Classical limit of the Partition functions

Hamiltonian operator of system containing N identical spinless ~~Particle~~ particles is

$$\hat{H} = \hat{K} + \hat{\Omega} \quad - (1)$$

where $\hat{K}$ is K.E operator

Ω is P.E. operator

If $\psi(r_1, \dots r_N)$ is wave function of system then

$$\hat{K}\psi(r_1, \dots r_N) = -\frac{\hbar^2}{2m}\sum_{i=1}^{N} \nabla_i^2 \psi(r_1, \dots r_N) \quad - (2)$$

and $\quad \hat{\Omega}\psi(r_1, \dots r_N) = \Omega(r_1 \dots r_N)\,\psi(r_1 \dots r_N) \quad - (3)$

where m is mass of particle

∇_i^2 is laplacian operator w.r.to r_i

$\Omega(r_1 \dots r_N)$, sum of two body potential

$$\Omega(r_1 \dots r_N) = \sum_{i<j} v_{ij} \quad - (4)$$

where $\quad v_{ij} \equiv v(|r_i - r_j|) \quad - (5)$

The partition function of system

$$Q_N(V,T) = Tr\, e^{-\beta \hat{H}} = \sum_n (\phi_n e^{-\beta \hat{H}} \phi_n) \quad - (6)$$

where $\phi_n(1 \dots N)$ is ~~no.~~ member of any complete ~~set~~ orthonormal set of wave function of system

$\phi_n^*(1 \dots N)$ is its complex conjugate.

where $(r_1 \cdots r_N)$ is replaced by $(1, \cdots N)$ for convenient

and Each ϕ_n satisfies normalized condition $\int \phi_n \phi_n^* d^{3N}r = 1$

for any operator $\hat{Q}$ is

$$(\phi_n \hat{Q} \phi_n) = \int d^{3N}r \; \phi_n^*(1, \cdots N) \hat{Q} \phi_n (1, \cdots N) \quad — (7)$$

ϕ_n is symmetric function of $r_1 \cdots r_N$ for boson system

ϕ_n is antisymmetric function of $r_1, \cdots, r_N$ for fermion system

If T is very high then partition function

$$Q_N(V,T) = \frac{1}{N! \, h^{3N}} \int d^{3N}p \, d^{3N}r \, e^{-\beta \hat{H}(P, r)} \quad — (8)$$

{ at high T, boson and fermion system $\rightarrow$ Boltzmann system

'h' is planck's constant and H is classical Hamiltonian

$$H(P, r) = \sum_{i=1}^{N} \frac{P_i^2}{2M} + \Omega(r_1 \cdots r_N) \quad — (9)$$

(i) <u>Free particles</u>

Consider ideal gas containing N particles for which P.E. of system i.e. $\Omega(1 \cdots N) = 0$

then H of free particles

$$\hat{H}(P, r) = \sum_{i=1}^{N} \frac{P_i^2}{2M} = \hat{k} \quad — (10)$$

i.e. H is set of N momenta

$$P \equiv (p_1, \ldots p_N) \quad \text{—(11)}$$

and satisfies eigen value eq

$$\hat{k}\,\phi_p(1 \ldots N) = K_p\,\phi_p(1 \ldots N) \quad \text{—(12)}$$

where

$$K_p = \frac{1}{2m}(p_1^2 + \ldots p_N^2) = \sum_i^N \epsilon_i \quad \text{—(13)}$$

with the periodic boundary condition

$$\left.\begin{aligned} u_{\vec{p}}(\vec{r}) &= \frac{1}{V^{1/2}} e^{-i p \cdot r/\hbar} \\ \text{with } \vec{p} &= \frac{2\pi\hbar}{L}\vec{n} \end{aligned}\right\} \text{—(14)}$$

$\left\{ \begin{array}{l} V = L^3 \\ \text{volume of system} \end{array} \right.$

the factor ensures normalization

$$\int |u_{\vec{p}}(\vec{r})|^2 d\vec{r} = 1$$

$\vec{n}$ is vector of integers $0, \pm 1, \pm 2 \ldots$

The total wave function is sum of permutation

$$\phi_p(1 \ldots N) = \frac{1}{\sqrt{N!}} \sum_P S_P\, P\left[u_{p_1}(1) \ldots u_{p_N}(N)\right] \quad \text{—(15)}$$

where $S_P = +1$ if particles are bosons

$$S_P = \text{sign } P = \begin{cases} \pm 1 & \text{if the particles are fermions} \\ +1 & \text{for even permutation} \\ -1 & \text{for odd permutation} \end{cases}$$

When we permute, we can either change the particles or change the momenta $p_1 \cdots p_N$, these will ~~be~~ give the same ~~result~~ permutation

$$\phi_p(1 \cdots N) = \frac{1}{\sqrt{N!}} \sum_P \delta_P \left[u_{p_1}(P1) \cdots u_{p_N}(PN) \right]$$
$$= \frac{1}{\sqrt{N!}} \sum_P \delta_P \left[u_{Pp_1}(1) \cdots u_{Pp_N}(N) \right] \quad — (16)$$

In the limit $V \to \infty$ then

$$\sum_p \to \frac{V}{\lambda^3} \int d^3p \quad — (17)$$

Therefore partition function

$$Q_N(V,T) = Tr\, e^{-\beta \hat{K}_p} = \sum_p (\phi_p e^{-\beta \hat{K}_p} \phi_p) = \sum_p \int d^{3N}r\, \phi_p^* e^{-\beta \hat{K}_p} \phi_p$$

$\{ H = K_p$

$$Tr\, e^{-\beta \hat{K}} = \frac{V^N}{N! \lambda^{3N}} \int d^{3N}p\, d^{3N}r\, |\phi_p(1 \cdots N)|^2 e^{-\beta \hat{K}_p}$$

$\{$ using eq^n (7) replaced $\Sigma \to \int$

— (18)

using eq^n (16), we get

~~$Tr\, e^{-\beta K_p}$~~ $$Tr\, e^{-\beta \hat{K}} = \frac{V^N}{N! \lambda^{3N}} \int dp^{3N} d^{3N}r\, e^{-\beta K_p} \times$$

~~$|\phi_p(1 \cdots N)|^2$~~

$$\frac{1}{(\sqrt{N!})^2} \left\{ \sum_P \delta_P \left[u_{p_1}^*(P1) \cdots u_{p_N}^*(PN) \right] \times \sum_{P'} \delta_{P'} \left[u_{P'p_1}^*(1) \cdots u_{P'p_N}(1) \right] \right.$$

$$Tr\, e^{-\beta \hat{K}} = \frac{V^N}{(N!)^2 \lambda^{3N}} \int d^{3N}p\, d^{3N}r\, e^{-\beta K_p} \left\{ \sum_P \sum_{P'} \left[u_{p_1}^*(P1) u_{P'p_P}(1) \right] \cdots \right.$$

$$\left[u_{p_N}^*(PN)\, u_{P'p_N}(N) \right] \quad — (19)$$

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[Now every term in p' sum will give the same contribution to the Integral in (19). Thus we may replace the above N! times any one term in p' sum]

The N-fold summation over the k_p all the permulations p' will contribut the same.

Therefore we can take only one term of them say $p_{p_1}' = p_1 \cdots p_{pN} = p_N$ and multiply by (N!)

Then result is

$$Tr\, e^{-\beta \hat{K}} = \frac{V^N}{N!\,\lambda^{3N}} \int d^{3N}_p\, d^{3N}_r\, e^{-\beta\left(\frac{p_1^2}{2M}+\frac{p_2^2}{2M}+\cdots\frac{p_N^2}{2M}\right)}$$
$$\times\left[\sum_P S_p\,[u^*_{p_1}(P1)\,u_{p_1}(1)\cdots[u^*_{p_N}(PN)\,u_{p_N}(N)]\right] \quad -(20)$$

$$= \frac{V^N}{N!\,\lambda^{3N}} \int d^{3N}_p\, d^{3N}_r\, e^{-\beta\left(\frac{p_1^2}{2M}+\cdots+\frac{p_N^2}{2M}\right)}$$
$$\frac{1}{V^N}\left[\sum_P S_p\, e^{+i/\hbar[\{p_1\cdot(P1-1)\cdots\cdots p_N\cdot(PN-N)]}\right] \quad -(21)$$

$$= \frac{1}{N!\,\lambda^{3N}} \sum_P S_p \left[\int d^{3N}_r \int\left[e^{-\frac{\beta p_1^2}{2M}+i/\hbar\, p_1\cdot(P1-1)}\right]dp_1 \cdots\right.$$
$$\left.\cdots \left[\int e^{-\frac{\beta p_N^2}{2M}+i/\hbar\, p_N\cdot(PN-N)}\right]dp_N\right] \quad -(22)$$

Integration is F.T. over Gaussian

$$Q_N(V,T) = \frac{1}{N!\,\lambda^{3N}} \int d^{3N}_r \left[\left(\frac{2\pi M k T}{h^2}\right)^{3/2 N} \sum_P S_p\,[f(P1-1)\cdots f(PN-N)]\right] \quad -(23)$$

where $f(x) = e^{-\frac{2\pi m k T}{h^2} x^2}$ is the F.T. of Gaussian

we know that thermal wave length

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

then finally we get

~~$Tr\, e^{-\beta \hat{K}} = \frac{1}{N!} \frac{1}{\lambda^{3N}} \left(\frac{1}{\lambda^{3N/2}} \right) \int d^{3N} r \sum_p \delta_p$~~

$$Tr\, e^{-\beta \hat{K}} = \frac{1}{N!\, \lambda^{3N}} \int d^{3N} r \left[\sum_p \delta_p \left[f(P1-1) \cdots f(PN-N) \right] \right] \quad (22)$$

$$\text{where } f(r) = \int d^{3N} p\, e^{-\frac{\beta p^2}{2m} + \frac{i}{\hbar} \vec{p} \cdot \vec{r}} = e^{-\pi r^2 / \lambda}$$

$$r = |\vec{r}|$$

from eqn (23)

$$Tr\, e^{-\beta \hat{K}} = \frac{1}{N!\, \lambda^{3N}} \int d^{3N} r \left[\sum_p \delta_p \left[f(Pr_1 - r_1) \cdots f(Pr_N - r_N) \right] \right] \quad - (24)$$

Where $\sum_p$ contains N terms

At high Tempr the integrand may be ~~ery~~ approximated as follow

(i) the term correspond to the unit permutation $P = 1$ is $[f(0)]^N = 1$ $\Big\{$ leading term in summation is when $Pr_i = r_i$

(ii) the second term will include one pair exchange (r_i and r_j then $f(r_i - r_j)\, f(r_i - r_j) = |f(r_i - r_j)|^2$

(iii) Next term will include triplets

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so we have

$$\sum_p \delta_p \left[f(p\vec{r}_1 - \vec{r}_1) \cdots f(p\vec{r}_N - \vec{r}_N) \right] = 1 \overset{\text{boson}}{\underset{\text{fermion}}{\pm}} \sum_{i<j} f_{ij} f_{ji} + \sum_{i<j<k} f_{ij} f_{jk} f_{ki} + \cdots \qquad (25)$$

where $f_{ij} = f(r_i - r_j)$

f_{ij} vanishes extremely rapidly if

$$|r_i - r_j| >> \lambda \quad \text{i.e. } f << 1 . \qquad (26)$$

Therefore when temp^r is so high that

$\lambda <<$ average interparticle distance

In otherwords when $n\lambda^3 = \frac{n h^3}{(2\pi m k T)^{3/2}} << 1$ — (27)

the system can be approximated by first term

$$Q_N(V,T) = Tr\, e^{-\beta \hat{K}}$$

$$= \frac{1}{N!\,\lambda^{3N}} \int d^{3N} r \; 1 = \frac{V^N}{N!\,\lambda^{3N}} \qquad (28)$$

This is Q_N for classical ideal gas

This shows that we get the ideal gas partition function from precise QM.

Let examine the first quantum correction to the classical partition function of ideal gas.

If $|r_i - r_j| >> \lambda$ and eq^n (25) approximates as

$$1 \pm \sum f_{ij}^2$$

to some order of approximation, we can write

$$1 \pm \sum_{i<j} f_{ij}^2 \simeq \prod_{i<j} (1 \pm f_{ij}^2) = \exp\left\{-\beta \sum_{i<j} v'_{ij}\right\} \qquad (29)$$

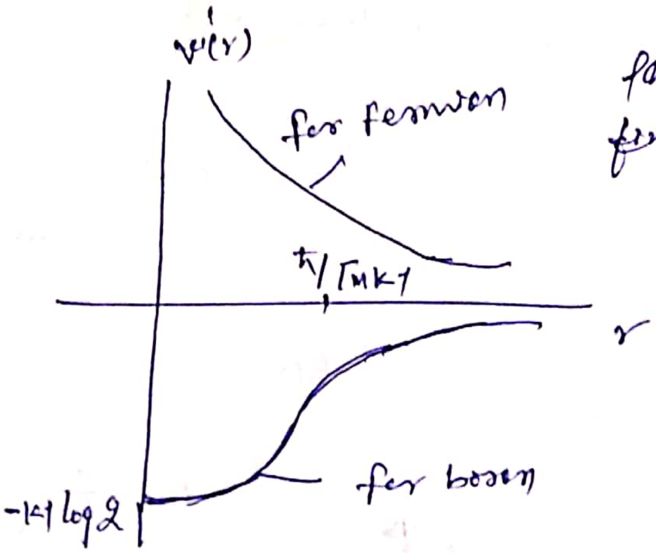
where

$$v'_{ij} \equiv -kT \log_e (1 \pm f_{ij}^2)$$

$$v'_{ij} = -kT \log\left[1 \pm \exp\left\{-\frac{2\pi (r_i - r_j)^2}{\lambda^2}\right\}\right] \qquad (30)$$

from eqn (24)

$$Tr\, e^{-\beta \hat{K}} = \frac{1}{N!\lambda^{3N}} \int d^{3N}r\, d^{3N}p \exp\left[-\beta \sum_l \frac{p_l^2}{2m} + \sum_{i<j} v'_{ij}\right] \qquad (31)$$



~~This shows that the first quantum~~

This shows that first quantum correction to the partition function of ideal gas has same effect as that of endowing the particles with an interparticle potential $v'(r)$ and treating the problems classically.

The potential $v'(r)$ is attractive for bosons and repulsive for fermions. This sometimes called as statistical attraction b/w bosons and statistical repulsion b/w fermions.

$v'(r)$ originates from the symmetric properties of wave function