $\Rightarrow \sum_i \delta n_i = 0$

$\sum n_i \varepsilon_i = E$ (constant) $\Rightarrow \sum_i \delta n_i \varepsilon_i = 0$ ——— (14a)

Eq. (14) is the condition to maximize $W(n_i)$ including ~~eq~~ conditions (14a)

Now to calculate $\ln W(n_i)$ we need to calculate $\ln w(i)$

For BOSE-EINSTEIN, we know

$$w(i) = \frac{(n_i + g_i - 1)!}{n_i! \, (g_i - 1)!}$$

$$\ln w(i) = \ln (n_i + g_i - 1)! - \ln n_i! - \ln (g_i - 1)!$$

Now, $(n_i + g_i) >> (n_i + g_i - 1)$ & $(g_i - 1) << g_i$

$\therefore \ln w(i) = \ln (n_i + g_i)! - \ln n_i! - \ln g_i!$

Stirling's relation

$$= (n_i + g_i) \ln (n_i + g_i) - (n_i + g_i) - n \ln n + n$$
$$- g_i \ln g_i + g_i$$

$$= n_i \ln (n_i + g_i) + g_i \ln (n_i + g_i) - (n_i + g_i) - n_i \ln n_i$$
$$+ n_i - g_i \ln g_i + g_i$$

$$= n_i \ln \left(\frac{n_i + g_i}{n_i} \right) + g_i \ln \left(\frac{n_i + g_i}{g_i} \right)$$

$$\ln w(i) = n_i \ln \left(\frac{g_i}{n_i} + 1 \right) + g_i \ln \left(1 + \frac{n_i}{g_i} \right)$$

$$\ln W(n_i) = \sum_i \ln w(i)$$

$$\ln W(n_i^\circ) = \sum_i n_i \ln\left(\frac{g_i^\circ}{n_i^\circ} + 1\right) + g_i \ln\left(1 + \frac{n_i^\circ}{g_i}\right)$$

In general

$$\ln W(n_i^\circ) = \sum_i n_i \ln\left(\frac{g_i^\circ}{n_i^\circ} - a\right) - \frac{g}{a} \ln\left(1 - a\frac{n_i^\circ}{g_i}\right) \quad (15)$$

if $a = -1$ for B.E case

$= +1$ for F.D case

$= 0$ for M.B case

Thus eq. (14) becomes

$$\sum_i \left[\ln\left(\frac{g_i^\circ}{n_i^\circ} - a\right) - \alpha - \beta\varepsilon_i\right]_{n_i^\circ = n_i^*} \delta n_i = 0 \quad (16)$$

Above eq. holds if

$$\ln\left(\frac{g_i^\circ}{n_i^*} - a\right) - \alpha - \beta\varepsilon_i = 0 \quad (17)$$

$$n_i^* = \frac{g_i^\circ}{e^{\alpha+\beta\varepsilon_i} + a} \quad (18)$$

or

$$\frac{n_i^*}{g_i} = \frac{1}{e^{\alpha+\beta\varepsilon_i} + a} \quad (18a)$$

i is the most probable no. of particles per energy level for i^{th} cell.

Above result does not depend on how the energy levels are grouped into cells, as long as $g_i >> 1$

$\Rightarrow$ Eq. (15) becomes

$$\frac{S}{k} \simeq \ln W(n_i^*) = \sum_i \left[n_i^* \ln\left(\frac{g_i}{n_i^*} - a\right) - \frac{g_i}{a} \ln\left(1 - a\frac{n_i^*}{g_i}\right) \right]$$

$$= \sum_i \left[n_i^* (\alpha + \beta\varepsilon_i) + \frac{g_i}{a} \ln\left(1 + a e^{-\alpha - \beta\varepsilon_i}\right) \right]$$

(19) $\longrightarrow$

$$= \alpha N + \beta E + \sum_i \frac{g_i}{a} \ln\left(1 + a e^{-\alpha - \beta\varepsilon_i}\right)$$

or $$\frac{1}{a} \sum_i g_i \ln\left(1 + a e^{-\alpha - \beta\varepsilon_i}\right) = \frac{S}{k} - \alpha N - \beta E \quad \text{— (20)}$$

$$\frac{1}{a} \sum_i g_i \ln\left(1 + a e^{-\alpha - \beta\varepsilon_i}\right) = \frac{S}{k} + \frac{\mu}{kT} N - \frac{1}{kT} E$$

$$= \frac{G - (E - TS)}{kT} = \frac{PV}{kT} \quad \text{— (22)}$$

$$\alpha = -\frac{\mu}{kT} \qquad \beta = \frac{1}{kT} \quad \text{— (21)}$$

$$\therefore \quad PV = \frac{kT}{a} \sum_i g_i \ln\left(1 + a e^{-\alpha - \beta\varepsilon_i}\right) \quad \text{— (23)}$$

For M-B case, $a \to 0$

$$PV = kT \sum_i g_i e^{-\alpha - \beta\varepsilon_i} = kT \sum_i n_i^*$$

$$\boxed{PV = NkT} \quad \text{— (24)}$$

Classical Ideal Gas.

The term $a^{-1}\sum( )$ is equal to $\frac{PV}{kT}$, is identical to q-potential of the ideal gas and contains microscopic properties of system

Ideal Gas In Other Quantum-Mechanical Ensembles

In the canonical ensemble, the partition function

$$Q_N(V,T) = \sum_E e^{-\beta E} \quad \text{——— (1)}$$

where E denotes energy eigenvalue satisfying

$$E = \sum_\varepsilon n_\varepsilon \varepsilon, \quad \text{——— (2)}$$

ε = single particle energy (s)

n_ε = no. of particles in single-particle energy state ε, satisfying

$$\sum_\varepsilon n_\varepsilon = N \quad \text{——— (3)}$$

Eq. (1) can be written as,

$$Q_N(V,T) = \sum_{(n_\varepsilon)} g(n_\varepsilon) e^{-\beta \sum_\varepsilon n_\varepsilon \varepsilon} \quad \text{——— (4)}$$

where $g(n_\varepsilon)$ is statistical weight factor corresponding to distribution set (n_ε) ——— (5)

Now, we know $g_{B\text{-}E}(n_\varepsilon) = 1$

$$g_{F\text{-}D}(n_\varepsilon) = \begin{cases} 1 & \text{if all } n_\varepsilon = 0 \text{ or } 1 \\ 0 & \text{otherwise} \end{cases} \quad \text{— (6)}$$

$$g_{M\text{-}B}(n_\varepsilon) = \prod_\varepsilon \frac{1}{n_\varepsilon!} \quad \text{— (7)}$$

we are considering here single-particle state as individual states, without grouping them into cells (i.e $g_i = 1$)

Substituting values in eq. (4)

M-B Canc

$$Q_N(V,T) = \sum_{n_\varepsilon}{}' g(n_\varepsilon) e^{-\beta \sum_\varepsilon n_\varepsilon \varepsilon}$$

$$= \sum_{n_\varepsilon}{}' \left[\left(\prod_\varepsilon \frac{1}{n_\varepsilon!} \right) \prod_\varepsilon \left(e^{-\beta\varepsilon} \right)^{n_\varepsilon} \right]$$

$$Q_N(V,T) = \frac{1}{N!} \sum_{n_\varepsilon}{}' \left[\frac{N!}{\prod_\varepsilon n_\varepsilon!} \prod_\varepsilon \left(e^{-\beta\varepsilon} \right)^{n_\varepsilon} \right] \quad \text{——— (8)}$$

using multinomial thm, we can write above eq. as

$$Q_N(V,T) = \frac{1}{N!} \left[\sum_\varepsilon e^{-\beta\varepsilon} \right]^N$$

$$= \frac{1}{N!} \left[Q_1(V,T) \right]^N \quad \text{——— (9)}$$

we can obtain $Q_1(V,T)$ for single-particle states with energies lying b/w ε & $\varepsilon + d\varepsilon$ as,

$$Q_1(V,T) \equiv \sum_\varepsilon e^{-\beta\varepsilon} \approx \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^\infty e^{-\beta\varepsilon} \varepsilon^{1/2} d\varepsilon$$

$$= \frac{V}{\lambda^3} \quad \text{——— (10)}$$

$$\lambda = \sqrt{\frac{h}{2\pi m k T}}$$

mean thermal wavelength of the particles

$$\Rightarrow \boxed{Q_N(V,T) = \frac{V^N}{N! \lambda^{3N}}} \quad \text{——— (11)}$$

from partition fn we can determine thermodynamic of system

Now, in GCE, the grand partition fn can be written as

$$\underline{Q}(z, V, T) = \sum_{N=0}^{\infty} z^N Q_N(V,T) = \exp\left(\frac{zV}{\lambda^3}\right) \quad (12)$$

Grand Partition fn

using eq. (5) & (6) in eq. (4) we get

$$Q_N(V,T) = \sum_{(n_\varepsilon)}{}' \left(e^{-\beta \sum n_\varepsilon \varepsilon}\right) \quad (13)$$

depending upon value of $g(n_\varepsilon)$, above eq. makes relevance to B-E or F-D statistics.

$$\text{So } \underline{Q}(z, V, T) = \sum_{N=0}^{\infty} \left[z^N \sum_{(n_\varepsilon)}{}' e^{-\beta \sum_\varepsilon n_\varepsilon \varepsilon} \right] \quad (14a)$$

$$= \sum_{N=0}^{\infty} \left[\sum_{(n_\varepsilon)}{}' \prod_\varepsilon \left(z e^{-\beta\varepsilon}\right)^{n_\varepsilon} \right] \quad (14b)$$

the primed summation is over all value of n_ε $\left(\Sigma n_\varepsilon = N\right)$, the second summation is over all possible values of N.

So this is equivalent to all possible value of n_ε, independently of one another

i.e we can write

$$\underline{Q}(z, V, T) = \sum_{n_0, n_1, \cdots} \left[\left(z e^{-\beta\varepsilon_0}\right)^{n_0} \left(z e^{-\beta\varepsilon_1}\right)^{n_1} \cdots \right]$$

$$= \left[\sum_{n_0} \left(z e^{-\beta\varepsilon_0}\right)^{n_0} \right] \left[\sum_{n_1} \left(z e^{-\beta\varepsilon_1}\right)^{n_1} \right] \cdots \quad (15)$$

$$\underline{Q}(z,V,T) = \begin{cases} \prod_{\varepsilon} \frac{1}{(1-ze^{-\beta\varepsilon})} & \text{in B-E case, } ze^{-\beta\varepsilon} < 1 \quad (114) \\ \prod_{\varepsilon} (1+ze^{-\beta\varepsilon}) & \text{in F-D case} \end{cases}$$

(16a) (16b)

$\because n_\varepsilon = 0,1,2\cdots$ B-E
$= 0$ or 1 in F-D

Now, we know q-potential is log of grand partition fn.

$$q(z,V,T) = \frac{PV}{KT} \equiv \ln \underline{Q}(z,V,T)$$

$$q(z,V,T) = \frac{PV}{KT} = \mp \sum_{\varepsilon} \ln(1 \mp ze^{-\beta\varepsilon}) \quad (17)$$

comparing with eq. (23), p-(110), for $g_i = 1$, in above eq. (17), upper sign is for Bose statistics & lower for Fermi statistics

Also, $$q(z,V,T) \equiv \frac{PV}{KT} = \frac{1}{a} \sum_{\varepsilon} \ln(1+az e^{-\beta\varepsilon}) \quad (18)$$

Q why we use eq. (7) for eq. (4) in Canonical case & eq. (5), (6) for eq. (4) in grand Canonical case?

Where in eq. (18) for $a = 0, -1, +1$ governs the corresponding statistics

Now, we know for M-B case, $a \to 0$

$$\therefore q_{M\text{-}B} = z \sum_{\varepsilon} e^{-\beta\varepsilon} = zQ_1 \quad \text{---(19)}$$

Now, we know that

$$\bar{N} \equiv z\left(\frac{\partial q}{\partial z}\right)_{V,T} = \sum_{\varepsilon} \frac{1}{z^{-1}e^{\beta\varepsilon} + a} \quad \text{---(20)}$$

&

$$\bar{E} \equiv -\left(\frac{\partial q}{\partial \beta}\right)_{z,V} = \sum_{\varepsilon} \frac{\varepsilon}{z^{-1}e^{\beta\varepsilon} + a} \quad \text{---(21)}$$

And, the mean occupation number $\langle n_\varepsilon \rangle$ of level ε is given by

$$\langle n_\varepsilon \rangle = \frac{1}{Q}\left[\frac{-1}{\beta}\left(\frac{\partial Q}{\partial \varepsilon}\right)_{z,T,\text{ all other } \varepsilon}\right]$$

$$\equiv \frac{-1}{\beta}\left(\frac{\partial q}{\partial \varepsilon}\right)$$

$$\langle n_\varepsilon \rangle = \frac{1}{z^{-1}e^{\beta\varepsilon} + a} \quad \text{---(22)}$$

? Discuss the behaviour of $\langle n_\varepsilon \rangle$ for three statistics ?

Occupation Number

We know that mean occupation no. is given by

$$\langle n_\varepsilon \rangle = \frac{1}{z^{-1} e^{\beta\varepsilon} + a} \quad \text{(A)}$$

Now $z = e^{-\alpha}$ so $z^{-1} = e^{\alpha}$

$$\langle n_\varepsilon \rangle = \frac{1}{e^{\alpha} e^{\beta\varepsilon} + a} = \frac{1}{e^{\alpha+\beta\varepsilon} + a} = \frac{n_i^*}{g_i} \quad \text{(B)}$$

eq. 18a p-109 Ideal gas in MCE

from eq. (20), (21) & (22) p-115, we get

$$\bar{N} \equiv \sum_\varepsilon \langle n_\varepsilon \rangle \quad \& \quad \bar{E} = \sum_\varepsilon \langle n_\varepsilon \rangle \varepsilon \quad \text{(C)}$$

Now, we can write $\langle n_\varepsilon \rangle$ as

$$\langle n_\varepsilon \rangle = \frac{1}{z^{-1} e^{\beta\varepsilon} + a} = \frac{1}{e^{\alpha+\beta\varepsilon} + a} = \frac{1}{e^{\left(\frac{-\mu}{KT} + \frac{1}{KT}\varepsilon\right)} + a}$$

$\alpha = -\frac{\mu}{KT}$, $\beta = \frac{1}{KT}$

$$\langle n_\varepsilon \rangle = \frac{1}{e^{\left(\frac{\varepsilon-\mu}{KT}\right)} + a}$$

For F.D Case, $a = 1$

$$\langle n_\varepsilon \rangle = \frac{1}{e^{\frac{\varepsilon-\mu}{KT}} + 1}$$

Now $\langle n_\varepsilon \rangle$ can never exceed unity, i.e $\langle n_\varepsilon \rangle = 0$ or 1

i) if $\varepsilon < \mu$ i.e $\varepsilon - \mu = -ive$, and $|\varepsilon - \mu| >> KT$, then $\langle n_\varepsilon \rangle \to 1$

ii) if $\varepsilon > \mu$ and $|\varepsilon - \mu| >> KT$, then $\langle n_\varepsilon \rangle \longrightarrow 0$

(iii) if $\varepsilon = \mu$, $\langle n_\varepsilon \rangle \to \frac{1}{2}$.

For B-E case :- $a = -1$

$$\langle n_\varepsilon \rangle = \frac{1}{e^{\left(\frac{\varepsilon-\mu}{kT}\right)} - 1}$$

$\to$ So, $\varepsilon > \mu$ for B-E case

$\to$ if $\varepsilon_0 = \mu$, $\langle n_\varepsilon \rangle \to \infty$ i.e occupancy of that energy level approaches infinite. And the system become condensed to one lowest energy state. This phenomenon is referred to as B-E condensate. (BEC)

$\to$ for $\mu < \varepsilon_0$, all values of $(\varepsilon - \mu) = +ive$, so $\langle n_\varepsilon \rangle$ is non singular.

$ze^{-\beta\varepsilon} \leq 1$ for B-E

$z \leq e^{\beta\varepsilon}$

$e^{-\alpha} < e^{\beta\varepsilon}$

$e^{\frac{\mu}{kT}} < e^{\frac{\varepsilon}{kT}}$

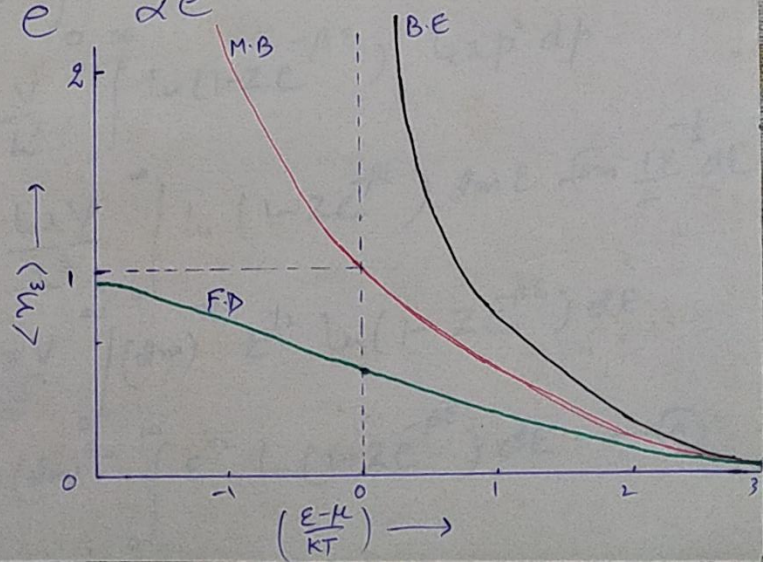
$\mu < \varepsilon$

for M-B case, $a = 0$

$$\langle n_\varepsilon \rangle = \frac{1}{e^{(\varepsilon-\mu)/kT}} = e^{(\mu-\varepsilon)/kT} \propto e^{-\varepsilon/kT}$$

So when $\varepsilon = \mu$

$\langle n_\varepsilon \rangle = 1$



THERMODYNAMICS OF IDEAL BOSE GAS

we know that for ideal Bose-Gas

$$q(z,V,T) \equiv \ln Q_G = \frac{PV}{kT} = -\sum_{\varepsilon} \ln(1 - ze^{-\beta\varepsilon}) \quad \boxed{a=-1} \quad \text{---(1)}$$

Eq. 18 P-114

$$\& \quad N \equiv \sum_{\varepsilon} \langle n_\varepsilon \rangle = \sum_{\varepsilon} \frac{1}{z^{-1}e^{\beta\varepsilon} - 1} \quad \text{---(2)}$$

Eq. 20 P-115

$z = e^{-\alpha} = e^{\mu/kT}$ ---(3)

where, the summation is over single-particle states. Now, for very large V, the spectrum of energy levels is continuous. Thus, the summation can be replaced with integration.

So, eq. (1) becomes

$$\frac{PV}{kT} = -\frac{1}{h^3}\int \ln(1 - ze^{-\beta\varepsilon})\, d^3q\, d^3p$$

$$= -\frac{V}{h^3}\int_0^\infty \ln(1 - ze^{-\beta\varepsilon})\, d^3p$$

$$= -\frac{V}{h^3}\int_0^\infty \ln(1 - ze^{-\beta\varepsilon})\, 4\pi p^2\, dp$$

$$= -\frac{4\pi V}{h^3}\int_0^\infty \ln(1 - ze^{-\beta\varepsilon})\, 2m\varepsilon \sqrt{2m}\, \frac{1}{2}\varepsilon^{-\frac{1}{2}}\, d\varepsilon$$

$$= -\frac{2\pi V}{h^3}\int_0^\infty (2m)^{3/2}\varepsilon^{1/2} \ln(1 - ze^{-\beta\varepsilon})\, d\varepsilon$$

$$\frac{PV}{kT} = \frac{-2\pi V (2m)^{3/2}}{h^3}\int_0^\infty \varepsilon^{1/2} \ln(1 - ze^{-\beta\varepsilon})\, d\varepsilon \quad \text{---(A)}$$

Illy $$N = \frac{2\pi V}{h^3}(2m)^{3/2}\int_0^\infty \frac{\varepsilon^{1/2}}{z^{-1}e^{\beta\varepsilon}-1}\,d\varepsilon$$ — (B)

Now, integration over $d\varepsilon$ ranges from $0 \to \infty$, i.e for $\varepsilon = 0$ eq. (A) & (B) given zero weight to level $\varepsilon = 0$.

So, the eq. (1) & (2) (consequently eq. (A) & (B)) has to be split into two parts (i) for $\varepsilon = 0$ (ii) Rest of single particle energy levels ε.

So, eq. (A) & (B) can be re-written as

$$\frac{PV}{kT} = \frac{-2\pi V}{h^3}(2m)^{3/2}\int_0^\infty \varepsilon^{1/2}\ln(1-ze^{-\beta\varepsilon})\,d\varepsilon - \ln(1-z)$$

$$\frac{P}{kT} = \frac{-2\pi}{h^3}(2m)^{3/2}\int_0^\infty \varepsilon^{1/2}\ln(1-ze^{-\beta\varepsilon})\,d\varepsilon - \frac{1}{V}\ln(1-z)$$ — (5)

Illy $$\frac{N}{V} = \frac{2\pi}{h^3}(2m)^{3/2}\int_0^\infty \frac{\varepsilon^{1/2}}{z^{-1}e^{\beta\varepsilon}-1} + \frac{1}{V}\frac{z}{1-z}$$ — (6)

No. of particles per unit vol. in $\varepsilon = 0$

Still taking zero, ∵ it will not contribute in integration

Now, Let N_0 be no. of particle in energy state $\varepsilon = 0$

i.e $N_0 = \langle n_0\rangle = \frac{z}{1-z}$ $\quad \langle n_0\rangle = 0, 1, 2, \ldots \infty$ B-E Case

Now when $\langle n_0\rangle = 0$, $z = 0$ & when $\langle n_0\rangle = \infty$, $z = 1$

$\Rightarrow \quad 0 \le z \le 1$

Now, as $z \to 1$, the $\varepsilon = 0$ state in eq. (6) gets occupied by significant no. of particles

OR the contribution of second term of eq. (6) becomes significant at $\varepsilon = 0$ when z approaches unity

This accumulation of particles into single state $\varepsilon = 0$ leads to the phenomenon of B-E condensate.

we now for $\varepsilon = 0$,

$$N_0 = \frac{z}{1-z} \quad \text{or} \quad z = \frac{N_0}{N_0+1}$$

& eq. (5)

Now, the last term can be written as

$$\frac{-1}{V}\ln(1-z) = -\frac{1}{V}\ln\left(1 - \frac{N_0}{N_0+1}\right) = \frac{1}{V}\ln(N_0+1)$$

Now, N_0 is no. of particles in $\varepsilon = 0$, have highest value N

the underlined above term $V^{-1}\ln(N_0+1)$ is atmost $O(N^{-1}\ln N)$

$(\because V \propto N)$

this term $\therefore$ is negligible for all values of z & hence may be dropped altogether.

$\therefore$ eq. (5) becomes.

$$\frac{P}{kT} = -\frac{2\pi}{h^3}(2m)^{3/2}\int_0^\infty \varepsilon^{1/2}\ln(1 - ze^{-\beta\varepsilon})\,d\varepsilon$$

put $x = \beta\varepsilon \quad dx = \beta\, d\varepsilon$

$$\frac{P}{kT} = \frac{-2\pi}{h^3}(2m)^{3/2}\int_0^\infty \left(\frac{x}{\beta}\right)^{1/2} \ln(1-ze^{-x})\,\frac{dx}{\beta}$$

$$= \frac{-2\pi}{h^3}(2\pi mkT)^{3/2}\int_0^\infty x^{1/2}\ln(1-ze^{-x})\,dx$$

$$= \frac{1}{\lambda^3} g_{5/2}(z) \quad \text{--- (7)} \quad \text{where } \lambda = \frac{h}{(2\pi mkT)^{1/2}}$$

Eq. (6) can be written as

$$\frac{N-N_0}{V} = \frac{2\pi(2mkT)^{3/2}}{h^3}\int_0^\infty \frac{x^{1/2}}{z^{-1}e^x - 1}$$ (9)

$$\frac{N-N_0}{V} = \frac{1}{\lambda^3} g_{3/2}(z) \quad \text{--- (8)} \qquad \lambda = \frac{h}{(2\pi mkT)^{1/2}}$$

where $g_\nu(z)$ are Bose-Einstein functions, defined as

$$g_\nu(z) = \frac{1}{\Gamma(\nu)}\int_0^\infty \frac{x^{\nu-1}\,dx}{z^{-1}e^x - 1} = z + \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} + \cdots$$ (10)

Now Internal energy of this system is given by

$$U = -\left(\frac{\partial}{\partial\beta}\ln Q\right)_{z,V} = kT^2\left\{\frac{\partial}{\partial T}\left(\frac{PV}{kT}\right)\right\}_{z,V}$$ (11)

$$= kT^2 V g_{5/2}(z)\left\{\frac{d}{dt}\left(\frac{1}{\lambda^5}\right)\right\} = \frac{3}{2}kT\frac{V}{\lambda^3} g_{5/2}(z)$$

or $$P = \frac{2}{3}\left(\frac{U}{V}\right) \quad \text{--- (12)}$$

Now, at high temperature, z will have small value $\therefore z = e^{-\tau}$

$z = e^{\frac{\mu}{kT}}$. Then, $N_0 = \frac{z}{1-z}$ will also be small as compare to N (total no. of particles in the system).

$\therefore$ we can write eq. (8) as follows.

$$\frac{N}{V} = \frac{2\pi(2mkT)^{3/2}}{h^3} \int_0^\infty \frac{x^{1/2}}{z^{-1}e^x - 1} = \frac{1}{\lambda^3} g_{3/2}(z)$$

Now let $n = \frac{N}{V}$ & $v = \frac{1}{n}$

$$\therefore \quad n = \frac{1}{\lambda^3} g_{3/2}(z)$$

$$\& \quad g_{3/2}(z) = \frac{\lambda^3}{v} \qquad \text{(b)}$$

$$\text{or} \quad z + \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \cdots = \frac{\lambda^3}{v}$$

In above eq. $\frac{\lambda^3}{v}$ is written as expansion of terms of z ($g_{3/2}(z)$). By inverting above eq. it is allowed to write z ($g_{3/2}(z)$) in terms of expansion of $\frac{\lambda^3}{v}$

Now from eq. (7)

$$\frac{P}{kT} = \frac{1}{\lambda^3} g_{5/2}(z)$$

$$\frac{PV}{kT} = \frac{V}{\lambda^3} g_{5/2}(z)$$

$$\frac{PV}{NkT} = \frac{V}{Nd^3} g_{S1/2}(z)$$

$$\frac{PV}{NkT} = \frac{n^{-1}}{d^3} g_{S1/2}(z) = \frac{v}{d^3} g_{S1/2}(z)$$

or $$\frac{PV}{NkT} = \frac{g_{S1/2}(z)}{\left(\frac{d^3}{v}\right)} \quad \text{——} \quad (C)$$

In above eq. also we are allowed to expand $g_{S1/2}(z)$ in term of d^3 by writing as

$$g_{S1/2}(z) = \sum_{l=1}^{\infty} a_l \left(\frac{d^3}{v}\right)^l$$

$\therefore$ Eq. (C) becomes

$$\frac{PV}{NkT} = \sum_{l=1}^{\infty} a_l \left(\frac{d^3}{v}\right)^{l-1} \quad \text{——} \quad (13)$$

The above eq. (13) represents equation of state in the form of <u>virial expansion</u>. Where a_l are called <u>virial coefficients</u> with values.

$$\left.\begin{aligned} a_1 &= 1, \quad a_2 = \frac{-1}{4\sqrt{2}} = -0.17678 \\ a_3 &= -\left(\frac{2}{9\sqrt{3}} - \frac{1}{8}\right) = -0.00330 \\ a_4 &= -\left(\frac{3}{32} + \frac{5}{32\sqrt{2}} - \frac{1}{2\sqrt{6}}\right) = -0.00011 \end{aligned}\right\} \quad \text{——} \quad (14)$$

$$\frac{PV}{NkT} = a_1 + a_2\left(\frac{\lambda^3}{v}\right) + a_3\left(\frac{\lambda^3}{v}\right)^2 + \cdots \quad \text{(D)}$$

Now $$C_v = \left(\frac{\partial U}{\partial T}\right)_{N,V} = \frac{\partial}{\partial T}\left(\frac{3}{2}PV\right)_{N,V} = \frac{3}{2}\frac{\partial}{\partial T}\left((PV)\right)_{N,V}$$

$$\frac{C_v}{Nk} = \frac{3}{2}\frac{\partial}{\partial T}\left(\frac{PV}{Nk}\right)_v$$

$$= \frac{3}{2}\left[\frac{\partial}{\partial T}\left(a_1 T + a_2\left(\frac{\lambda^3}{v}\right)T + a_3\left(\frac{\lambda^3}{v}\right)^2 T + \cdots\right]\right.$$

$$= \frac{3}{2}\frac{\partial}{\partial T}\left[T\sum_{l=1}^{\infty} a_l\left(\frac{\lambda^3}{v}\right)^{l-1}\right] \leftarrow \{\text{Diff. w.r.t } T \text{ by product rule}\}$$

$$= \frac{3}{2}\sum_{l=1}^{\infty}\frac{5-3l}{2}a_l\left(\frac{\lambda^3}{v}\right)^{l-1}$$

Put value of a_l & l

$$\frac{C_v}{Nk} = \frac{3}{2}\left[1 + 0.0884\left(\frac{\lambda^3}{v}\right) + 0.0066\left(\frac{\lambda^3}{v}\right)^2 + 0.0004\left(\frac{\lambda^3}{v}\right)^3 + \cdots\right] \quad \text{(15)}$$

Now as $T \to \infty$, $\lambda \to 0$

$\therefore$ eq. (D) becomes

$$\frac{PV}{NkT} = 1, \quad \underline{\underline{PV = NkT}}$$

& eq. (15) becomes $\frac{C_v}{Nk} = \frac{3}{2}$, $\underline{\underline{C_v = \frac{3}{2}Nk}}$.

$\Rightarrow$ At high temp, ideal Bose gas behaves like a classical ideal gas

Low Temperature, Since $\lambda \propto \frac{1}{T}$, so at low temperature λ becomes significant.

So eq. (8) becomes

$$\frac{N-N_0}{V} = \frac{g_{3/2}(z)}{\lambda^3} = \frac{(2\pi m kT)^{3/2}}{h^3} g_{3/2}(z)$$

or $$\frac{N_e}{V} = \frac{(2\pi m kT)^{3/2}}{h^3} g_{3/2}(z) \quad (16)$$ where $N_e = N - N_0$

N_e is no. of particles in the excited state ($\epsilon \neq 0$)

Now, unless z gets extremely close to unity, $N_e \simeq N$

And we know $0 \leq z \leq 1$,

$\Rightarrow$ for $g_{3/2}(z)$ increases monotonically with z & is bounded, with largest value ($z=1$)

$$g_{3/2}(1) = 1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + \cdots \simeq 2.612 \quad (17)$$

or we can write $g_{3/2}(z) \leq 2.612$ (18)

$\therefore$ Eq. (16) becomes.

$$N_e \leq V \frac{(2\pi m kT)^{3/2}}{h^3} (2.612) \quad (19)$$

Eq. (19) gives the total no. of particles (for V, $\& T$) in all the excited state taken together is bounded.

Now, as long as the actual no. of particles in the system is less than this limiting value, everything is well and good, practically all the particles in the system are distributed over the excited states, where the precise value of z is determined by eq (16) with $N_e \simeq N$.

However, if the actual no. of particles exceed this limiting value, then the excited states will hold no. of particles

$$N_e = \frac{V\,(2\pi m KT)^{3/2}}{h^3}\, 2.612 \qquad \text{——} (20)$$

& rest will be pushed into the ground state $\varepsilon = 0$

i.e $$N_0 = N - \left\{\frac{V(2\pi m KT)^{3/2}}{h^3}\, 2.612\right\} \qquad \text{——} (21)$$

where precise value of z is now determined by

$$z = \frac{N_0}{N_0+1} \simeq 1 - \frac{1}{N_0} \simeq 1 \qquad (\text{As } N_0 \text{ is very large}) \qquad (22)$$

This phenomenon of macroscopically large no. of particles accumulating in a single quantum state ($\varepsilon = 0$) is generally referred to as the phenomenon of Bose-Einstein condensation.

This phenomenon has familiarity with vapor condensation into liquid (OR is it!)

The B-E-C occurs when no. of particle exceed N_e. So, the condition of BEC is

$$N > \frac{VT^{3/2}(2\pi mk)^{3/2}}{h^3} 2.613 \quad \text{---} (23)$$

or if we hold N & V constant & vary T

$$T < T_c = \frac{h^2}{2\pi mk}\left[\frac{N}{V\,2.613}\right]^{2/3} \quad \text{---} (24)$$

where, T_c is the characteristic temperature that depends on the particle mass m & the particle density $\frac{N}{V}$ in the system.

Accordingly, for $T < T_c$, the system is a mixture of two phases.

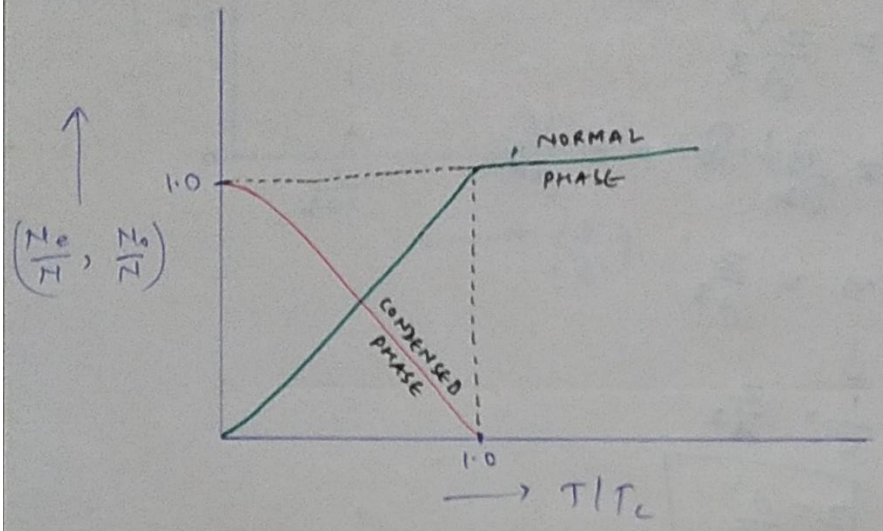
(i) Normal phase, consisting of $N_e \{= N\left(\frac{T}{T_c}\right)^{3/2}\}$ particles distributed over the excited states ($\varepsilon \neq 0$)

(ii) a condensed phase, consisting of $N_0 \{= N - N_e\}$ particles accumulated in the ground state ($\varepsilon = 0$).

The variation of normal & condensed phase with temperature is as shown in figure.

for $T \to T_c$, the condensate fraction varies as

$$\frac{N_0}{N} = 1 - \left(\frac{T}{T_c}\right)^{3/2} \simeq \frac{3}{2}\left(\frac{T_c - T}{T_c}\right) \quad \text{——} (25)$$



To plot z Vs T, it is similar to plot z Vs $\left(\frac{v}{\lambda^3}\right)$ $\because \lambda \propto \frac{1}{T}$

$\therefore$ for $0 \le z \le 1$, maximum $g_{3/2}(1) = 2.612$

$\therefore$ for $0 \le \left(\frac{v}{\lambda^3}\right) \le (2.612)^{-1} \simeq 0 \le T \le T_c$

And we know for low temp $z \simeq 1$.,

$\because z = \frac{N_0}{1+N_0} = \frac{1}{1+\frac{1}{N_0}}$

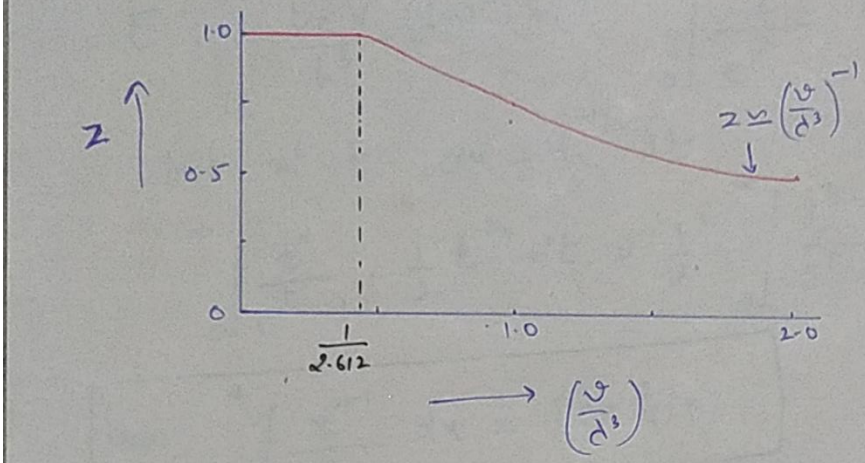
$z = \left(1+\frac{1}{N_0}\right)^{-1} \simeq 1 - \frac{1}{N_0}$

$z \simeq 1$ as low T, $N_0 \to$ max!

Now for $\left(\frac{v}{\lambda^3}\right) > (2.612)^{-1}$, $z < 1$ & is determined by relation (

$$g_{3/2}(z) = \left(\frac{\lambda^3}{v}\right) < 2.612 \quad \text{——} (26) \quad (\text{eq. } 8) \quad p\text{-}121$$

for $\left(\frac{v}{\lambda^3}\right) \gg 1$, $g_{3/2}(z) \ll 1$ & hence $z \ll 1$ under these circumstances $g_{3/2}(z) \simeq z$, so $z \simeq \frac{\lambda^3}{v}$ (eq. 5, p-122) which is the classical case.



C_v Vs T

For low temperature (i.e $T < T_c$), when $z \simeq 1$

we know $E = \sum_\varepsilon \langle n_\varepsilon \rangle \varepsilon$

$$= \sum_\varepsilon \frac{1}{z^{-1} e^{\beta\varepsilon} - 1} \varepsilon$$

$$= \sum_\varepsilon \frac{1}{e^{\beta\varepsilon} - 1} \varepsilon \quad (\because z \simeq 1)$$

Converting summation into integral

$$E = \frac{V 4\pi}{h^3} \int_0^\infty \frac{p^2}{2m} \frac{1}{e^{p^2/2mkT} - 1} p^2 dp.$$

put $\frac{p^2}{2mkT} = x^2 \quad dx = \frac{dp}{(2mkT)^{1/2}}$

$$E = \frac{V \cdot 4\pi}{h^3} \int_0^\infty \frac{x^2 kT \cdot x^2 (2mkT)(2mkT)^{1/2}}{e^{x^2} - 1} dx$$

$$E = \frac{4\pi V}{h^3}(2m)^{3/2}(kT)^{5/2}\int_0^\infty \frac{x^4}{e^{x^2}-1}\,dx$$

put $x^2 = t$, $dx = \frac{t^{-1/2}}{2}\,dt$

$$\int_0^\infty \frac{t^2}{e^t-1}\cdot\frac{1}{2}t^{-1/2}\,dt = \frac{1}{2}\int_0^\infty \frac{t^{3/2}\,dt}{e^t-1} = \frac{1}{2}\int_0^\infty \frac{t^{\frac{5}{2}-1}}{e^t-1}\,dt$$

Now, $\int_0^\infty \frac{x^{n-1}}{e^x-1}\,dx = \Gamma(n)\,\xi(n)$

So above integral becomes. $\frac{1}{2}\times\Gamma\left(\frac{5}{2}\right)\xi\left(\frac{5}{2}\right)$

which is equal to $\frac{1}{2}\times\frac{3}{2}\times\frac{1}{2}\times\sqrt{\pi}\times 1.341 = \frac{3}{8}\sqrt{\pi}(1.341)$

So, $E = \frac{4\pi V}{h^3}(2m)^{3/2}(kT)^{5/2}\times\frac{3}{8}\sqrt{\pi}\times 1.341$

$$T_c = \frac{h^2}{2\pi mk}\left[\frac{N}{V\,2.612}\right]^{2/3} \quad \text{(eq. 24, P-127)}$$

$$\frac{N}{V\cdot(2.612)} = \left[T_c\,\frac{2\pi mk}{h^2}\right]^{3/2}$$

$$V = \frac{N}{2.612}\left[\frac{h^2}{2\pi mkT_c}\right]^{3/2}$$

$$\therefore E = \frac{4\pi}{h^3}\frac{N}{2.612}\left[\frac{h^2}{2\pi mkT_c}\right]^{3/2}\cdot(2m)^{3/2}(kT)^{5/2}\,\frac{3}{8}\sqrt{\pi}\,(1.341)$$

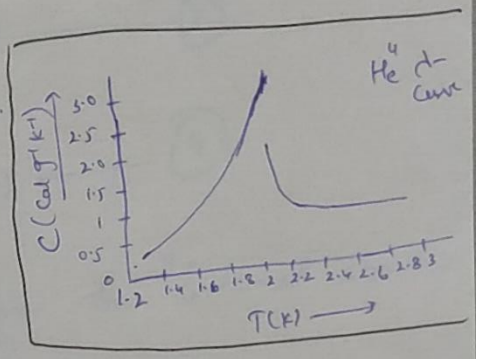
$$\therefore \quad E = 0.77\, NkT\, \frac{T^{3/2}}{T_c^{3/2}}$$

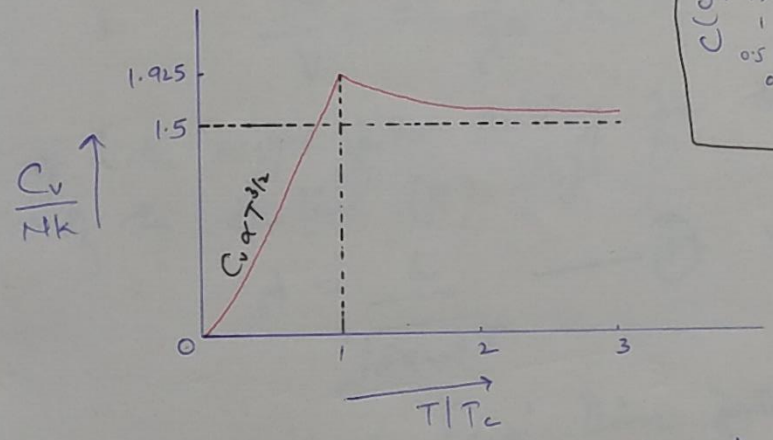
$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = 0.77 \times \frac{5}{2} Nk \left(\frac{T}{T_c}\right)^{3/2}$$

$$C_v = 1.93\, Nk \left(\frac{T}{T_c}\right)^{3/2}$$

As $T \to 0K$ $\quad C_v \to 0$

$T \to T_c$ $\quad C_v = 1.93\, Nk$





Q why He^4 forms BEC but not He^3 ?

THERMODYNAMICS OF IDEAL FERMI GAS

we know for Ideal Fermi Gas

$$\frac{PV}{kT} = \ln \mathcal{Q} = \sum_\varepsilon \ln\left(1 + z e^{-\beta\varepsilon}\right) \longrightarrow (1)$$

$$\& \quad N \equiv \sum \langle n_\varepsilon \rangle = \sum_\varepsilon \frac{1}{z^{-1} e^{\beta\varepsilon} + 1} \longrightarrow (2)$$

$\langle n_\varepsilon \rangle = 0$, when $z = 0$

$\langle n_\varepsilon \rangle = 1$, when $z = \infty$

$0 \le z \le \infty$

BEC can not occur in Fermi Gas because of the restriction imposed by Pauli's Exclusion Principle. (However, low T Fermi Gas display its own quantum behavior)

The summation in eq. ① & ②, if replaced with integration, can be represented as

$$\frac{P}{kT} = \frac{g}{\lambda^3} f_{5/2}(z) \quad \text{——} ③$$

&

$$\frac{N}{V} = \frac{g}{\lambda^3} f_{3/2}(z) \quad \text{——} ④$$

g is the weight factor arising from the "internal structure" of the particle (e.g. spin)

$$\lambda = \frac{h}{\sqrt{2\pi m k T}} \quad \text{——} ⑤$$ mean thermal wavelength

while $f_\nu(z)$ are Fermi-Dirac functions, defined as

$$f_\nu(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty \frac{x^{\nu-1}}{z^{-1} e^x + 1} dx = z - \frac{z^2}{2^\nu} + \frac{z^3}{3^\nu} - \cdots$$

——— ③ └ ⑥

Combining eq. ③ & ④ we get equation of state of the Fermi Gas.

Now, internal energy U of the Fermi gas

$$U = -\left(\frac{\partial}{\partial \beta} \ln Q\right)_{z,V}$$

$$U = kT^2 \left(\frac{\partial}{\partial T} \ln Q\right)_{z,V} \qquad \text{(using eq ③, ④)}$$

$$U = \frac{3}{2} kT \frac{gV}{\lambda^3} f_{5/2}(z) = \frac{3}{2} NkT \frac{f_{5/2}(z)}{f_{3/2}(z)} \quad \text{— ⑦}$$

$$\Rightarrow \boxed{P = \frac{2}{3} \frac{U}{V}} \quad \text{— ⑧}$$

Now specific heat C_v, $C_v = \left(\frac{\partial U}{\partial T}\right)_{N,V}$

$$C_v = \frac{3}{2} Nk \frac{\partial}{\partial T}\left(T \cdot \frac{f_{5/2}(z)}{f_{3/2}(z)}\right)$$

$$= \frac{3}{2} Nk \left\{ \frac{f_{5/2}(z)}{f_{3/2}(z)} + \frac{T}{f_{3/2}(z)} \frac{\partial}{\partial T} f_{5/2}(z) + T f_{5/2}^{(z)} \frac{\partial}{\partial T} \frac{1}{f_{3/2}^{(z)}} \right\}$$

Now $\frac{\partial}{\partial z} f_\nu(z) = \frac{1}{z} f_{\nu-1}^{(z)}$

& $\frac{1}{z}\left(\frac{\partial z}{\partial t}\right)_{V,N} = \frac{-3}{2T} \frac{f_{3/2}(z)}{f_{1/2}(z)}$ — ⑨

$$\therefore C_v = \frac{3}{2} Nk \frac{f_{5/2}(z)}{f_{3/2}(z)} + \frac{\frac{3}{2} NkT}{f_{3/2}(z)} \frac{\partial f_{5/2}(z)}{\partial z} \frac{\partial z}{\partial T} + \frac{3}{2} NkT f_{5/2}^{(z)}$$

$$(-1) f_{3/2}^{-2}(z) \frac{\partial f_{3/2}(z)}{\partial z} \frac{\partial z}{\partial T}$$

$$\frac{\partial}{\partial T} f_{3/2}(z) = \frac{\partial}{\partial T}\left(\frac{Nd^3}{Vg}\right)$$

$$\frac{\partial}{\partial z} f_{3/2}(z) \frac{\partial z}{\partial T} = \frac{-3}{2T} \frac{Nd^3}{Vg}$$

$$\frac{1}{z} f_{1/2}(z) \frac{\partial z}{\partial T} = \frac{-3}{2T} \frac{Nd^3}{Vg}$$

$$\frac{1}{z} \frac{\partial z}{\partial T} = \frac{-3}{2T} \frac{f_{3/2}(z)}{f_{1/2}(z)}$$

$$C_v = \frac{3}{2}Nk\frac{f_{5/2}(z)}{f_{3/2}(z)} + \frac{\frac{3}{2}NkT}{f_{3/2}(z)}\frac{1}{z}f_{3/2}(z)\cdot\left(\frac{-3}{2T}\right)\frac{f_{3/2}(z)}{f_{1/2}(z)}\cdot z$$

$$+ \frac{3}{2}NkT\, f_{5/2}(z)\,(-1)\frac{1}{f_{3/2}(z)}\frac{1}{z}f_{1/2}(z)\left(\frac{-3}{2T}\right)\frac{f_{3/2}(z)}{f_{1/2}(z)}z$$

$$C_v = \frac{3}{2}Nk\frac{f_{5/2}(z)}{f_{3/2}(z)} - \frac{9}{4}Nk\frac{f_{3/2}(z)}{f_{1/2}(z)} + \frac{9}{4}Nk\frac{f_{5/2}(z)}{f_{3/2}(z)}$$

$$C_v = Nk\left[\frac{15}{4}\frac{f_{5/2}(z)}{f_{3/2}(z)} - \frac{9}{4}\frac{f_{3/2}(z)}{f_{1/2}(z)}\right]$$

$$\frac{C_v}{Nk} = \frac{15}{4}\frac{f_{5/2}(z)}{f_{3/2}(z)} - \frac{9}{4}\frac{f_{3/2}(z)}{f_{1/2}(z)} \quad \text{——} (10)$$

Now, Helmholtz free energy

$$G = A + PV \quad \text{or} \quad A = G - PV$$

$$A \equiv N\mu - PV$$

$$= N\left[kT\ln z - \frac{2}{3}U\right]$$

$$A = N\left[kT\ln z - \frac{3}{2}kT\frac{f_{5/2}(z)}{f_{3/2}(z)}\right] \quad \text{eq. 7 p-133.}$$

$$A = NkT\left[\ln z - \frac{f_{5/2}(z)}{f_{3/2}(z)}\right] \quad \text{——} (11)$$

Entropy, $S = \frac{U-A}{T}$

$$= \frac{3}{2}Nk\,\frac{f_{5/2}(z)}{f_{3/2}(z)} - Nk\left[\ln z - \frac{f_{5/2}(z)}{f_{3/2}(z)}\right]$$

$$= \frac{5}{2}Nk\,\frac{f_{5/2}(z)}{f_{3/2}(z)} - Nk\ln z$$

$$S = Nk\left[\frac{5}{2}\,\frac{f_{5/2}(z)}{f_{3/2}(z)} - \ln z\right] \quad \text{---(12)}$$

Non-degenerate Classical Ideal gas Case:-
i.e if density of gas is very low and/or its temperature is very high

i.e $f_{3/2}(z) = \frac{nd^3}{g} = \frac{nh^3}{g(2\pi mkT)^{3/2}} << 1$ ---(13)

(from eq. (4))

then for $z << 1$, $f_\nu(z) \simeq z$

then eq. (8), (11) & (12) becomes.

$$P = \frac{NkT}{V}, \quad U = \frac{3}{2}NkT, \quad C_v = \frac{3}{2}Nk. \quad \text{---(14)}$$

$$A = NkT\left\{\ln\left(\frac{nd^3}{g}\right) - 1\right\}. \quad \text{---(15)}$$

$$S = Nk\left[\frac{5}{2} - \ln\left(\frac{nd^3}{g}\right)\right]. \quad \text{---(16)}$$

Now, invert the series in eq. (4) to obtain an expansion for z in powers of $\left(\frac{nd^3}{g}\right)$ & substituting in eq. (3)

$$\frac{PV}{NkT} = \sum_{l=1}^{\infty} (-1)^{l-1} a_l \left(\frac{d^3}{gv}\right)^{l-1} \quad \text{——— (17)} \qquad v = \frac{1}{n}$$

Hly $C_v = \frac{3}{2} Nk \sum_{l=1}^{\infty} (-1)^{l-1} \frac{5-3l}{2} a_l \left(\frac{d^3}{gv}\right)^{l-1}$

$$= \frac{3}{2} Nk \left[1 - 0.0884\left(\frac{d^3}{gv}\right) + 0.0066\left(\frac{d^3}{gv}\right)^2 - 0.0004\left(\frac{d^3}{gv}\right)^3 + \dots\right] \quad \text{——— (18)}$$

(Here z is smaller than unity, but not very small)

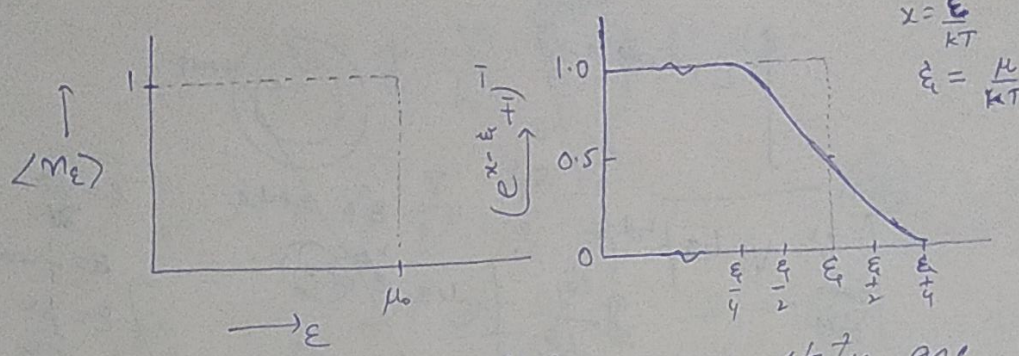
Thus at finite temp, C_v is smaller than $\frac{3}{2}Nk$.

Now, as $\frac{nd^3}{g} >> 1$ (i.e gas is degenerate), and for $\frac{nd^3}{g} \to \infty$, gas is completely degenerate.

Let us consider completely degenerate case i.e $T \to 0$ $\left(\frac{nd^3}{g} \to \infty\right)$. Now, the mean occupation no. becomes

$$\langle n_\varepsilon \rangle \equiv \frac{1}{e^{(\varepsilon-\mu)/kT} + 1} = \begin{cases} 1 & \text{for } \varepsilon < \mu_0 \\ 0 & \text{for } \varepsilon > \mu_0 \end{cases} \quad \text{——— (19)}$$

where μ_0 is the chemical potential of the system at $T=0$. The function $\langle n_\varepsilon \rangle$ will be a step function



At $T=0$, all single particle energy states are completely filled upto $\varepsilon = \mu_0$, with one particle in each state.

while above μ_0 ($\varepsilon > \mu_0$), all single particle energy states are empty. This level (boundary) which demarcates between filled & empty energy levels is called "fermi level".

The limiting value of "μ_0" is called fermi energy, with corresponding momentum called fermi momentum (p_f)

Now, we can write $\int_0^{\varepsilon_f} a(\varepsilon)\, d\varepsilon = N$ ——— (20)

$a(\varepsilon)$ denotes the density of states of the system

$$a(\varepsilon)\, d\varepsilon = g \frac{V}{h^3} 4\pi p^2 dp \quad \text{——— (21)}$$

we can also write $\int_0^{p_f} a(p)\, dp = N$

$$N = g \cdot \frac{V}{h^3} \int_0^{p_F} 4\pi p^2 \, dp$$

$$N = g \frac{V}{h^3} \cdot \frac{4\pi}{3} p_F^3 \quad \text{——— (22)}$$

$$\Rightarrow \quad p_F = \left(\frac{3N}{4\pi g V}\right)^{1/3} h \quad \text{——— (23)}$$

Now $\quad \varepsilon_F = \left(\frac{3N}{4\pi g V}\right)^{2/3} \frac{h^2}{2m} = \left(\frac{6\pi^2 n}{g}\right)^{2/3} \frac{\hbar^2}{2m}$ ——— (24)

Now, the ground-state, or zero-point energy of the system

$$E_0 = g \int_0^{p_F} \frac{4\pi V}{h^3} \left(\frac{p^2}{2m}\right) p^2 \, dp$$

$$= \frac{4\pi g V}{2m h^3} \int_0^{p_F} p^4 \, dp$$

$$E_0 = \frac{2\pi g V}{5m h^3} p_F^5 \quad \text{——— (25)}$$

from eq (21) & (25)

$$\frac{E_0}{N} = \frac{3p_F^2}{10m} = \frac{3}{5}\varepsilon_F \quad \text{——— (26)}$$

from eq. (8) p-133

$P_0 = \frac{2}{3}\left(\frac{E_0}{V}\right)$ is the ground state pressure of the system.

from eq. (26)

$$P_0 = \frac{2}{5} n \varepsilon_F \quad \text{---(27)}$$

where $n = \frac{N}{V}$

putting value of ε_F from eq. (24), we get

$$P_0 = \left(\frac{6\pi^2}{g}\right)^{2/3} \frac{\hbar^2}{5m} n^{5/3} \propto n^{5/3} \quad \text{---(28)}$$

$\Rightarrow$ At $T=0$, the particle constituting the system cannot settle down into single energy state. (as we had in the Bose case) and are therefore spread over a requisite no. of lowest available energy states.

Now, at low but finite temperature, z is finite. (still large than unity)

$\therefore$ we can write

$$f_{5/2}(z) = \frac{8}{15\pi^{1/2}} (\ln z)^{5/2} \left[1 + \frac{5\pi^2}{8} (\ln z)^{-2} + \cdots\right] \quad \text{---(30)}$$

$$f_{3/2}(z) = \frac{4}{3\pi^{1/2}} (\ln z)^{3/2} \left[1 + \frac{\pi^2}{8} (\ln z)^{-2} + \cdots\right] \quad \text{---(31)}$$

& $$f_{1/2}(z) = \frac{2}{\pi^{1/2}} (\ln z)^{\frac{1}{2}} \left[1 - \frac{\pi^2}{24} (\ln z)^{-2} + \cdots\right] \quad \text{---(32)}$$

Now, we know for ideal Fermi Gas

$$\frac{P}{kT} = \frac{g}{\lambda^3} f_{5/2}(z) \quad , \quad \frac{N}{V} = \frac{g}{\lambda^3} f_{3/2}(z)$$

using eq. (31)

$$\frac{N}{V} = \frac{4\pi g}{3}\left(\frac{2m}{h^2}\right)^{3/2}(kT\ln z)^{3/2}\left[1 + \frac{\pi^2}{8}(\ln z)^{-2} + \cdots\right] \quad (33)$$

In zeroth approximation, i.e including 1st term only

$$\frac{N}{V} = \frac{4\pi g}{3}\left(\frac{2m}{h^2}\right)^{3/2}(kT\ln z)^{3/2}$$

$$(kT\ln z)^{3/2} = \frac{N}{V}\cdot\frac{3}{4\pi g}\left(\frac{h^2}{2m}\right)^{3/2}$$

$$kT\ln z \equiv \left(\frac{3N}{4\pi g V}\right)^{2/3}\frac{h^2}{2m} \simeq \mu \quad (34)$$

$$\mu = kT\ln z$$

$\Downarrow$

fermi energy (Eq 24)

In the next approximation (first two terms of $f_{3/2}(z)$)

$$\frac{N}{V} = \frac{g}{\lambda^3}\frac{4}{3\pi^{1/2}}(\ln z)^{3/2}\left[1 + \frac{\pi^2}{8}(\ln z)^{-2}\right]$$

$$kT\ln z = \frac{3N}{4\pi}\frac{N}{V} = \frac{4\pi g}{3}\left(\frac{2m}{h^2}\right)^{3/2}(kT\ln z)^{3/2}\left[1 + \frac{\pi^2}{8}(\ln z)^{-2}\right]$$

$$(kT\ln z)^{3/2} = \frac{3N}{4\pi gV}\left(\frac{h^2}{2m}\right)^{3/2}\left[1+\frac{\pi^2}{8}(\ln z)^{-2}\right]^{-1} \quad (141)$$

$$kT\ln z = \left(\frac{3N}{4\pi gV}\right)^{2/3}\left(\frac{h^2}{2m}\right)\left[1+\frac{\pi^2}{8}(\ln z)^{-2}\right]^{-2/3}$$

$$\mu = kT\ln z = \varepsilon_F\left[1-\frac{\pi^2}{12}\left(\frac{kT}{\varepsilon_F}\right)^2\right] \quad \text{—— (35)}$$

→ using series approxi.

Now, to calculate U, use value of $f_{5/2}(z)$, $f_{3/2}(z)$

in eq. (7)

i.e $U = \frac{3}{2}NkT\,\frac{f_{5/2}(z)}{f_{3/2}(z)}$

$$\frac{U}{N} = \frac{3}{2}kT\;\frac{\frac{8}{15\pi^{1/2}}(\ln z)^{5/2}\left[1+\frac{5\pi^2}{8}(\ln z)^{-2}+\cdots\right]}{\frac{4}{3\pi^{1/2}}(\ln z)^{3/2}\left[1+\frac{\pi^2}{8}(\ln z)^{-2}+\cdots\right]}$$

$$= \frac{3}{2}kT\times\frac{2}{5}\ln z\left[1+\frac{\pi^2}{2}(\ln z)^{-2}+\cdots\right]$$

$$\frac{U}{N} = \frac{3}{5}(kT\ln z)\left[1+\frac{\pi^2}{2}(\ln z)^{-2}+\cdots\right] \quad \text{—— (36)}$$

$$= \frac{3}{5}\varepsilon_F\left[1+\frac{\pi^2}{2}(\ln z)^{-2}+\cdots\right]\left[1-\frac{\pi^2}{12}\left(\frac{kT}{\varepsilon_F}\right)^2\right]^{-1}$$

from eq. (35)

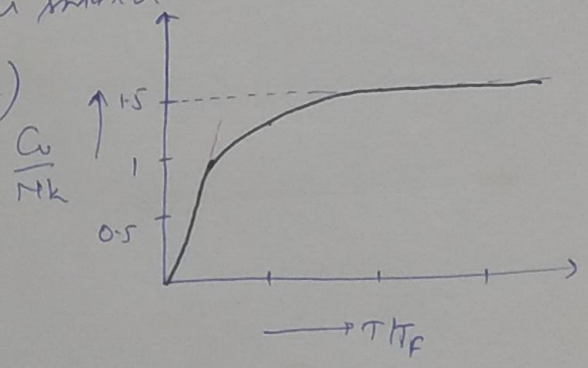
$$\frac{U}{N} = \frac{3}{5}\varepsilon_F\left[1+\frac{5\pi^2}{12}\left(\frac{kT}{\varepsilon_F}\right)^2+\cdots\right] \quad \text{—— (37)}$$

The pressure of the gas is then given by

$$P = \frac{2}{3}\frac{U}{V} = \frac{2}{3} n \varepsilon_F \left[1 + \frac{5\pi^2}{12}\left(\frac{kT}{\varepsilon_F}\right)^2 + \cdots\right] \quad (38)$$

Now, $\frac{C_v}{Nk} = \left(\frac{\partial U}{\partial T}\right)_{N,V} = \frac{\pi^2}{2}\frac{kT}{\varepsilon_F} + \cdots$ from eq. (37) (39)

for $T \ll T_F$ (T_F is fermi temp), the specific heat varies linearly with temp.. The magnitude however is smaller than $\frac{3}{2}Nk$ (Classical value)



We know Helmholtz free energy,

$$\frac{A}{N} = \mu - \frac{PV}{N}$$

$$= \frac{3}{5}\varepsilon_F\left[1 - \frac{5\pi^2}{12}\left(\frac{kT}{\varepsilon_F}\right)^2 + \cdots\right] \quad (40)$$

And entropy $\frac{S}{Nk} = \frac{\pi^2}{2}\frac{kT}{\varepsilon_F} + \cdots$ (41)