Classical Statistical mechanics, canonical partition function

$$Z = \frac{1}{N!} \int \frac{d^{3N}p \, d^{3N}q}{h^{3N}} e^{-\beta H(p,q)} \quad ; \quad \beta = \frac{1}{k_B T}$$

e.g. free gas (later) $H = \sum_{j=1}^{3N} \frac{p_j^2}{2m}$

What is Z? (thermodynamically)

$$Z = \int_0^\infty dE\, \Gamma(E)\, e^{-E/k_BT} = \int_0^\infty dE\, e^{\frac{1}{k_B} S(E) - \frac{E}{k_BT}}$$

$$= \int_0^\infty dE\, e^{-\frac{1}{k_BT}(E-TS)} = \int_0^\infty dE\, e^{-\beta A(E)}$$

free energy

smallest A dominates

$$Z \approx C e^{-\beta A(E)}$$

min is correct A.

$$\ln Z = \underbrace{\ln C}_{\text{goes away } N \to \infty} - \beta A$$

$$\boxed{A = -k_B T \ln Z}$$ gives $A(T, V, N)$

and allows to derive all thermodynamics through

$$dA = -S\,dT - p\,dV + \mu\,dN$$

Check subleading term

$$A(E) = A(\bar{E}) + \frac{\partial A}{\partial E}(E-\bar{E}) + \frac{1}{2}\frac{\partial^2 A}{\partial E^2}(E-\bar{E})^2 + \dots$$

$A(\bar{E})$: minimum

$\frac{\partial A}{\partial E} = 0$

fixed T

$$A = E - TS \Rightarrow \left(\frac{\partial A}{\partial E}\right)_T = 1 - T\frac{\partial S}{\partial E} = 0$$

$\frac{\partial S}{\partial E}$: $1/T$

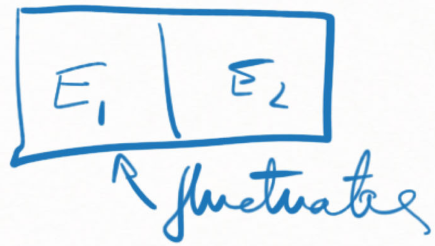
$$\frac{\partial^2 A}{\partial E^2} = -T\frac{\partial^2 S}{\partial E^2} = -T\frac{\partial(1/T)}{\partial E} = \frac{T}{T^2}\left(\frac{\partial T}{\partial E}\right)_V = \frac{1}{C_V T}$$

$$A \simeq A(\bar{E}) + \frac{1}{2}\frac{1}{C_V T}(E-\bar{E})^2$$

$$Z = e^{-\beta A(\bar{E})} \int_0^\infty dE\, e^{-\frac{\beta}{2C_V T}(E-\bar{E})^2} \simeq e^{-\beta A}\sqrt{\frac{2\pi C_V T}{\beta}}$$

$$\ln Z = \underbrace{-\beta A}_{\sim N} + \underbrace{\frac{1}{2}\ln\big(\underbrace{2\pi C_V k_B T^2}_{N}\big)}_{\ln N \ll N} \qquad (\ln 10^{23} \simeq 53)$$

Energy fluctuations



$$\langle E \rangle = \frac{\int_0^\infty dE\, E\, \Gamma(E)\, e^{-\beta E}}{\underbrace{\int_0^\infty dE\, \Gamma(E)\, e^{-\beta E}}_{Z}} = -\frac{\partial}{\partial \beta} \ln Z$$

$$\boxed{\begin{aligned} \langle E^2 \rangle &= \frac{\partial^2 Z/\partial \beta^2}{Z} = \frac{\int E^2 \Gamma(E) e^{-\beta E}}{\int \Gamma(E) e^{-\beta E}} \\ &= \frac{1}{Z}\frac{\partial}{\partial \beta}\left(Z \frac{\partial \ln Z}{\partial \beta}\right) = \left(\frac{\partial \ln Z}{\partial \beta}\right)^2 + \frac{\partial^2 \ln Z}{\partial \beta^2} \end{aligned}}$$

$$\langle (E - \langle E \rangle)^2 \rangle = \langle E^2 \rangle - \langle E \rangle^2$$

$$= \partial^2 \ln Z/\partial \beta^2 = -\frac{\partial}{\partial \beta} E$$

$$\langle (\Delta E)^2 \rangle = -\frac{\partial E}{\partial \beta} = +\frac{\partial E}{\partial T}\left(T \frac{1}{k_B \beta^2}\right) \qquad \beta = \frac{1}{k_B T}$$

$$= C_V k_B T^2$$

$$\Delta E = \sqrt{\langle (\Delta E)^2 \rangle} = \sqrt{\underbrace{C_V k_B T^2}_{N}} \sim \sqrt{N} \quad \text{(big)}$$

def.

but $\frac{\Delta E}{E} \sim \frac{1}{\sqrt{N}}$ small $10^{23} \Rightarrow \frac{\Delta E}{E} \sim 10^{-12}$

In canonical $P_n = \dfrac{e^{-\beta E_n}}{Z}$

$$S \overset{?}{=} -k_B \sum_n P_n \ln P_n = -k_B \langle \ln P_n \rangle$$

$$= -k_B \sum_n P_n \left(-\beta E_n - \ln Z \right) = \beta k_B \langle E \rangle + k_B \underbrace{\ln Z}_{-\beta A}$$

$$= \frac{E}{T} - \frac{A}{T} = \frac{TS}{T} = \underline{S} \checkmark$$ (works for canonical)

When is $S = -k_B \sum_n p_n \ln p_n$ maximum

$$F = -k_B \sum_n p_n \ln p_n + \lambda \left(\sum_n p_n - 1 \right)$$

Lagrange multiplier

$$\frac{\partial F}{\partial p_n} = -k_B (\ln p_n + 1) + \lambda = 0 \Rightarrow \ln p_n = \frac{\lambda}{k_B} - 1$$

p_n indep. of n $\Rightarrow$ $p_n = \frac{1}{\Gamma(E)}$ microcanonical

Suppose we allow E to fluctuate with $\langle E \rangle = \bar{E}$ fixed

$$F = -k_B \sum_n P_n \ln P_n + \lambda \left(\sum_n P_n - 1 \right) + \chi \left(\sum_n E_n P_n - \bar{E} \right)$$

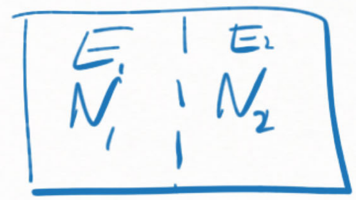
$$\frac{\partial F}{\partial P_n} = -k_B \ln P_n - k_B + \lambda + \chi E_n = 0$$

$$\ln P_n = -1 + \frac{\lambda}{k_B} + \frac{\chi E_n}{k_B} \Rightarrow P_n = C e^{\frac{\chi E_n}{k_B}}$$

$$\chi = -1/T \quad < 0 \text{ for convergence}$$

$$\boxed{P_n = \frac{1}{Z} e^{-\beta E_n}}$$

Grand canonical



$\Xi \rightarrow$ Xi

$$\Xi = \sum_n e^{-\beta E_n + \beta \mu N_n}$$

$$= \int_0^\infty dN \; e^{-\beta(A - \mu N)}$$

$$\rightarrow \quad \ln \Xi = -\beta A + \beta \mu N = -\beta E + \beta T S + \beta \mu N$$

$$k_B T \ln \Xi = TS - E + \mu N$$

Gibbs-Duhem relation

Consider a function $f(x_1, \ldots x_n)$ /

$$f^{(j)} = \frac{\partial f}{\partial x_j}$$

$$f(\lambda x_1, \ldots \lambda x_n) = \lambda^a f(x_1 \ldots x_n)$$

$\partial/\partial\lambda$

$$\sum_{j=1}^{n} x_j f^{(j)}(\lambda x_1, \ldots \lambda x_n) = a \lambda^{a-1} f \overset{\lambda=1}{\Longrightarrow} \boxed{\sum_{j=1}^{n} x_j \frac{\partial f}{\partial x_j} = a f}$$

$E(S, V, N)$ extensive $\quad E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N)$

$$S \underbrace{\frac{\partial E}{\partial S}}_{T} + V \underbrace{\frac{\partial E}{\partial V}}_{-p} + N \underbrace{\frac{\partial E}{\partial N}}_{\mu} = E$$

$$\Rightarrow \boxed{E = TS - pV + \mu N}$$

extensive

recall $G = E - TS + pV \; ; \; G(p, T) \quad \Rightarrow \boxed{\mu = \frac{G}{N}}$

and also

$$k_B T \ln \Xi = TS - E + \mu N = pV$$

$$\boxed{k_B \ln \Xi = \frac{pV}{T}}$$

$$P_n = \frac{1}{\Xi} e^{-\beta E_n + \beta\mu N_n} \quad ; \quad \Xi = \sum_n e^{-\beta E_n + \beta\mu N_n}$$

$$\langle E_n \rangle = -\frac{\partial}{\partial\beta} \ln \Xi \quad ; \quad \langle N_n \rangle = \frac{1}{\beta} \frac{\partial \ln \Xi}{\partial \mu}$$

$$-k_B \sum_n P_n \ln P_n = -k_B \sum_n P_n \left(-\beta E_n + \beta\mu N_n - \ln \Xi\right)$$

$$= \beta k_B E - \beta k_B \mu N + k_B \ln \Xi = \frac{E}{T} - \frac{\mu N}{T} + \frac{PV}{T} = S \; \underline{\checkmark}$$

We can also do

$$F = -k_B \sum_n p_n \ln p_n + \lambda \left(\sum_n p_n - 1 \right) +$$

$$+ \chi \left(\sum_n p_n E_n - \bar{E} \right) + \xi \left(\sum_n p_n N_n - \bar{N} \right)$$

and do $\partial F / \partial p_n = 0$ to get p_n.