ISOBARIC - ISOTHERMAL ENSEMBLE

Two steps: a) define partition function
b) connection with thermodynamics

$$\Delta(N,p,T) = \int_0^\infty dV\, e^{-\beta p V} \underbrace{Q(N,V,T)}_{\text{canonical partition function}} \qquad \boxed{\text{partition function}}$$

$$G(N,p,T) \underset{(*)}{=} -kT \ln \Delta(N,p,T) \qquad \boxed{\text{Gibbs free energy}}$$

How do we verify that this definition is correct.

Two properties of G: $\begin{cases} G = E - TS + pV \\ S = -\left(\frac{\partial G}{\partial T}\right)_{p,N} \end{cases}$

We verify that definition (*) satisfies

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

The energy in thermodynamics is identified with $\langle H \rangle$, the average of H in the ensemble

The volume in thermodynamics is identified with $\langle V \rangle$, the average of V in the ensemble

NOTE: V fluctuates

probability to observe a volume V:

$$= \frac{1}{\Delta(N,p,T)} e^{-\beta p V} Q(N,V,T)$$

$$T\left(\frac{\partial G}{\partial T}\right)_{p,N} = T\left[-k\ln\Delta - kT\frac{1}{\Delta}\frac{\partial\Delta}{\partial T}\right]$$

$$= G - kT^2\frac{1}{\Delta}\frac{\partial\Delta}{\partial T}$$

$$\Delta = \int dV\,\frac{d^{3N}p\,d^{3N}q}{h^{3N}N!}\,e^{-\beta(H+pV)}$$

$$\frac{\partial\Delta}{\partial\beta} = +\int dV\,\frac{d^{3N}p\,d^{3N}q}{h^{3N}N!}\,e^{-\beta(H+pV)}\left[-(H+pV)\right]$$

$$= -\Delta\langle H+pV\rangle$$

$$\beta = \frac{1}{kT} \qquad \frac{\partial\beta}{\partial T} = -\frac{1}{kT^2}$$

$$\frac{\partial\Delta}{\partial T} = -\frac{1}{kT^2}\frac{\partial\Delta}{\partial\beta}$$

Therefore

$$T\left(\frac{\partial G}{\partial T}\right)_{p,N} = G + \frac{1}{\Delta}\frac{\partial\Delta}{\partial\beta} = G - \langle H\rangle - p\langle V\rangle$$

This is exactly the relation we wished to prove

Ideal gas

$$\Delta(N,p,T) = \int_0^\infty dV\, e^{-\beta p V} \frac{V^N}{\lambda^{3N} N!} \qquad \beta p V = x$$

$$= (\beta p)^{-(N+1)} \frac{1}{\lambda^{3N} N!} \underbrace{\int dx\, e^{-x} x^N}_{\Gamma(N+1) = N!}$$

$$= (\beta p)^{-(N+1)} \frac{1}{\lambda^{3N}}$$

$$G = -kT \ln \left[\frac{1}{(\beta p \lambda^3)^N} \cdot \frac{1}{\beta p} \right]$$

$$= NkT \ln(\beta p \lambda^3) + \underbrace{kT \ln \beta p}_{\text{non extensive } (O(1)) \text{ negligible}}$$

$$= NkT \ln\left(\frac{p\lambda^3}{kT}\right)$$

Comparison with canonical-ensemble results

$$F = NkT \ln(\rho\lambda^3) - NkT$$
$$= NkT \ln\left(\frac{p\lambda^3}{kT}\right) - NkT$$

Eq. of state $\boxed{\begin{aligned} p &= \rho k T \\ pV &= NkT \end{aligned}}$

$$G = F + pV =$$
$$= NkT \ln\left(\frac{p\lambda^3}{kT}\right) - NkT + NkT$$
$$= NkT \ln\left(\frac{p\lambda^3}{kT}\right)$$

[This is the canonical result for μ]

Also $G = N\mu = NkT(\rho\lambda^3) = NkT \ln\left(\frac{p\lambda^3}{kT}\right)$