GRAND CANONICAL ENSEMBLE

Partition function

$$\Xi(\mu,V,T) = \sum_{N=0}^{\infty} e^{\beta\mu N} \underbrace{Q(N,V,T)}_{\text{canonical partition function}}$$

$$\Omega(\mu,V,T) = -kT \ln \Xi(\mu,V,T)$$ grand-canonical potential

NOTE: N fluctuates. Probability to have N particles

$$\frac{1}{\Xi(\mu,V,T)} e^{\beta\mu N} Q(N,V,T)$$

To prove the definition is correct:

Thermodynamics ; $\Omega = E - TS - \mu N \qquad S = -\left(\frac{\partial\Omega}{\partial T}\right)_{\mu,V}$

Therefore we should verify that

$$\Omega = \langle H \rangle + T\left(\frac{\partial\Omega}{\partial T}\right)_{\mu,V} - \mu\langle N\rangle$$

The proof (left as an <u>exercise</u>) is the same as that in the isobaric-isothermal ensemble

IDEAL GAS ; $Q = \dfrac{V^N}{\lambda^{3N} N!}$

$$\Xi(\mu,V,T) = \sum_{N=0}^{\infty} e^{\beta\mu N} \frac{V^N}{\lambda^{3N} N!} = \sum_{N=0}^{\infty} \frac{1}{N!}\left(\frac{e^{\beta\mu} V}{\lambda^3}\right)^N$$

$$= \exp\left(\frac{e^{\beta\mu} V}{\lambda^3}\right)$$

$$\Omega = -kT \frac{e^{\beta\mu} V}{\lambda^3}$$

A) CHECK: (We use, e.g., canonical results)

extensivity requires $\Omega = -pV$

But $pV = NkT$

$$\mu = kT \ln \rho\lambda^3 \longrightarrow \lambda^3 \frac{N}{V} = e^{\beta\mu} \longrightarrow N = \frac{Ve^{\beta\mu}}{\lambda^3}$$

Therefore

$$\Omega = -pV = -NkT = -kTV\frac{e^{\beta\mu}}{\lambda^3} \qquad \underline{\text{OK}}$$

B) Calculation of $\langle N \rangle$ (N in thermodynamics)

$$\Omega = -kTV\frac{e^{\beta\mu}}{\lambda^3}$$

$$d\Omega = -SdT - pdV - Nd\mu$$

$$N = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} = +\overbrace{kT\,V\frac{1}{\lambda^3}e^{\beta\mu}\,\beta}^{=1} = \frac{Ve^{\beta\mu}}{\lambda^3}$$

it coincides with above equation

If we use the definitions

$$N = -kT\frac{1}{\Xi}\frac{\partial\Xi}{\partial\mu} = +\overbrace{kT\frac{1}{\Xi}\sum_N \beta}^{=1} N e^{\beta\mu N} Q(N,V,T)$$

$$= \frac{1}{\Xi}\sum_N N e^{\beta\mu N} Q(N,V,T) = \langle N \rangle$$