Classical limit of Quantum Statistics.

Recall the quantum partition functions:

$$\ln \mathcal{Z}(\mu, V, T) = \pm \sum_j \ln \left[1 \pm e^{\beta(\mu - \epsilon_j)}\right] \quad \text{—— (1)}$$

$\pm$ refers to F.D & B.E. respectively

To show that for large systems ($N \to \infty$), the classical limit ($\Lambda(T) << \rho^{-1/3}$) of (1) yields the canonical partition function:

$$Z(N, V, T) = \frac{1}{N!}\left(\frac{2\pi m}{\beta}\right)^{3N/2} \frac{1}{h^{3N}} \quad !.$$

Proof: Classical limit $\Lambda(T) << \rho^{-1/3}$ ... $\rho = N/V$

$\Lambda(T)$: de-Broglie wavelength.

is achieved by joint limits $\beta \to 0$, $\rho \to 0$

Now $N = \sum_j \langle n_j \rangle = \sum_j \frac{1}{e^{\beta(\epsilon_j - \mu)} \pm 1}$

$\pm$: FD/BE

$\therefore$ Average density $\rho = \frac{1}{V} \cdot \sum_j \langle n_j \rangle$ —— (2)

~~Thus high~~

In the limit $\beta \to 0$ & $\rho \to 0$, more states are empty!

$\therefore$ we can safely assume that $\langle n_j \rangle << 1$.

{Each term in the summation ② is very small}

$\therefore \quad e^{\beta(\epsilon_j - \mu)} >> 1.$ {FD/BE behave same way!} —— (*)

R.H.S is j independent, thus we say

$$-\beta\mu >> 1.$$

$$\therefore \quad \langle n_j \rangle \approx e^{-\beta(\epsilon_j - \mu)} \quad \text{—— ③}$$

$$\therefore \quad N = \sum_j \langle n_j \rangle = \left(\sum_j e^{-\beta\epsilon_j}\right) e^{\beta\mu} \quad \text{—— ④}$$

$$\therefore \quad e^{\beta\mu} = \frac{N}{\sum_j e^{-\beta\epsilon_j}} \quad \text{—— ⑤}$$

from ③ & ④, we write :

$$\frac{\langle n_j \rangle}{N} = p_j = \frac{e^{-\beta\epsilon_j}}{\sum_j e^{-\beta\epsilon_j}} \quad \text{—— ⑥}$$

"Classical Boltzmann probability"

p_j = probability of finding a particle in j^{th} level.

$e^{-\beta\epsilon_j}$ = Boltzmann factor

$\sum_j e^{-\beta\epsilon_j}$ = Single particle partition f^n:

from (6), we say : $p_j \propto e^{-\beta\epsilon_j}$

Now recall the canonical partition function:

$$\ln Z(N, V, T) = -\beta F \quad \text{(7)}$$

F → Helmholtz free energy.

& Grand canonical partition function :

$$\ln \mathcal{Z}(\mu, V, T) = -\beta \mathcal{G} = \beta PV \quad \text{(8)}$$

$\mathcal{G}$ → Grand potential

$\because \quad F = E - TS$

& $\quad G = \mu N = E + PV - TS = F + PV$

we write, $\quad \mu N = F + PV \quad \text{(9)}$

Substituting for F & PV from (7) & (8), into (9)

$$\ln \mathcal{Z} = -\beta \mu N + \ln \mathcal{Z}$$

Substituting for $\ln \mathcal{Z}$ from (1)

$$\ln Z = -\beta \mu N \pm \sum_j \ln \left[1 \pm e^{\beta(\mu - \epsilon_j)}\right]$$

$\pm$: F.D / B.E

$\therefore$ in classical limit Eq^n (*), $e^{\beta(\epsilon_j - \mu)} >> 1$

$\therefore$ $e^{\beta(\mu - \epsilon_j)} << 1$

& expanding $\ln(1+x) = x - x^2/2 + \dots$

we get: $\ln Z = -\beta \mu N + \sum_j e^{\beta(\mu - \epsilon_j)}$

Now substituting for $\beta\mu$ (from (5)) & $\sum_j e^{\beta(\mu - \epsilon_j)}$ from (4)

$$\ln Z = -N\left(\ln N - \ln \sum_j e^{-\beta \epsilon_j}\right) + N$$

$$= -\ln N! + \ln\left(\sum_j e^{-\beta \epsilon_j}\right)^N$$

$$\therefore \quad Z = \frac{\left(\sum_j e^{-\beta \epsilon_j}\right)^N}{N!} = \frac{(Z_1)^N}{N!} \quad \text{—— (10)}$$

$$Z_1 = \sum_j e^{-\beta \epsilon_j} \equiv \text{Single particle partition } f^n.$$

Notice $N!$ naturally emerges from Quantum mechanics.

Finally we can use eq^n (18), to write for canonical partition of an ideal gas:

$$Z = \frac{1}{N!} \left(\int\int\int_{-\infty}^{+\infty} \frac{e^{-\frac{\beta \hbar^2 k^2}{2m}}}{(2\pi/L)^3} dk_x \, dk_y \, dk_z \right)^N$$

$$= \frac{V^N}{N! \, (2\pi)^{3N}} \left(\int_{-\infty}^{+\infty} e^{-\frac{\beta \hbar^2 k_x^2}{2m}} dk_x \right)^{3N} = \frac{V^N}{N! \, (2\pi)^{3N}} \left(\frac{2\pi m}{\beta \hbar^2} \right)^{3N/2}$$

$$= \frac{V^N}{N!} \left(\frac{2\pi m}{\beta} \right)^{3N/2} \frac{1}{h^{3N}}$$

"Classical partition f^n of an ideal gas in NVT"