Lecture 5 –

Canonical Ensemble

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:

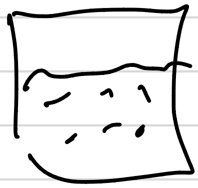
$$\langle A \rangle = \sum_{n \in states} P(n) A(n)$$

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

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

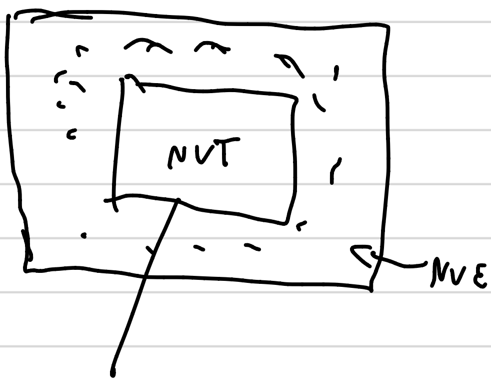
But we don't live in an isolated closed system ⇒

Chemistry usually happens at const

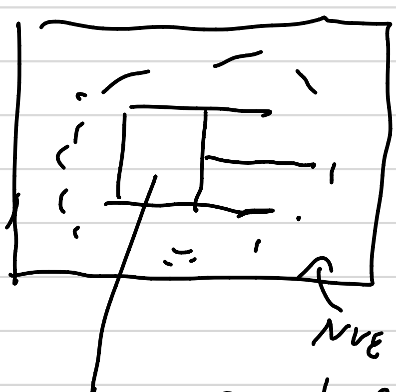
T & V  or T & P 

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

First, how is this dealt with in classical thermo



impermeable to particles, rigid, can exchange heat



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

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

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

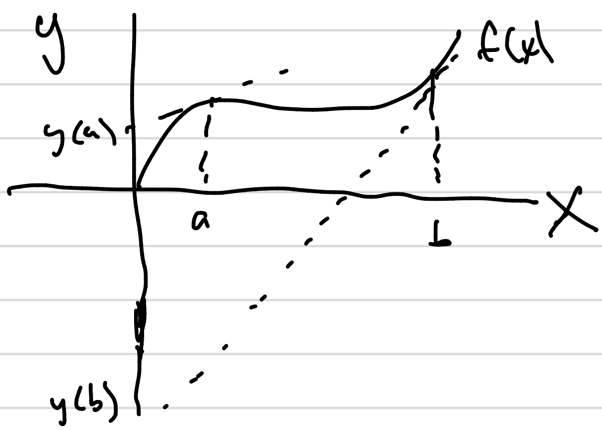
$$dE = TdS - PdV + \mu dN$$

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

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



The conj of x is u

$u = \left(\partial f/\partial x\right) = f'(x)$

$x = (f')^{-1}(u)$
$= \phi(u)$

Slope intercept says

$f(a) = \underbrace{f'(a)}_{u(a)}\, a + y(a)$

$f(b) = u(b)\, b + y(b)$

in general $f(x) = u(x)x + y(x)$

$y(x) = f(x) - u(x)x$

new func $\tilde{f}(u) = f(x(u)) - x(u)\, \partial f/\partial x$

Eg. New func $A(N,V,T) = \mathcal{E}(N,V,S) - S\left(\partial \mathcal{E}/\partial S\right)_{N,V} = \mathcal{E}(N,V,S) - TS$

$\tilde{f}$ u above x above

A is the "Helmholz 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 $A = E - TS \Rightarrow dA = dE - TdS - SdT$

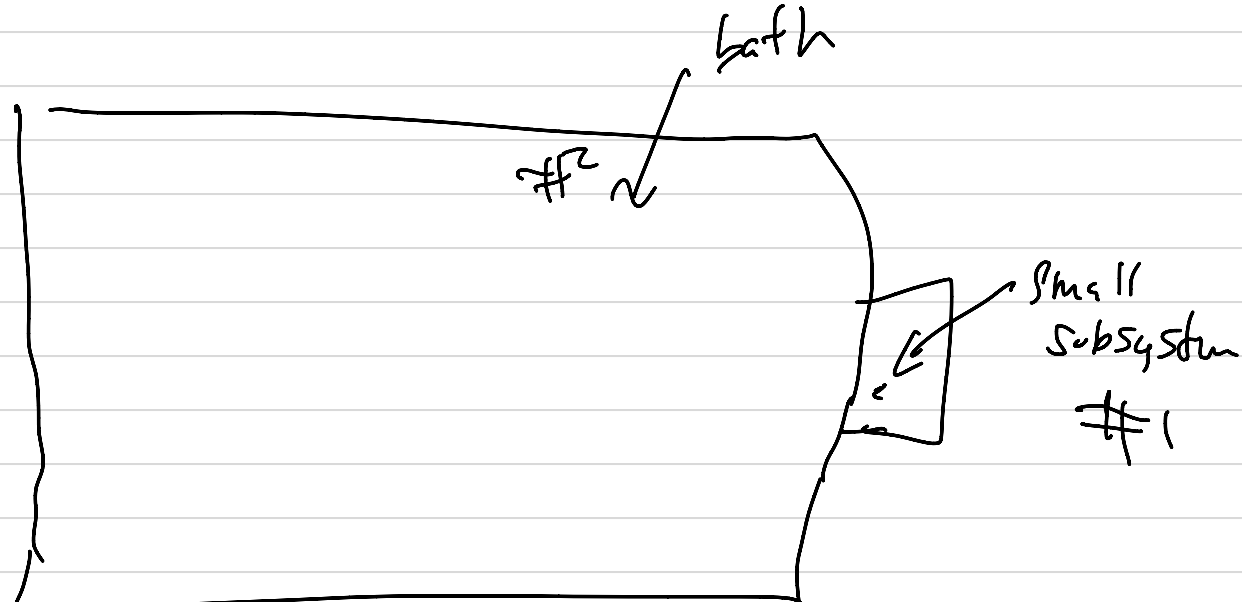
$$= (TdS - PdV + \mu dN) - TdS - SdT$$

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

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

☆

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



$$E_{total} = \mathcal{H}(p,q) = \mathcal{H}_1(p',q') + \mathcal{H}_2(p'',q'')$$

Integrate over coordinates (p'', q''), this is a type of what we call "coarse-graining", reduce complexity of system. May cover this more later

What is $f(p', q')$ prob of state in subsystem.

$$f(p', q') = \frac{\int dp'' dq'' \, \delta\left(\mathcal{H}(p,q) - \mathcal{H}_1(p', q') - \mathcal{H}_2(p'', q'')\right)}{\Omega(N, V, \mathcal{E})} \leftarrow \text{const}$$

Since system 1 is small, expand function around $\mathcal{H}_1(p', q') = 0$, convenient to expand $\ln(f)$

Remember $\phi(x) = \phi(a) + (x-a)\phi'(a) + \frac{(x-a)^2}{2}\phi''(a) + \ldots$

$$= \sum_{n=0}^{\infty} \phi^{(n)}(a) \frac{(x-a)^n}{n!} \quad \text{taylor series}$$

$$\log f(p', q') = \log \int dp'' dq'' \, \delta\left(\mathcal{H}(p,q) - \mathcal{H}_1(p', q') - \mathcal{H}_2(p'', q'')\right) - \underset{\text{ignore}}{\text{const}}$$

first order

large system

$$\approx \log \int dp'' dq'' \, \delta\left(\mathcal{H}(p,q) - \mathcal{H}_2(p', q')\right)$$

$$+ \left(\frac{\partial}{\partial \mathcal{H}_1} \log \int dp'' dq'' \, \delta\left(\mathcal{H}(p,q) - \mathcal{H}_1(p', q') - \mathcal{H}_2(p'', q'')\right)\right)\Bigg|_{\mathcal{H}_1 = 0} \mathcal{H}_1$$

$$+ \ldots$$

lets shorten $\mathcal{H}(p,q)=\mathcal{E}$ and use property of delta func

$$\partial/\partial H_1\, \delta(H_1+H_2-\mathcal{E}) = -\frac{\partial}{\partial\mathcal{E}}\delta(H_1+H_2-\mathcal{E})$$

note, using this here. is skipping some steps

so $\log f \approx \log\int dp''dq''\,\delta(\mathcal{H}_2(p'',q'')-\mathcal{E})$

$$-\left(\partial/\partial\mathcal{E}\log\int dp''dq''\,\delta(H_1+H_2-\mathcal{E})\Big|_{\mathcal{H}_1=0}\right)\mathcal{H}_1(p',q')$$

$$\parallel$$

$$\left(\partial/\partial\mathcal{E}\log\int\delta(H_2-\mathcal{E})\right)\mathcal{H}_1(p',q')$$

$$\log\int dp''dq''\,\delta(H_2(p'',q''-\mathcal{E}))| = \Omega_2(N_2,V_2,\mathcal{E}_2)$$

$$= S_2/k$$

$$\log f \approx \frac{S_2}{k} - \mathcal{H}_1(p',q')\frac{\partial}{\partial\mathcal{E}}\frac{S_2}{k}(N_2,V_2,\mathcal{E}_2)$$

$$\log f \approx \underbrace{S_2/k}_{\text{const}} - \mathcal{H}_1(p',q')/kT_2 \qquad T_2 \approx T$$

so $f \propto \exp(-\mathcal{H}_1(p',q')/kT)$ ✓

The normalized prob of seeing a state is

$$f(p,q) = e^{-\mathcal{H}(p,q)/k_BT}\Big/\int dp\int dq\, e^{-\mathcal{H}(p,q)/k_BT}$$

we often call denominator Z

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

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

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

for systems of indistinguishable particles, usually write

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

$$f(q',p') = \frac{1/N!h^{3N}\, e^{-\beta H(q',p')}}{Q(N,V,T)}$$

($\frac{1}{N!h^{3N}}$ cancel out to give same prob. func.)

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

insert delta func

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

$$= \int_0^\infty dE\, e^{-\beta E} \cdot \underbrace{\frac{1}{N!h^{3N}} \int dp^{3N} dq^{3N}\, \delta(H(p,q)-E)}_{\frac{1}{E_0}\Omega(N,V,E)}$$

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

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

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