# Equivalence Canonical / G Can Ensembles

the grand canonical partition function is

$$Z_{gc}(\mu) = \sum_{N=0}^{\infty} \underbrace{e^{\beta\mu N}}_{\text{fugacity}} Z_{con}(N)$$

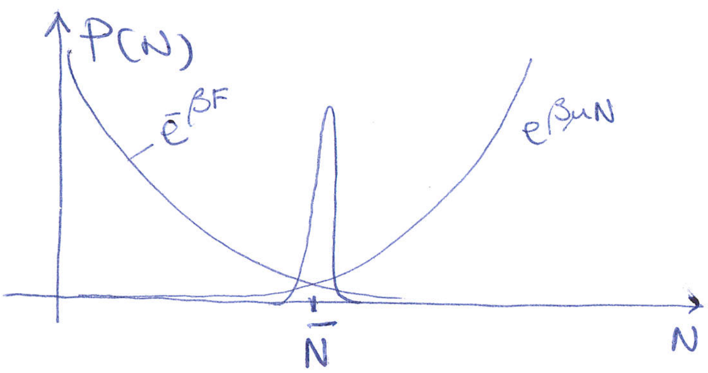
The expression is fairly similar to that which relates Canonical & Microcanonical

$$Z_{con}(T) = \int \frac{dE}{\Delta} e^{-\beta E} Z_{micro}(E)$$

Equivalence follows the same steps

The

$$\frac{e^{\beta\mu N} \overbrace{Z_{con}(N)}^{e^{-\beta F}}}{Z_{gcon}} = P(N)$$ probability distribution of N




Steepest descent

$\bar{N} \,|\, \frac{\partial}{\partial N}\left[F(N) - \mu N\right] = 0$

remember from thermodynamics

$$\left(\frac{\partial F}{\partial N}\right)_{V,T} = \mu \longrightarrow \text{system chem pot}$$

while the $\mu$ here is the bath chem pot

therefore the existence of ~~maximum~~ minimum of

$$F(N) - \mu N \Rightarrow \mu_S = \mu_B \text{ equilibrium condition}$$

$$\mathcal{Z}_{gcan} = e^{-\beta[F(\bar{N}) - \mu \bar{N}]} \sum_0^\infty {}_N \, e^{-\beta\left[\frac{\partial^2}{\partial N^2} F(N) - \mu N\right]\frac{(N-\bar{N})^2}{2}}$$

stability condition

$$\frac{\partial^2}{\partial N^2}(F(N) - \mu N)\Big|_{N=\bar{N}} > 0$$

$$\left(\frac{\partial}{\partial N}\mu\right)\Big|_{N=\bar{N}} > 0$$

let us express in variables $N, V, T$ $\quad \frac{\partial \mu}{\partial N}$

Extensivity of $F(N)$ means

$F(\lambda V) = \lambda F(V)$ homogeneous function of degree one

set $\lambda = 1/N$

$$F\left(\frac{V}{N}\right) = \frac{1}{N} F(V) \Rightarrow F(V) = N F\left(\frac{V}{N}\right)$$

specific Helmholtz free en

$v$ specific volume

$$F(V,N) = N f\left(\frac{V}{N}, T, 1\right)$$

$$\frac{\partial F}{\partial N} = f\left(\frac{V}{N}, T, 1\right) + N \frac{\partial f}{\partial v}\frac{\partial v}{\partial N} = f(v,T) - v\frac{\partial f}{\partial v}$$

$$-\frac{V}{N^2} \Rightarrow -\frac{v}{N} \qquad + N\frac{\partial f}{\partial N}$$

$$\cancel{\frac{\partial^2 F}{\partial N^2} = -\frac{v}{N}\frac{\partial f}{\partial v}}$$

$$\frac{\partial^2 F}{\partial N} = \cancel{\frac{\partial f}{\partial v}\frac{\partial v}{\partial N}} - \cancel{\frac{\partial v}{\partial N}\frac{\partial f}{\partial v}} - v\frac{\partial^2 f}{\partial v^2}\frac{\partial v}{\partial N} = \frac{v^2}{N}\frac{\partial^2 f}{\partial v^2}$$

remember

$$-\frac{\partial F}{\partial V} = P \qquad P = -\frac{\partial N f}{\partial N v} = -\frac{\partial f}{\partial v}$$

$$\frac{\partial^2 F}{\partial N^2} = -\frac{v^2}{N}\frac{\partial P}{\partial v}$$

$$k_T = -\frac{1}{V}\frac{\partial V}{\partial P} = -\frac{1}{v}\frac{\partial v}{\partial P} \qquad \frac{\partial P}{\partial v} = -\frac{1}{v k_T}$$

$$\frac{\partial^2 F}{\partial N^2} = +\frac{v^{\cancel{2}}}{N}\frac{1}{\cancel{v} k_T} = \frac{V}{N^2 k_T} = \frac{1}{\rho N k_T}$$

$$\boxed{\sigma_N^2 = \rho N k_T k_B T}$$ fluctuations of the number

$$\langle N^2\rangle - \langle N\rangle^2 = k_B T \underbrace{\left[\rho N \left(-\frac{1}{V}\frac{\partial V}{\partial P}\right)_T\right]}_{\left(\frac{\partial N}{\partial \mu}\right)_T}$$

linear response

$$Z_{gcan} = e^{-\beta(F(\bar{N})-\mu\bar{N})}\sqrt{2\pi\sigma_N^2}$$

$$-\frac{1}{\beta}\ln Z_{gcan} = \underbrace{F(\bar{N})-\mu\bar{N}}_{\text{grand-Potential}} \cancel{\underbrace{-\frac{1}{2\beta}\ln 2\pi\sigma^2_{(N)}}_{\mathcal{O}(\ln N)}}$$

$$\Omega = F-\mu N$$

Thermodynamic relations

$$F-\mu N = -PV$$

$$U-TS-\mu N+PV=0$$

Gibbs-Duhem relation