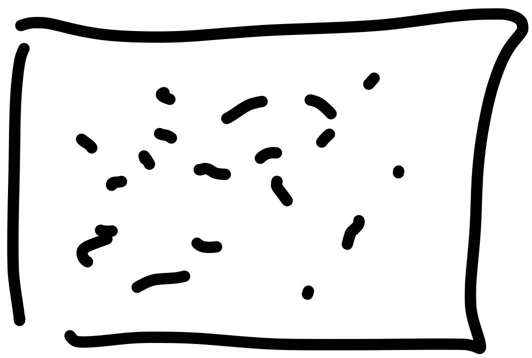
Lecture 6 - Microcanonical to Canonical

Previously:

N, V, E:



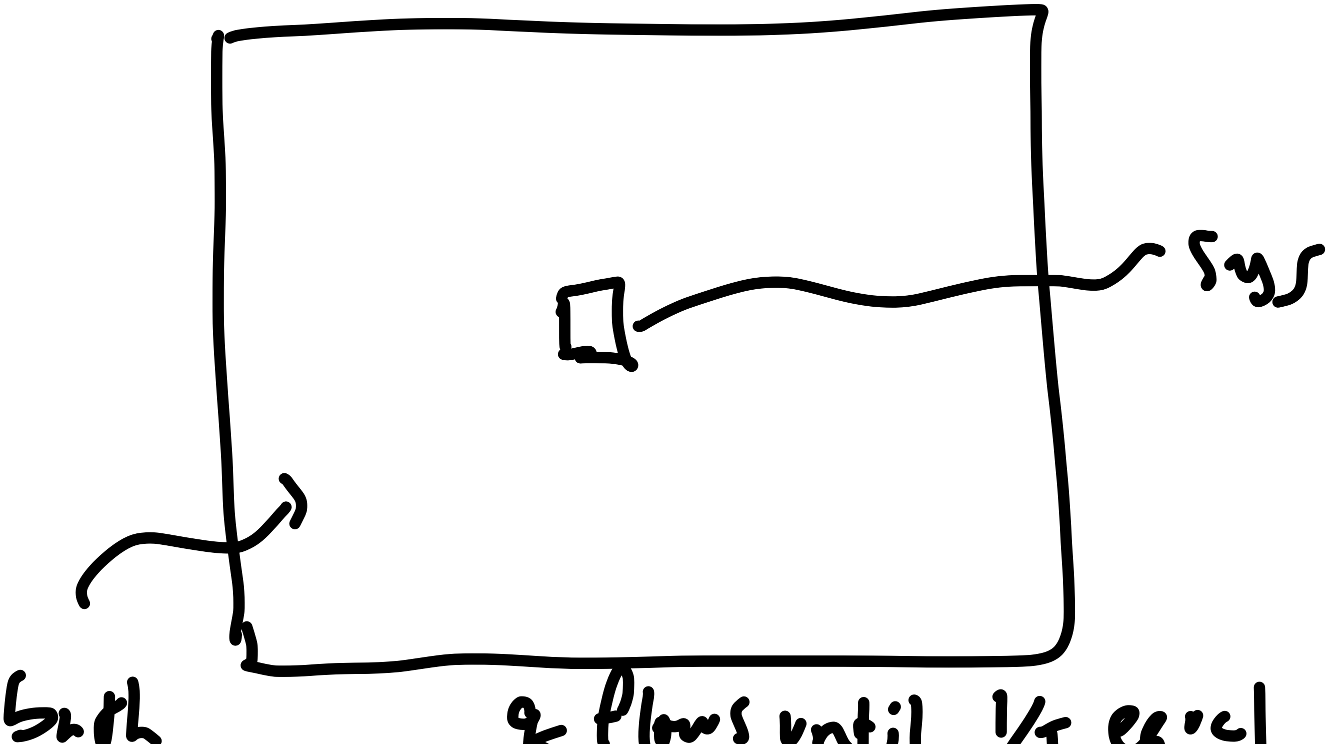
$$P(\vec{x}) \propto \begin{cases} \dfrac{1}{\Omega(N,V,E)} & \text{if } \mathcal{H}(x) = E \\ 0 & \text{otherwise} \end{cases}$$

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

N, V, T:

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

but why?



q flows until $1/T$ equal

Total: $\Omega = \Omega_{sys}\,\Omega_{bath}$

$\Omega_{bath}(N, V, E_{bath})$

$E_{tot} = E_{bath} + E_{sys}$ is const

Suppose system has config $\vec{X}$

$E_{sys} = \mathcal{H}(X) \Rightarrow E_{bath} = E - E_{sys}$ fixed

$P(\vec{X}) \propto \Omega_b(N, V, E_b)$

$$S(N,V,\mathcal{E}_b) \approx S(N,V,\mathcal{E}_{tot}) + (\mathcal{E}_b - \mathcal{E}_{tot})\frac{dS}{d\mathcal{E}_b} + \cancel{\frac{1}{2}(\mathcal{E}_b - \mathcal{E}_{tot})^2 \frac{\partial^2 S^2}{\partial \mathcal{E}_b}} + \dots$$

$$S(N,V,\mathcal{E}_b) \approx \text{const} - \mathcal{E}_{sys} \cdot \frac{1}{T_{bath}} = \frac{1}{T}$$

$$\parallel$$

$$k_b \ln \Omega(N,V,\mathcal{E}_b)$$

$$\Omega(N,V,\mathcal{E}_b) \propto e^{-\mathcal{E}_{sys} \cdot \frac{1}{k_B T}}$$

so $P(x) \propto e^{-\mathcal{H}(x)/k_B T}$ ✓

$$P(x) = \frac{1}{Z} e^{-\mathcal{H}(x)/k_B T}$$

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

Often, define

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

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

$$= e^{-\beta \mathcal{H}(x)} \big/ Z(N, V, T)$$

Can write Q in another useful way:

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

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

$$= \int_0^\infty d\mathcal{E} \underbrace{\left[\frac{1}{h^{3N} N!} \int dx\, \delta(\mathcal{H}(x) - \mathcal{E}) \right]}_{\frac{1}{\mathcal{E}_0} \Omega(N, V, \mathcal{E})} e^{-\beta \mathcal{E}}$$

← system

$$= \frac{1}{\mathcal{E}_0} \int_0^\infty d\mathcal{E} \underbrace{\Omega(N, V, \mathcal{E})}_{\substack{\text{degeneracy} \\ \text{density of states } W(\mathcal{E})}} e^{-\beta \mathcal{E}}$$

[laplace transform]

$$P_{sys}(\mathcal{E}) \propto W(\mathcal{E}) e^{-\beta \mathcal{E}}$$

More thermodynamics

To derive more, need to know how ensembles are connected in classical thermo

Microcanonical:
$S(N, V, E)$ is fundamental, max @ eq

$$dS = \left(\frac{\partial S}{\partial N}\right) dN + \left(\frac{\partial S}{\partial V}\right) dV + \left(\frac{\partial S}{\partial E}\right) dE$$

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

at same time, 1st law

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

here $E(N, V, S)$ but can't measure S

In math, can replace an argument by a conjugate variable through <u>legendre transform</u> to get a new function

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

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

Helmholtz free energy

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

$$= d\mathcal{E} - d[TS] = \underbrace{d\mathcal{E} - TdS}\, - SdT$$

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

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

A is thermodynamic potential for N, V, T, minimized @ eq

Now will show $A = -k_B T \ln Z$

$= -\frac{1}{\beta} \ln Z$

like entropy $\longrightarrow$

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

$$\frac{\partial A}{\partial T} = \frac{\partial A}{\partial \beta} \cdot \frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2} \frac{\partial A}{\partial \beta}$$

so $T \frac{\partial A}{\partial T} = -\beta \frac{\partial A}{\partial \beta}$

already showed $\langle \mathcal{E} \rangle = -\frac{\partial \ln Z}{\partial \beta}$

$$A = -\frac{\partial \ln Z}{\partial \beta} - \beta \frac{\partial A}{\partial \beta} \rightsquigarrow \int \rightarrow \left[\frac{1}{\beta^2} \ln Z - \frac{1}{\beta} \frac{\partial \ln Z}{\partial \beta}\right]$$

$= -\frac{1}{\beta} \ln Z$ ✓

So $A = -k_B T \ln Z \quad = -k_B T \ln Q + \text{const}$

Consider ideal gas

$$Q = \frac{1}{N!\, h^{3N}} \int d\vec{x} \int d\vec{p}\, e^{-\beta \sum p_i^2/2m}$$

$$= \frac{1}{N!\, h^{3N}} V^N \cdot (2\pi m k_B T)^{3/2 N}$$

$$= \frac{1}{N!} V^N \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2} N}$$

$$= \frac{1}{N!} \left(\frac{V}{\Lambda^3} \right)^N$$

$$E = -\frac{\partial \ln Q}{\partial \beta} = -\frac{\partial}{\partial \beta} \left[\ln \left(\beta^{-\frac{3}{2} N} \right) \right]$$

$$= 3/2\, N k_B T \checkmark$$

$$P = -\frac{\partial A}{\partial V} = k_B T \frac{\partial \ln Q}{\partial V} \Rightarrow PV = N k_B T \checkmark$$