Canonical & other ensembles

If we know all states of a system, and their probabilites then we can predict any observable

$$\langle A \rangle = \sum_{n \in \text{states}} P(n) A(n)$$

<u>Closed</u> <u>isolated</u> system $\quad P(n) \propto \frac{1}{\Omega}$

constant N, V, E, $\Omega(N,V,E)$ – # states

$$\langle A \rangle = \int d\vec{p}\, d\vec{q}\; A(\vec{p},\vec{q})\, \delta(\mathcal{H}(\vec{p},\vec{q}) - E) \,/\, \Omega(N,V,E)$$

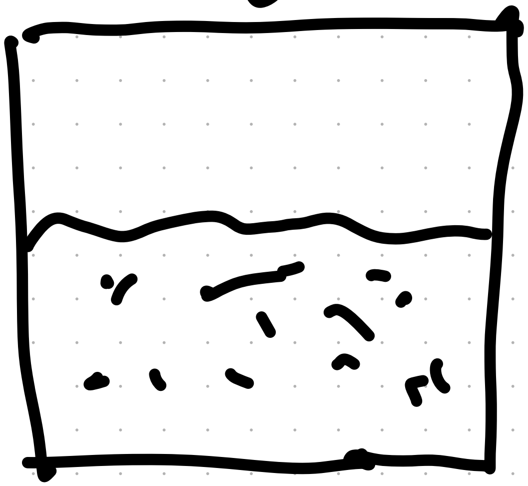
$$\Omega = \text{const} \int d\vec{p}\, d\vec{q}\; \delta(\mathcal{H}(\vec{p},\vec{q}) - E)$$

Experiments don't happen

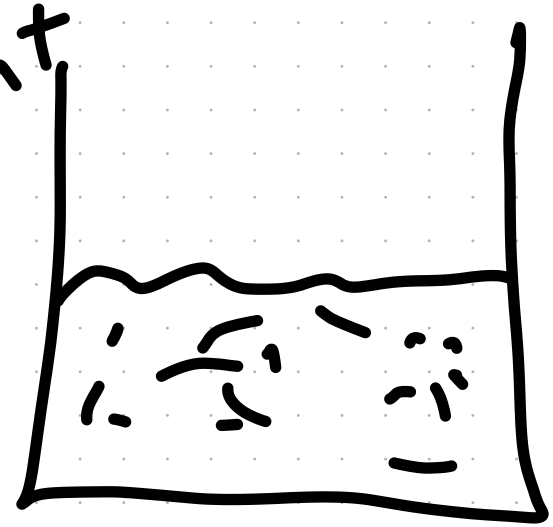
insolated, closed systms

Chemistry

const
T, V

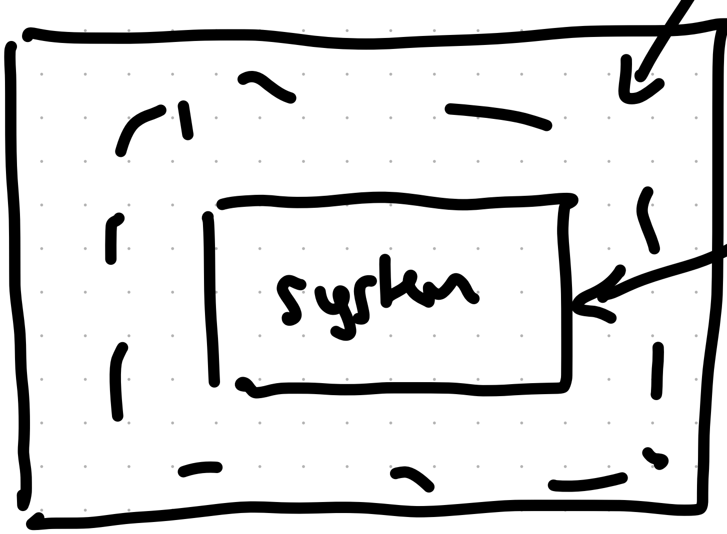


constant
T, P

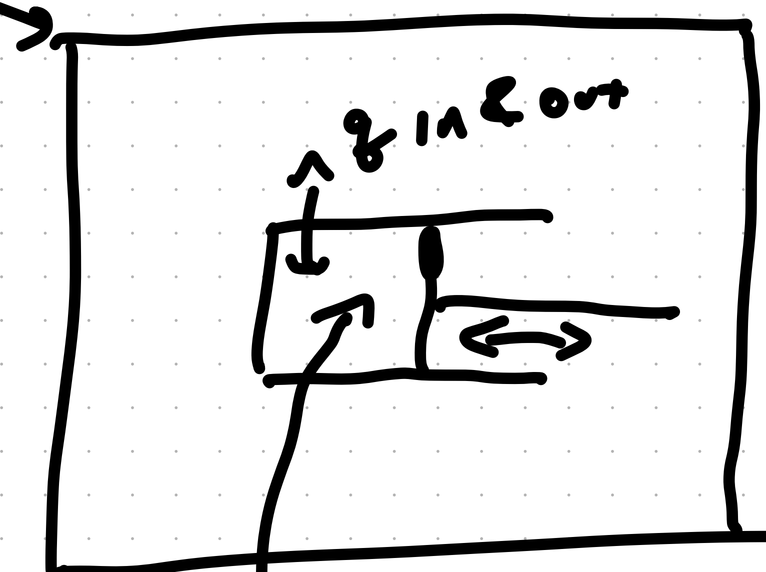


system
N, V, T

N, V, E



exchange
q



N, P, T const

Microcanonical

$S(N, V, \mathcal{E})$ – maximized at equilibrium

$$dS = \left(\frac{\partial S}{\partial \mathcal{E}}\right)_{V,N} d\mathcal{E} + \left(\frac{\partial S}{\partial V}\right)_{\mathcal{E},N} dV + \left(\frac{\partial S}{\partial N}\right)_{V,\mathcal{E}} dN$$

$$= \frac{1}{T} d\mathcal{E} + \frac{P}{T} dV - \left(\frac{\mu}{T}\right) dN$$

$$d\mathcal{E} = T\,dS - P\,dV + \mu\,dN$$

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from S $\nearrow$ $\mathcal{E}$ is a function of S, V, N

$\mathcal{E}(N, V, S)$ state function

$$d\mathcal{E} = \left(\frac{\partial \mathcal{E}}{\partial S}\right)_{V,N} dS + \left(\frac{\partial \mathcal{E}}{\partial V}\right)_{S,N} dV + \left(\frac{\partial \mathcal{E}}{\partial N}\right)_{V,S} dN$$

$\nearrow$ chain rule

$$T = \left(\frac{\partial \mathcal{E}}{\partial S}\right)_{N,P} \qquad P = -\left(\frac{\partial \mathcal{E}}{\partial V}\right)_{S,N}$$

$$\mu = \left(\frac{\partial \mathcal{E}}{\partial N}\right)_{S,N}$$

$\mathcal{E}(N, V, S)$ – S is not measurable

Legendre transform

replace a variable, with a conjugate variable

$$A(N, V, \underline{\underline{T}}) = \mathcal{E}(N, V, \underline{\underline{S}}) - S\left(\frac{\partial \mathcal{E}}{\partial S}\right)_{N,V}$$

$$= \mathcal{E} - TS$$

"Helmholtz free energy"

$$A(N,V,T) = \mathcal{E} - TS$$

$$dA = \left(\frac{\partial A}{\partial T}\right)_{V,N} dT + \left(\frac{\partial A}{\partial V}\right)_{T,N} dV + \left(\frac{\partial A}{\partial N}\right)_{V,T} dN$$

$$A = \mathcal{E} - TS$$

$$d\mathcal{E} = T\underline{dS} - PdV + \mu dN$$

$$\begin{aligned} d(A) &= d(\mathcal{E} - TS) \\ &= d\mathcal{E} - d(TS) \\ &= d\mathcal{E} - \underline{TdS} - SdT \\ &= -SdT - PdV + \mu dN \end{aligned}$$

$$-S = \left(\frac{\partial A}{\partial T}\right)_{N,V} \quad \underbrace{-P = \left(\frac{\partial A}{\partial V}\right)_{N,T} \quad \left(\frac{\partial A}{\partial N}\right) = \mu}$$

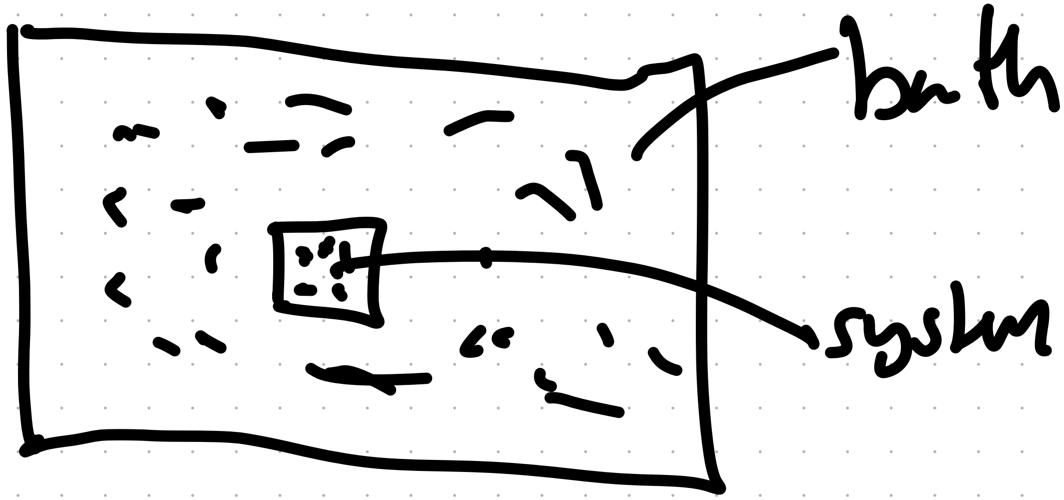
A is like Energy

$A(N, V, T)$

fundamental "energy"

for const N, V, T

("thermodynamic potentials")



$$\underbrace{\begin{array}{l} q_1, q_2 \cdots q_{3N} \\ p_1, p_2 \cdots p_{3N} \end{array}}_{\text{system}} \rightarrow \vec{X} = (\vec{q}^{\,sys}, \vec{p}^{\,sys})$$

$$\mathcal{H}_{total} = \mathcal{H}_{system} + \mathcal{H}_{bath}$$

$$E_{total} = E_{sys} + E_{bath} \quad \text{constant}$$

$$S_{total} = S_{sys} + S_{bath}$$

Suppose system has config. $\vec{x}$

$$\mathcal{E}_{system} = \mathcal{H}_{sys}(\vec{x})$$

1 arrangement of system

$$\Omega_b(N_b, V_b, \mathcal{E}_{tot} - \mathcal{E}_{sys}) \propto \underbrace{f(\vec{x})}_{\text{prob of sys to be in } \vec{x}}$$

$$S_{bath} = k_B \log \Omega_b(N_b, V_b, \mathcal{E}_b)$$

$$\mathcal{E}_b = \mathcal{E}_{total} - \mathcal{E}_{syst} \approx \mathcal{E}_{tot}$$

$$S_{bath}(\mathcal{E}_b) \approx S_{bath}(\mathcal{E}_{total})$$

$$+ \left(\frac{\partial}{\partial \mathcal{E}_b} S\right)\underbrace{(\mathcal{E}_b - \mathcal{E})}_{\mathcal{E}_b \text{ close to } \mathcal{E}} = -\mathcal{E}_{syst}$$

$$\cancel{+ \frac{1}{2}\left(\frac{\partial^2}{\partial \mathcal{E}_b} S\right)(\mathcal{E}_b - \mathcal{E})^2 + \cdots}$$

$$S_{bath} \approx \text{const} - \mathcal{E}_{sys} \cdot \underbrace{\left(\frac{\partial S}{\partial \mathcal{E}_{bath}}\right)_{N,V}}_{T_{bath}^{-1}}$$

$$\approx \text{const} - \frac{\mathcal{E}_{sys}}{T_{bath}}$$

$$= \text{const} - \mathcal{E}_{sys}/T \text{ @ eq.}$$

$$S_{bath}(N, V, \underset{\mathcal{E}_{sys}}{\cancel{\mathcal{E}_{\sigma}}}) \approx const - \frac{\mathcal{E}_{sys}}{T}$$

$$\parallel$$

$$k_B \log(\Omega(N, V, \mathcal{E}_{bath}))$$

$$\underbrace{\Omega(N, V, \mathcal{E}_{bath})}_{\propto f(\vec{X})} \approx e^{const} \cdot e^{-\mathcal{E}_{sys}/k_B T}$$

$$\mathcal{E}_{sys} = \mathcal{H}(\vec{X})$$

$$f(\vec{X}) \underset{const\ N, V, T}{\propto} e^{-\mathcal{H}(\vec{X})/k_B T}$$

<u>Boltzmann</u>

$$f(\vec{X}) \propto e^{-\mathcal{H}(X)/k_BT} = \frac{e^{-\mathcal{H}/k_BT}}{Z(N,V,T)}$$

const N, V, T

$$Z(N,V,T) = \int d\vec{q} \int d\vec{p}\, e^{-\mathcal{H}(\vec{q},\vec{p})/k_BT}$$

partition function

canonical ensemble

particle system

discrete system

$$Z = \sum_{n \text{ states}} e^{-\varepsilon_n/k_BT}$$

$$Q(N,V,T) = \frac{1}{\underline{h}^{3N}\underline{N}!}\int d\vec{x}\, e^{-\mathcal{H}(\vec{x})/k_BT}$$

$$f(\vec{x}) = \frac{1}{h^{3N}N!}e^{-\mathcal{H}(\vec{x})/k_BT} \Big/ Q(N,V,T)$$

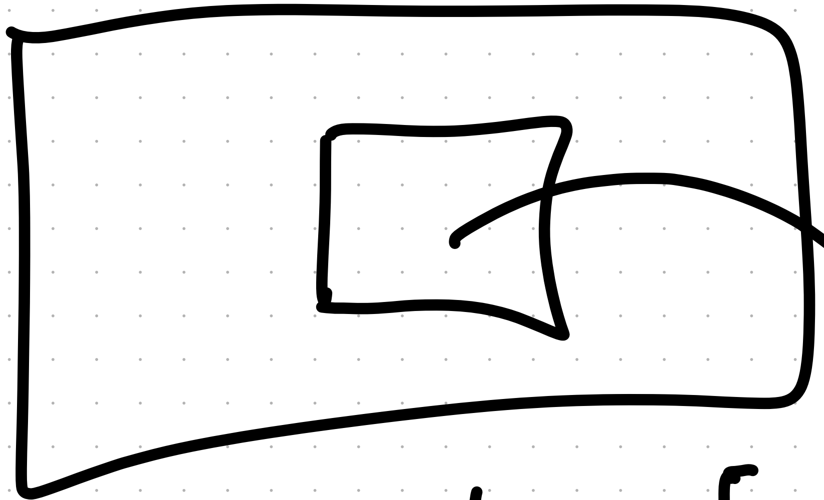
$$= e^{-\mathcal{H}(\vec{x})/k_BT} \Big/ Z(N,V,T)$$

$$Q(N,V,T) = \frac{1}{h^{3N} N!} \int d\vec{x}\, e^{-\mathcal{H}(x)/k_B T}$$

$$= \frac{1}{N!\, h^{3N}} \int d\vec{x} \int_0^\infty d\varepsilon\, \delta(\mathcal{H}(\vec{x}) - \varepsilon)\, e^{-\varepsilon/k_B T}$$

$$= \int_0^\infty d\varepsilon\, e^{-\varepsilon/k_B T} \left[\underbrace{\frac{1}{N!\, h^{3N}} \int d\vec{x}\, \delta(\mathcal{H}(\vec{x}) - \varepsilon)}_{\frac{1}{\varepsilon_0} \Omega(N,V,\varepsilon)} \right]$$

$$= \frac{1}{\varepsilon_0} \int_0^\infty d\varepsilon\, e^{-\varepsilon/k_B T}\, \underbrace{\Omega(N,V,\varepsilon)}_{\text{system}}$$



$\Omega_{sys}(N, V, \mathcal{E}_{sys})$

prob of seeing

$\mathcal{E}_{sys} = \mathcal{E}'$

$$P(\mathcal{E}_{sys} = \mathcal{E}') \propto e^{-\mathcal{E}'/k_BT}$$

$$Q = \int_0^{\mathcal{E}_{total}} P(\mathcal{E}')\,\Omega_{sys}(N, V, \mathcal{E}')\,d\mathcal{E}'$$

discrete $\quad Q = \sum \Omega(\mathcal{E}_n)\,e^{-\mathcal{E}_n/k_BT}$

$$Z = \sum_{\text{all states } n} e^{-\varepsilon_n / k_B T}$$

$$= N_{\varepsilon_1} e^{-\varepsilon_1 / k_B T} + N_{\varepsilon_2} e^{-\varepsilon_2 / k_B T}$$

$$+ \cdots$$

$$= \sum_{\varepsilon} \underbrace{\omega(\varepsilon)}_{\Omega(N, V, \varepsilon)} e^{-\varepsilon / k_B T}$$

$$A(N,V,T) = \mathcal{E} - TS$$

$$= \mathcal{E} - T\left(\frac{\partial A}{\partial T}\right)$$

$$\langle B \rangle = \int dX\, B(X)\, e^{-\mathcal{H}(x)/k_B T} \cdot \frac{1}{Z}$$

$$\langle \mathcal{E} \rangle = \int dX\, \mathcal{E}(X)\, e^{-\mathcal{H}(x)/k_B T} \cdot \frac{1}{Z}$$

$$Z = \int d\vec{X}\, e^{-\mathcal{H}(x)/k_B T} = \int d\vec{X}\, e^{-\beta \mathcal{H}(x)}$$

$$\beta \equiv (k_B T)^{-1}$$

$$\langle \mathcal{E} \rangle = \int dx\, \mathcal{H}(x)\, e^{-\beta \mathcal{H}(x)} / Z$$

$$Z = \int dx\, e^{-\beta \mathcal{H}(x)}$$

$$\frac{\partial Z}{\partial \beta} = \int dx \left(\frac{\partial}{\partial \beta} e^{-\beta \mathcal{H}(x)} \right)$$

$$= \int dx - \mathcal{H}(x)\, e^{-\beta \mathcal{H}(x)}$$

$$\frac{\partial \log x}{\partial x} = \frac{1}{x}$$

$$-\frac{\partial}{\partial \beta}\left(\log Z\right) = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

$$= \frac{1}{Z}\cdot\int \mathcal{H}(x)\, e^{-\beta \mathcal{H}(x)}\, d\vec{x}$$

$$= \langle E \rangle$$

$$A = E - T\left(\frac{\partial A}{\partial T}\right) =$$

$$= -\frac{\partial}{\partial \beta}\log Z - T\left(\frac{\partial A}{\partial T}\right)$$

$$\boxed{A = -k_B T \log Z}$$