Canonical Ensemble pt 3

Previouly - discrete systems

m energy energy levels

A copies of our sytem

prob of being in state $i \in \{1 \dots m\}$

$$= p_i = e^{-\beta \varepsilon_i} \Big/ \sum e^{-\beta \varepsilon_i} \quad \left(= \frac{N_i}{A} \right)$$

(degenerate) = same ε

$$Q = \sum_{i=1}^{M} e^{-\beta \varepsilon_i} = \sum_{\varepsilon_i} e^{-\beta \varepsilon_i} \underbrace{\omega(\varepsilon_i)}_{\text{"density of states"}}$$

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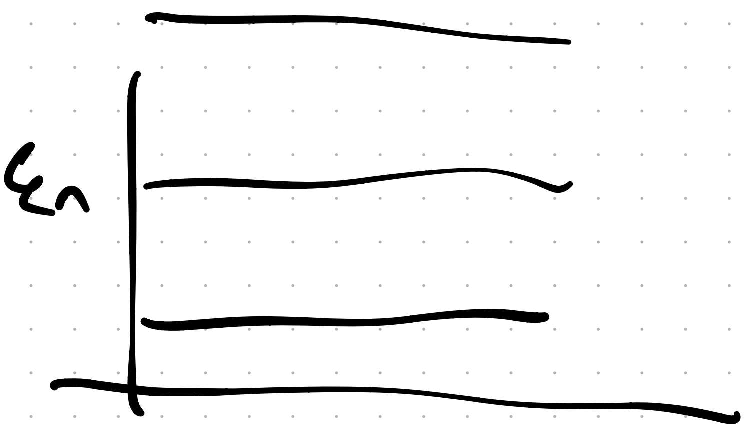
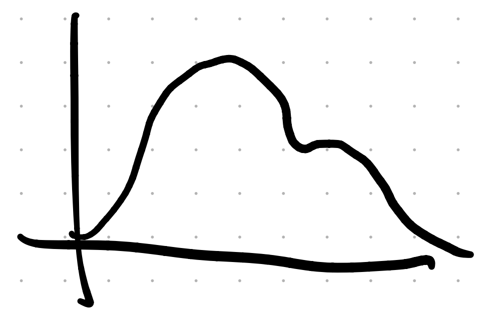
eg particle in a box $\quad \varepsilon_n = \dfrac{h^2 n^2}{8 m L^2}$ in 1d



closer together as
$L \to \infty$
thermodynamic limit



$$Q = \sum_{\varepsilon_i} \omega(\varepsilon_i) e^{-\beta\varepsilon_i} \xrightarrow[\substack{n \text{ states} \\ \to \infty}]{} \sum_{n=0}^{\infty} \omega(\varepsilon_n) e^{-\beta\varepsilon_n}$$

If the energies are close together

$$\varepsilon_n = \varepsilon_0 + n\Delta\varepsilon$$

$S \to \varepsilon$ Legendre

$\Omega \to Q$

$$Q = \sum_{n=0}^{\infty} \omega(\varepsilon_n) e^{-\beta\varepsilon_n} \cdot \frac{\Delta\varepsilon}{\Delta\varepsilon} = \frac{1}{\Delta\varepsilon} \sum_{n=0}^{\infty} \omega(\varepsilon) e^{-\beta\varepsilon_n} \Delta\varepsilon$$

$$\Delta\varepsilon \to 0 \Rightarrow \underbrace{\frac{1}{d\varepsilon}}_{\text{constant}} \int_0^{\infty} d\varepsilon\, \omega(\varepsilon) e^{-\beta\varepsilon} = Q$$

[Laplace transform]

$$Q = \frac{1}{d\varepsilon} \int_0^\infty d\varepsilon \, e^{-\beta\varepsilon} \, \omega(\varepsilon)$$

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

thermo properties are all derivatives of A

$$\ln(aX) = \ln(a) + \ln(X)$$

$$Z = \int d\varepsilon \, \omega(\varepsilon) e^{-\beta\varepsilon} \qquad \frac{\partial \ln Z}{\partial X} = \frac{\partial \ln Q}{\partial X}$$

Ideal gas

1 particle in 1d $\qquad p = mv$

Classical mechanics has

$$\mathcal{E} = KE + PE = \frac{1}{2}m\vec{v}^2 + U(\vec{x})$$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \frac{1}{2}m\vec{v}^2 = p^2/2m$

ideal gas means $U(\vec{x}) = 0$

Partition function turns out

$$Q = \frac{1}{h}\int_{-L}^{L} dx \int_{-\infty}^{\infty} dp\, e^{-\beta \mathcal{E}(x,p)}$$

$$Q = \frac{1}{h}\int_{-L}^{L} dx \int_{-\infty}^{\infty} dp \, e^{-\beta p^2/2m}$$

$$\int_{-L}^{L} dx = 2L = \text{"}V\text{"}$$

$$Q = \frac{V}{h}\int_{-\infty}^{\infty} e^{-p^2/2mk_BT} \, dp \qquad \sigma^2 = mk_BT$$

$$= \sqrt{2\pi\sigma^2} \cdot \frac{V}{h} = V \cdot \sqrt{\frac{2\pi m k_BT}{h^2}} = V/\Lambda$$

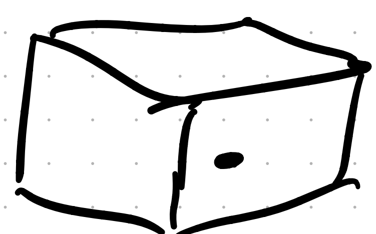
In 3d: $\mathcal{E} = p_x^2/2m + p_y^2/2m + p_z^2/2m$

$$e^{a+b+c} = e^a e^b e^c$$

$$Q = \frac{1}{h^3} \underbrace{\int dx\,dy\,dz}_{V} \int dp_x\,dp_y\,dp_z\, e^{-\beta\mathcal{E}}$$

$$= V/h^3 \cdot \int_{-\infty}^{\infty} dp_x\, e^{-p_x^2/2m} \int_{-\infty}^{\infty} dp_y\, e^{-p_y^2/2m} \int_{-\infty}^{\infty} dp_z\, e^{-p_z^2/2m}$$

$$= V/\Lambda^3 \leftarrow$$



$$\Lambda = \sqrt{h^2/2\pi m k_B T}$$

N particles in a box & distinguishable

$$\mathcal{E} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} \qquad \vec{p}^{\,2} = p_x^2 + p_y^2 + p_z^2$$

$$e^{-\beta \mathcal{E}(p_1, p_2, \ldots, p_N)} = \left[e^{-\beta \vec{p}_1^{\,2}/2m}\right]\left[e^{-\beta \vec{p}_2^{\,2}/2m}\right] \cdots$$

$$Q = \int d\vec{p}_1 \int d\vec{p}_2 \cdots = \left[\int dp\, e^{-\beta p^2/2m}\right]^N$$

N independent particles $Q(N,V,T) = q^N$

Turns out that if particles are indistinguishable

So the number of states is to big

by a factor of $N!$

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

ideal gas $Q(N, V, T) = q^N / N!$

$q = V / \Lambda^3$

$$Q = q^N / N! \qquad q = V/\Lambda^3 \qquad \Lambda = \sqrt{\frac{h^2}{2\pi m k_B T}}$$

$$\downarrow$$

$$\mathcal{E} = -\frac{\partial \ln Q}{\partial \beta} = -\frac{\partial}{\partial \beta}\left[\ln\left(q^N / N!\right)\right]$$

$$= -\frac{\partial}{\partial \beta}\left[N \ln q \cancel{- \ln N!}\right]$$

$$= -\frac{\partial}{\partial \beta} N \ln\left[V/\Lambda^3\right] \qquad \ln\left(\frac{V}{\Lambda^3}\right) = \ln \cancel{V} - 3\ln\Lambda$$

$$= 3N \frac{\partial}{\partial \beta} \ln(\Lambda)$$

$$\mathcal{E} = 3N \frac{\partial \ln \Lambda}{\partial \beta} \qquad \Lambda = \sqrt{\frac{h^2}{2\pi m k_B T}}$$

$$= \sqrt{\frac{h^2\beta}{2\pi m}} = \beta^{1/2} \cdot \text{const}$$

$$= 3N \frac{\partial \left[\ln \beta^{1/2} + \ln \text{const} \right]}{\partial \beta}$$

$$q = V/\Lambda^3$$

$$= \frac{3N}{2} \frac{\partial \ln \beta}{\partial \beta} = \frac{3N}{2} \cdot \frac{1}{\beta} \frac{\partial \beta}{\partial \beta} = \frac{3}{2} N k_B T$$

$$= 3/2\, nRT \; \bigstar$$

$$A = -k_B T \ln Q = -k_B T \ln\left[\frac{q^N}{N!}\right]$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = +k_B T \frac{\partial \ln(q^N/N!)}{\partial V}$$

$$q = V/\Lambda^3$$

$$P = +k_B T \frac{\partial \ln V^N}{\partial V} = N k_B T \cdot \frac{1}{V}$$

$$PV = nRT$$

Other Ensembles

Got partition functions by derivatives with lagrange multipliers

for N, V, T maximized S w/ contraints

$$\sum_{i=1}^{m} N_i = A$$

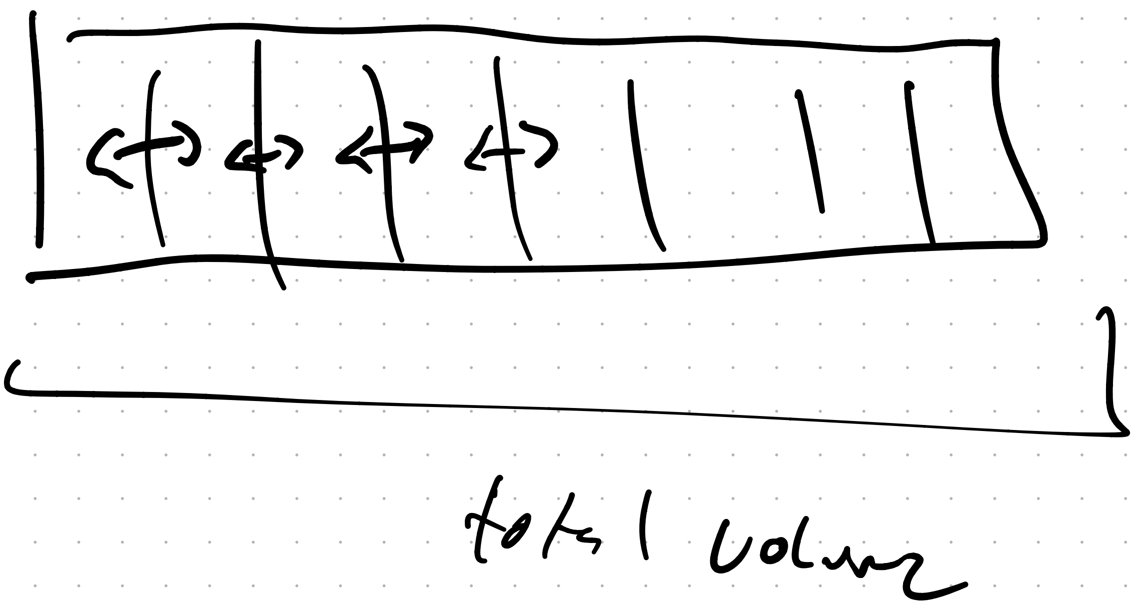
$$\sum_{i=1}^{m} N_i \varepsilon_i = \varepsilon_{total}$$

Suppose we want n, P, T (isothermal isobarbaric)

at constant pressure, system changes size

U changes until

$p_{in} = p_{out}$ @ Eq



extra constraint

$\sum N_j V_j = V_{total}$

↑ discrete volumes

Result

$$\Theta(n,p,T) = \sum_{j=1}^{n} \sum_{i=1}^{m} e^{-\beta E_{ij}} e^{-\beta p V_j}$$ (depends on volume)

$$= \sum_{j=1}^{n} e^{-\beta p V_j} \, Q(N, V_j, T)$$

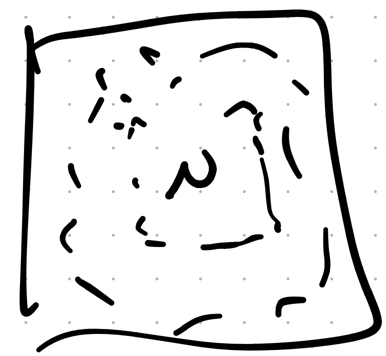
$$\Theta(n,p,T) = \frac{1}{V_0} \int_0^\infty dV \, e^{-\beta p V} \, Q(N,V,T)$$ [Laplace transform]

$$G = -k_B T \ln \Theta(n, p, T)$$

one other

Grand canonical

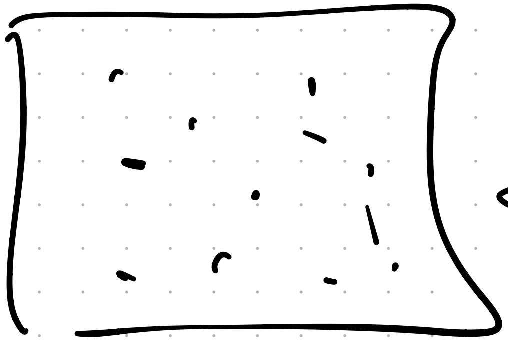
constant (μ, V, T)



$$\Xi = \sum_{N=0}^{\infty} e^{\beta \mu N} Q(N, V, T)$$

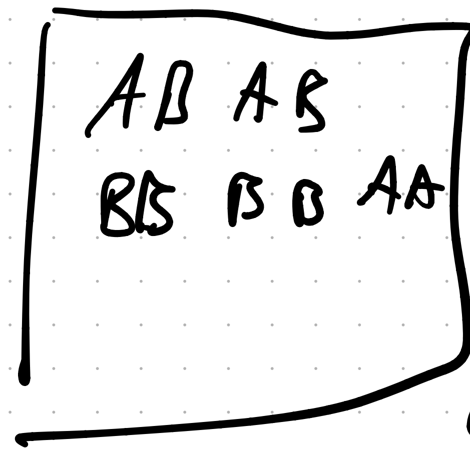
grand potential $\Phi = -k_B T \ln \Xi$

Discrete models are very valuable



(0, 1)

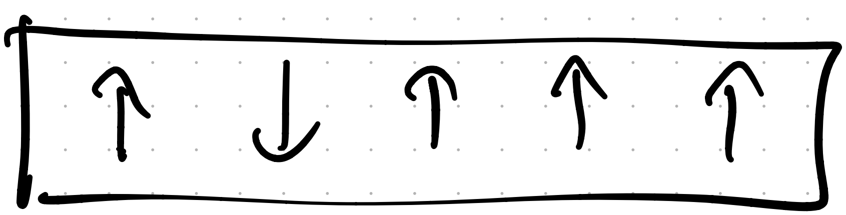
lattice gas



(A, B)

chemical eq

Next time



(interacting)
Ising model