Lecture 6 - Microcanonical to Canonical

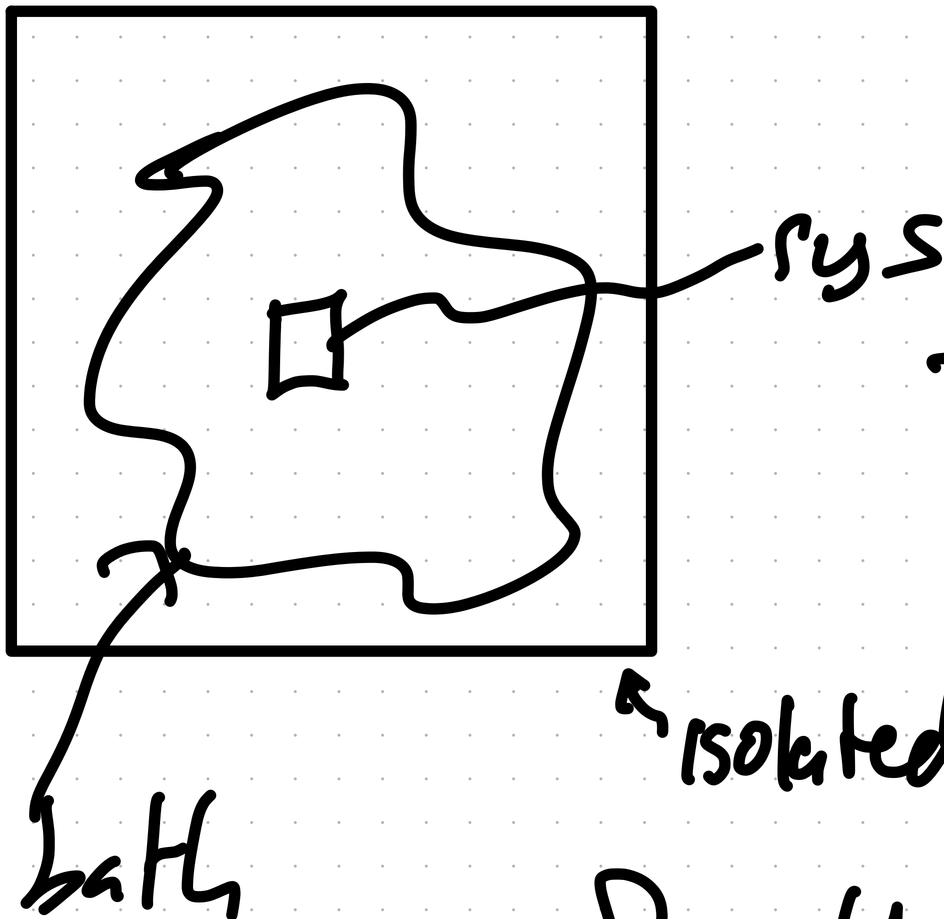
Microcanonical: Const N, V, E

$$P(\vec{X}) \propto \begin{cases} \frac{1}{\Omega(N,V,E)} & \mathcal{H}(x)=E \\ 0 & \text{otherwise} \end{cases}$$

$x_1 \ldots x_{3N}, p_1 \ldots p_{3N}$

$$S = k_B \ln \Omega(N,V,E)$$

N, V, T $\quad P(\vec{X}) \propto e^{-\mathcal{H}(x)/k_B T}$



Total # $= \Omega_t(N, V, \varepsilon)$

$= \Omega_{sys} \cdot \Omega_{bath}$

$$= \Omega_{bath}(N_{bath}, V_{bath}, \varepsilon_{bath}) \cdot \Omega_{sys}(N_{sys}, V_{sys}, \varepsilon_{sys})$$

$N_{bath} \gg N_{sys}$ $\quad$ $\varepsilon_{bath} \gg \varepsilon_{sys}$

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

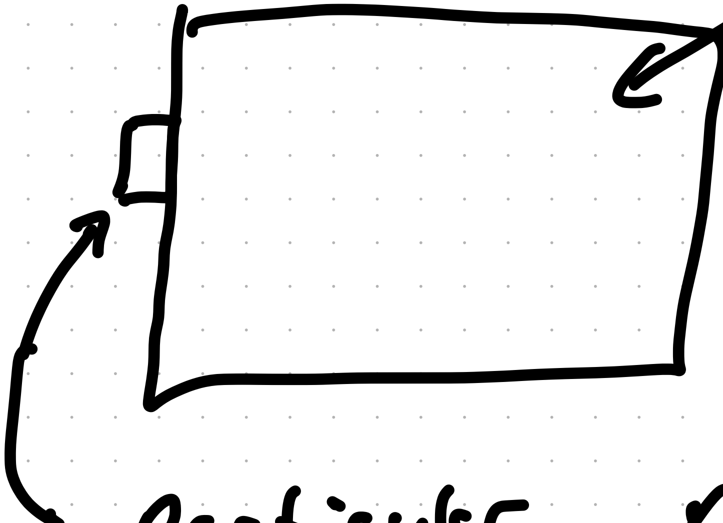
@ eq $\quad \frac{1}{T_{bath}} = \frac{1}{T_{sys}} = \frac{1}{T}$

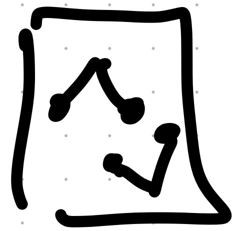
$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V}$$

Just consider system:

$$P(\vec{X}_{sys}) \propto \Omega_b(N, V, E_{bath})$$

$\mathcal{E}_{bath} = \mathcal{E}_{total} - \mathcal{H}(x)$





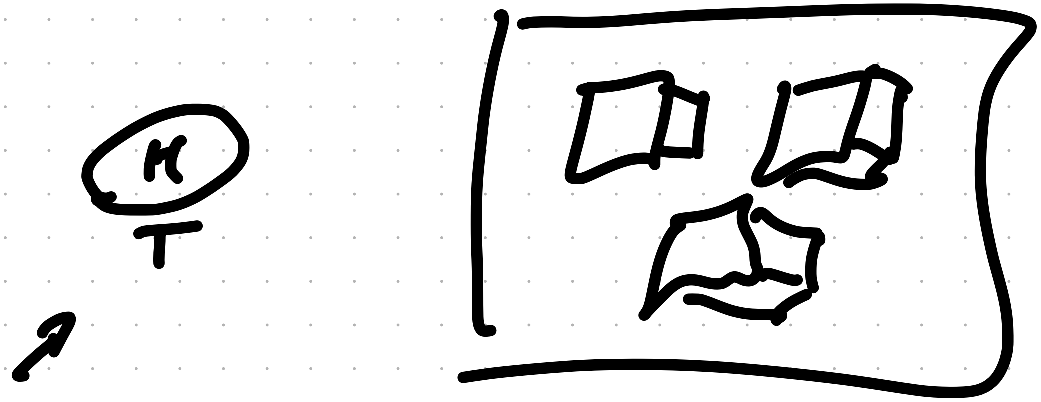
$\mathcal{E}_{sys} = \mathcal{H}(\vec{x}_{sys})$

particuler $\quad x_1, x_2, \ldots$

$p_1, p_2, \ldots$

$$P(\vec{X}_{sys}) \propto \Omega_{bath}(N_{bath}, V_{bath}, \mathcal{E}_{bath})$$

$$P(X_{sys+bath}) \propto \frac{1}{\Omega_{sys} \cdot \Omega_{bath}}$$



states $= 2 \cdot 6^3$

Sys $= T$, T has energy -2

$E_{total} = \sum \text{dice} + H/T = 6$

computational assignment

$$S(N, V, \varepsilon_b) = k_B \ln \Omega_b$$

Idea: taylor series $\varepsilon_b \approx \varepsilon_{total}$

$$P(x_{sys}) \propto \Omega_b = e^{\ln \Omega_b} = e^{S/k_B}$$

very very small

$$S(N_b, V_b, \varepsilon_b) \approx S(N_b, V_b, \varepsilon_{tot}) + \underbrace{(\varepsilon_b - \varepsilon_{tot})}_{-\varepsilon_{sys}} \underbrace{\left.\frac{dS}{d\varepsilon_b}\right|_{\varepsilon_b^*}}_{1/T} \cancel{+ O((\varepsilon_b - \varepsilon_{tot})^2)} \ldots$$

$$S_{bath} \approx C - \varepsilon_{sys}/T \Rightarrow P(x_{sys}) \propto e^{-\varepsilon_{sys}/k_B T}$$

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

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

$$\beta = 1/k_B T$$

Another partition function

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

N indisting. particles

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

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

$$= \frac{1}{h^{3N} N!} \int d\vec{x}_{sys} \int_0^\infty dE\, \delta(\mathcal{H}(x) - E)\, e^{-\beta E}$$

$$= \int_0^\infty dE \underbrace{\left[\frac{1}{h^{3N} N!} \int d\vec{x}_{sys}\, \delta(\mathcal{H}(x) - E) \right]}_{\Omega_{sys}(N,V,E)} e^{-\beta E}$$

$$= \frac{1}{E_0} \int_0^\infty dE\, \Omega(N,V,E)\, e^{-\beta E}$$

Laplace transform

degeneracy, density of states

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

$$P(x) \propto e^{-\beta\mathcal{H}(x)}$$

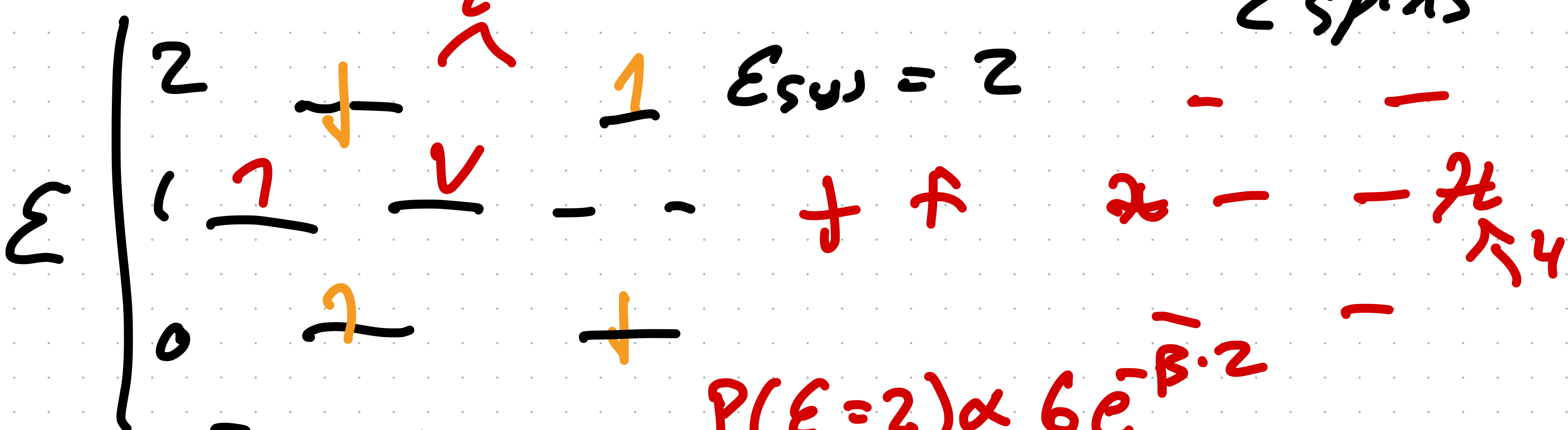
$$P(\varepsilon) \propto \underbrace{\omega(\varepsilon)}_{\text{density of states}}e^{-\beta\varepsilon}$$

16

$$P(\varepsilon=1) \propto 8e^{-\beta\varepsilon_1}$$

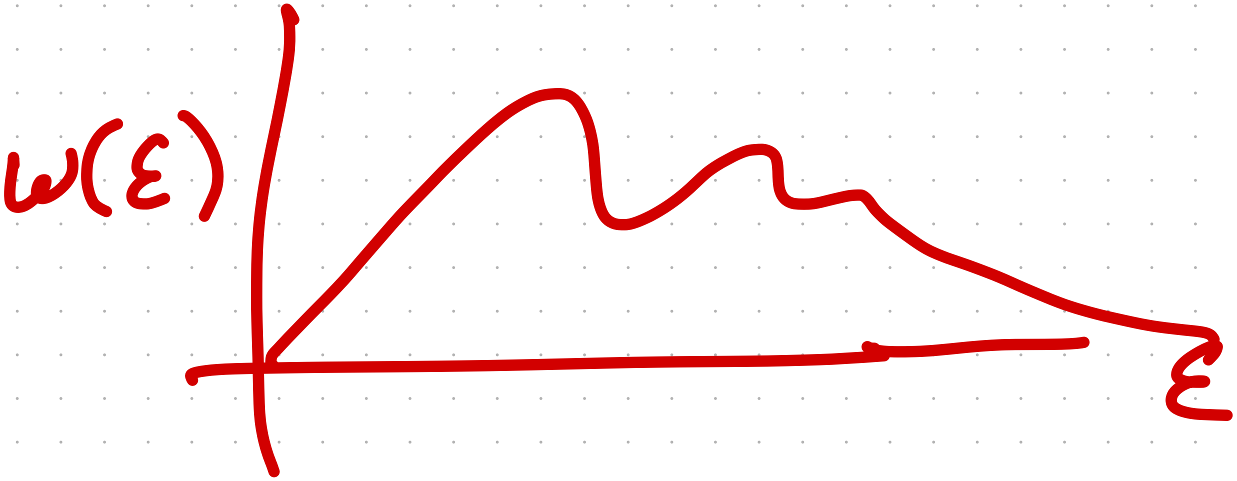
2 spins

$\varepsilon_{sys} = 2$



$$P(\varepsilon=2) \propto 6e^{-\beta\cdot 2}$$

2 spins



More Thermodynamics

Microcanonical: $-S$ is thermodynamic pot

$S(N, V, \varepsilon)$

$$dS = \underbrace{\left(\frac{\partial S}{\partial N}\right)_{V,\varepsilon}}_{-\mu/T} dN + \underbrace{\left(\frac{\partial S}{\partial \varepsilon}\right)_{N,V}}_{1/T} d\varepsilon + \underbrace{\left(\frac{\partial S}{\partial V}\right)_{N,\varepsilon}}_{P/T} dV$$

$$d\varepsilon = T\,dS - P\,dV + \mu\,dN$$

$\varepsilon(S, V, N)$

In mathematics: Legendre transformation

Legendre tranformation

mapping between 2 functions

one argument is replaced

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

$$\left(\frac{\partial S}{\partial E}\right) = \frac{1}{T}$$

$$A(N,V,T) = E - TS$$ [Helmholz free energy]

eg

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

$G = \underbrace{\mathcal{E} - TS + PV}_{N, P, T}$

$H = \mathcal{E} + PV$

N, P, S

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

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

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

$$= \mu\,dN - P\,dV - S\,dT$$

$$\left(\frac{dA}{\partial N}\right)_{N,T} = \mu \qquad \left(\frac{\partial A}{\partial V}\right|_{N,T} = -? \qquad \left(\frac{\partial A}{\partial T}\right)_{N,V} = -S$$

$$\underbrace{A = -k_B T \ln Z}_{\text{assume \& check}} = -\frac{1}{\beta} \ln Z$$

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

$$\mathcal{E} = -\frac{\partial \ln Z}{\partial \beta}$$

$$\frac{\partial A}{\partial T} = \frac{\partial A}{\partial \beta} \cdot \frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2} \frac{\partial A}{\partial \beta} \qquad \left(\frac{1}{k_B T}\right)$$

$$T \frac{\partial A}{\partial T} = -\frac{1}{k_B T} \frac{\partial A}{\partial \beta} = -\beta \frac{\partial A}{\partial \beta}$$

$$A = -\frac{\partial \ln Z}{\partial \beta} - \beta \frac{\partial A}{\partial \beta}$$

$$A = -\frac{\partial \ln z}{\partial \beta} - \beta \frac{\partial A}{\partial \beta}$$

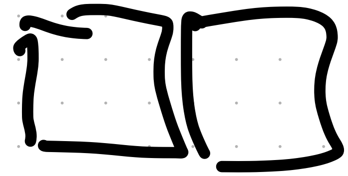
[check $A = -\frac{1}{\beta}\ln z$?]

$$\frac{\partial A}{\partial \beta} = +\frac{1}{\beta^2}\ln z - \frac{1}{\beta}\frac{\partial \ln z}{\partial \beta}$$

$$-\beta\frac{\partial A}{\partial \beta} = -\frac{1}{\beta}\ln z + \frac{\partial \ln z}{\partial \beta}$$

$$A = -\frac{1}{\beta}\ln z \quad \checkmark$$

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



Ideal gas:

$$Z = \underbrace{\int_0^L dx^{3N}} \int dp^{3N}\, e^{-\beta \sum p_i^2/2m}$$

$$= L^{3N} \cdot \left[(2\pi m k_B T)^{1/2} \right]^{3N}$$

$$= V^N \left[(2\pi m k_B T)^{3/2} \right]^N$$

$$Q = \frac{1}{h^{3N} N!} Z = \frac{1}{N!} \left[\frac{V}{\Lambda^3} \right]^N$$

$$Z = V^N \left[(2\pi m k_B T)^{3/2} \right]^N$$

$$A = -k_B T \ln Z$$

$$P = -\frac{\partial A}{\partial V} = +k_B T \frac{\partial \ln Z}{\partial V}$$

$N \ln V$ + stuff

$$P = k_B T \, N/V \implies PV = N k_B T \checkmark$$

$$\mathcal{E} = A + TS = A + T \frac{\partial A}{\partial T} \stackrel{?}{=} \frac{3}{2} N k_B T$$

HW?

const N, V, E

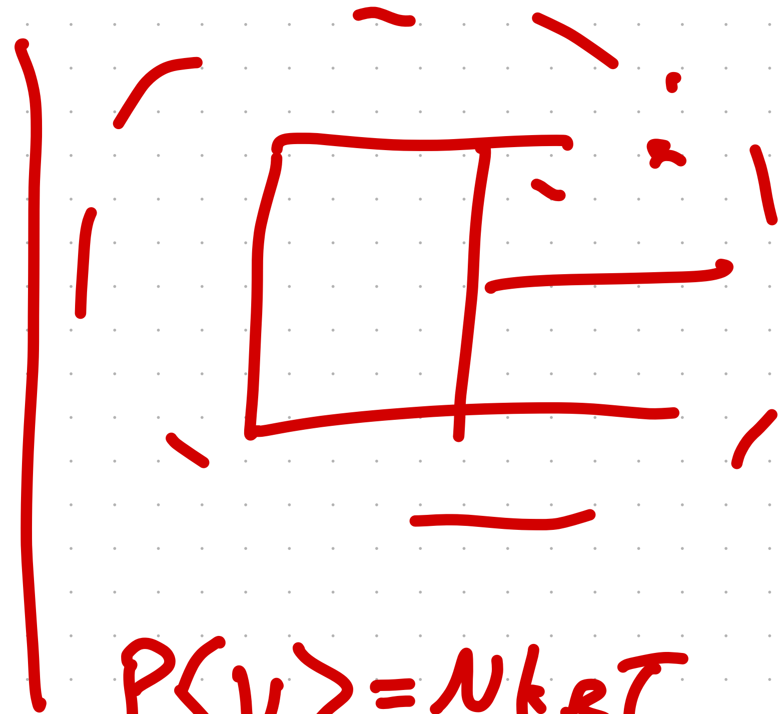
$$PV = Nk_BT$$

average quantities

const N, V, T

$$PV = Nk_BT$$

average quantity



$$P\langle V\rangle = Nk_BT$$

const N, P, T