Canonical Ensemble

Discuss HW1 survey

Other thermodynamic ensembles

Idea: Our hypothesis before was that if we could enumerate all the states of a system and the likelyhood of seeing them, then we could predict any observable:

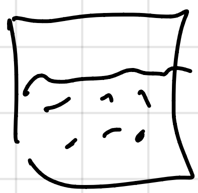
$$\langle A \rangle = \sum_{n \in \text{states}} P(n) A(n)$$

For closed isolated system, const N, V, E we expect all states to have the same weight, $\Omega(N,V,E)$ states

$$\langle A \rangle = \int d\vec{q}\, d\vec{p}\, \delta(H(p,q) - E)\, A(p,q) \Big/ \int d\vec{q}\, d\vec{p}\, \delta(H(p,q) - E)$$

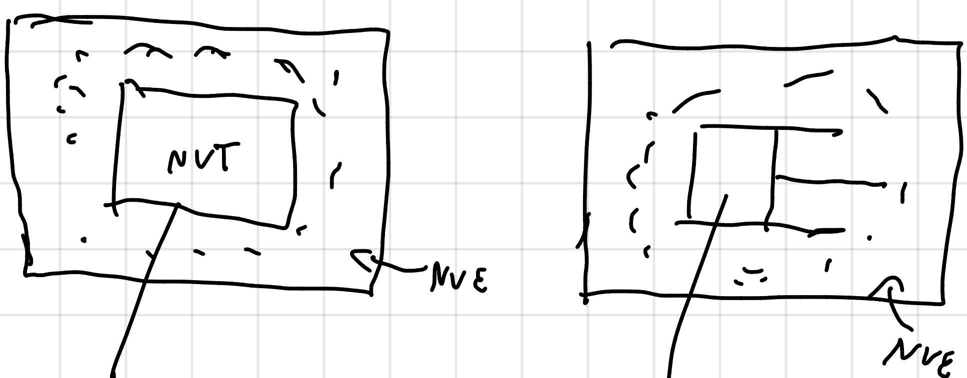
But we don't live in an isolated closed system $\Rightarrow$

Chemistry usually happens at const

T & V  or T & P 

So we have to see how likely a configuration is under these conditions

First, how is this dealt with in classical thermo



(can also have permeable membrane, eg μ, V, T

Impermeable to particles, rigid, can exchange heat

NPT can exchange heat, change volume (can show pressure equilibrates @ eq)

In microcanonical Ensemble we had $S(N, V, E)$ &

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

lets rewrite in terms of E, b/c that may be easier to think about

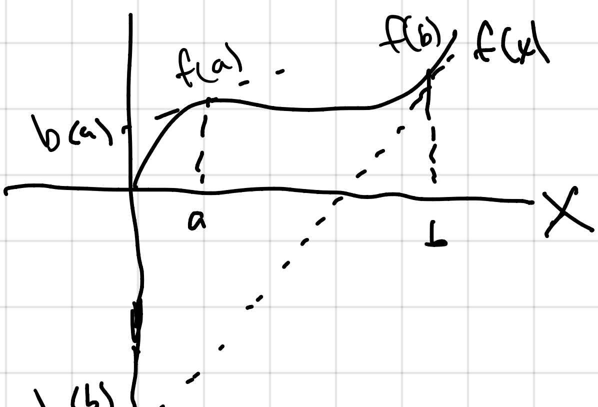
$$dE = T dS - P dV + \mu dN$$

This means $T = \left(\partial E/\partial S\right)_{N,V}$ $\quad P = -\left(\partial E/\partial V\right)_{S,N}$ $\quad \mu = \left(\dfrac{\partial E}{\partial N}\right)_{S,V}$

And $E(N,V,S)$ is a state function.

T, $-P$, and μ are called conjugate variables of S, V & N respectively

If we want a thermodynamic state function that depends on a conjugate variable instead of a current variable we have a trick called a Legendre transform



$$c(x) = \frac{df(x)}{dx} = f'(x) \Rightarrow x(c) = (f')^{-1}(c)$$

$$f(x) = x\frac{df(x)}{dx} + b(x) = x\,c(x) + b(x)$$

$$b(x) = f(x) - x\,c(x)$$

define new func $\tilde{b}(c) = f(x(c)) - x(c)\,c(x)$

Eg. have $E(\overbrace{N,V,S}^{\text{all extensive}})$ of our system, but can't measure S...

New func $\underbrace{A}_{b(T)}(N,V,\underbrace{T}_{c\text{ above}}) = E(N,V,S) - \underbrace{S}_{x\text{ above}}\left(\partial E/\partial S\right)_{N,V} = \underline{\underline{E(N,V,S) - TS}}$

A is the "Helmholtz free energy"

Chain rule for $A(N,V,T)$ gives

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

but $A = E - TS \Rightarrow dA = dE - TdS - SdT$

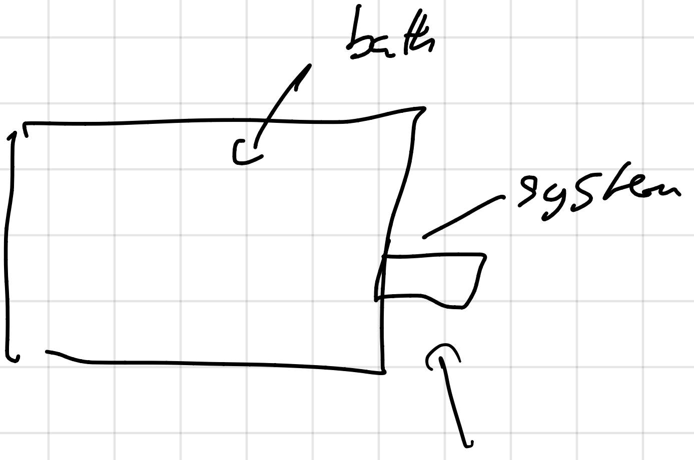
$$= (TdS - PdV + \mu dN) - TdS - SdT$$

$$= -SdT - PdV + \mu dN$$

$$\Rightarrow \left(\partial A/\partial T\right)_{N,V} = -S \quad \underbrace{\left(\frac{\partial A}{\partial V}\right)_{N,T} = -P \quad \left(\frac{\partial A}{\partial N}\right)_{V,T} = \mu}_{A \text{ is like an energy}}$$

☆

This is all classical thermo. To derive things based on a particle basis, we need to figure out how likely a state is, ie the inside of the partition function



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

$$\Rightarrow E_{total} = E_{sys} + E_{bath}$$

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

$\vec{q}, \vec{p} = \vec{X}$

Suppose the particles in the system have certain $\vec{p}, \vec{q}$, w/ $\mathcal{E}_{sys} = \mathcal{H}_{sys}(p,q)$. The bath can be arranged many ways:

$$\Omega_b(N_b, V_b, \mathcal{E} - \mathcal{E}_{sys}) \propto f(q,p)$$

$\mathcal{E} = \mathcal{E}_{sys} + \mathcal{E}_{bath}$ & $\mathcal{E}_{sys}$ small $\Rightarrow$ $\mathcal{E} - \mathcal{E}_{bath}$ is small

Consider $S_{bath}(N_{bath}, V_{bath}, \mathcal{E}_{bath}) = S_{bath}(\mathcal{E}_b)$

$$S_{bath}(\mathcal{E}_b) \approx S_{bath}(\mathcal{E}) + \left(\frac{d}{d\mathcal{E}_b} S\right)\Big|_{\mathcal{E}=\mathcal{E}_{bath}} \underbrace{(\mathcal{E}_b - \mathcal{E})}_{\sim \mathcal{E}_{sys}} + \ldots$$

$$\approx S_{bath}(\mathcal{E}) - \frac{1}{T}\mathcal{E}_{sys}$$

$$K \log \Omega_b(N_b, V_b, \mathcal{E}_b) \approx \text{const} - \mathcal{E}_{sys}/T$$

$$f(q,p) \propto \Omega_b(N_b, V_b, \mathcal{E}_b) = \text{const} \cdot e^{-\mathcal{E}_{sys}/k_B T}$$

$$\propto e^{-\mathcal{H}_{sys}(\vec{x})/k_B T}$$

$$f(q,p) = e^{-\mathcal{H}_{sys}(\vec{x})/k_B T} / Z, \qquad Z = \int d\vec{x}\, e^{-\beta \mathcal{H}_{sys}(x)}$$

and this is true even for systems where we're not thinking about particle systems, so

$$Z = \int d\vec{x}\, e^{-\beta H(x)} \qquad \text{where} \quad \beta = 1/k_B T$$

or for discrete systems $Z = \sum_n e^{-\beta E_n}$

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for N indistinguishable particles, often write

$$Q(N,V,T) = \frac{1}{h^{3N} N!} \int dp^{3N} dq^{3N}\, e^{-\beta \mathcal{H}(q,p)}$$

and

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

cancels out

$$= e^{-\beta \mathcal{H}(p,q)} \Big/ Z(N,V,T) \quad \checkmark$$

What is the connection between Q & $\Omega(N,V,E)$?

insert delta func

$$Q(N,V,T) = \frac{1}{N!\,h^{3N}} \int dp^{3N} dq^{3N} \int_0^\infty dE\, \delta(H-E)\, e^{-\beta E}$$

$$= \int_0^\infty dE\, e^{-\beta E} \cdot \underbrace{\frac{1}{N!\,h^{3N}} \int dp^{3N} dq^{3N}\, \delta(H(p,q)-E)}_{\frac{1}{\varepsilon_0}\Omega(N,V,E)}$$

$$Q(N,V,T) = \frac{1}{\varepsilon_0}\int_0^{\infty} d\varepsilon \, \overbrace{e^{-\beta\varepsilon}}^{P(\varepsilon)} \, \Omega(N,V,\varepsilon)$$

so the canonical partition function is averaging the number of states at each energy if they have weight $e^{-\beta\varepsilon}$

Discrete, $Q(N,V,T) = \sum_{\varepsilon} \Omega(N,V,\varepsilon) e^{-\varepsilon/k_B T}$