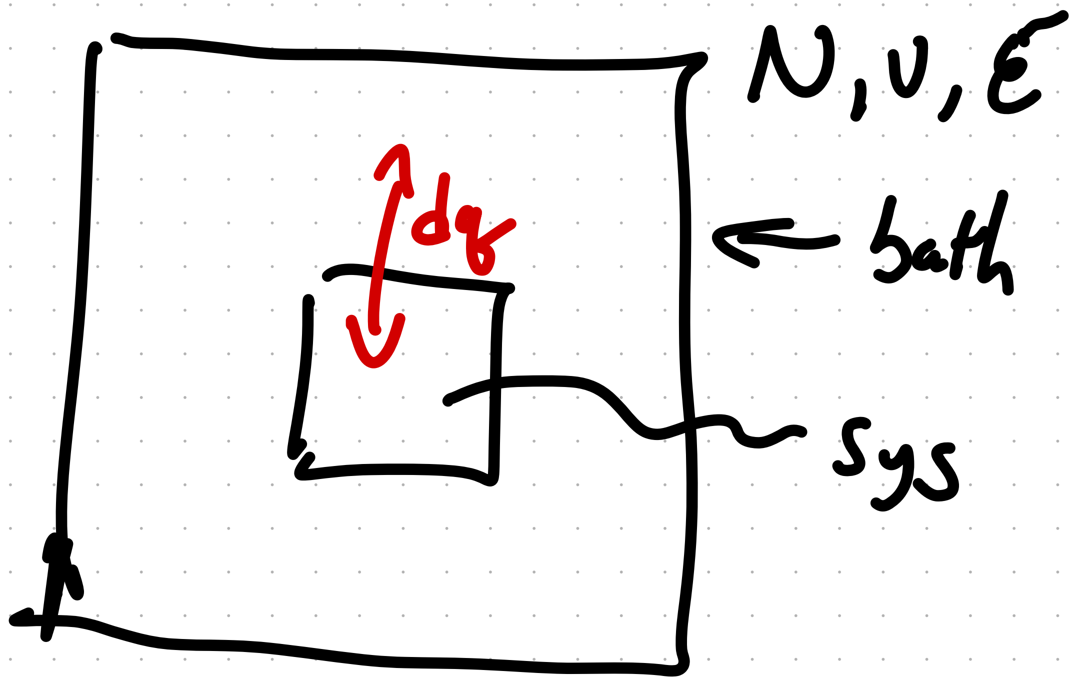
Constant pressure, constant chemical pot.

Before, we studied const

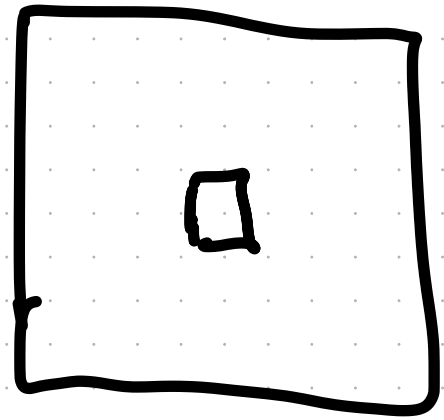
N, V, T



maximize entropy of whole thing

get $T_{in} = T_{out}$ $P(X_{system}) = e^{-\mathcal{H}_{sys}/k_BT} / Z$

Reminder:



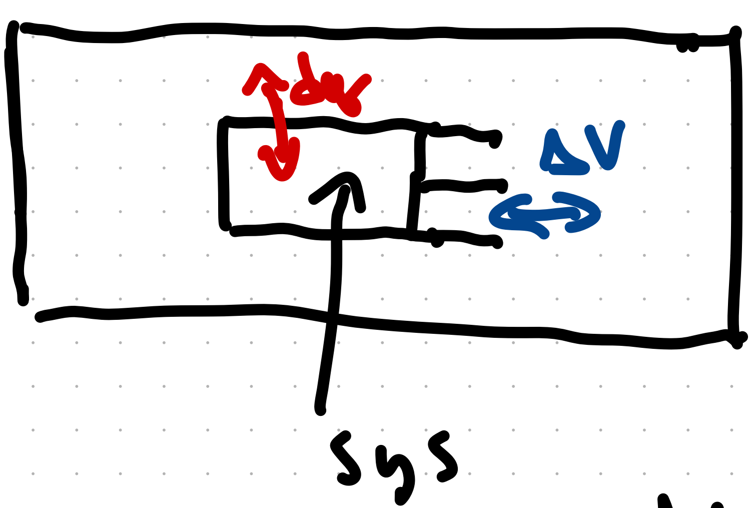
$$\varepsilon_{tot} = \varepsilon_b + \varepsilon_s$$

$$\varepsilon_{tot} - \varepsilon_{bath} \approx 0$$

$$S_{bath}(N_{bath}, V_{bath}, \varepsilon_{bath}) \approx S_{bath}(\varepsilon_{tot}) + \underbrace{\left(\frac{\partial S_b}{\partial \varepsilon_b}\right)}_{\frac{1}{T_{bath}}} \overbrace{(\varepsilon_b - \varepsilon_{tot})}^{-\varepsilon_{sys}} + \cdots$$

$$S_{bath} = k_B \ln \Omega_{bath}$$

$$\Omega_{bath} \approx \underbrace{e^{S_{bath}/k_B}}_{const} \, e^{-\varepsilon_{sys}/k_B T_{bath}} \propto P(X)$$



$\in N, V, E$

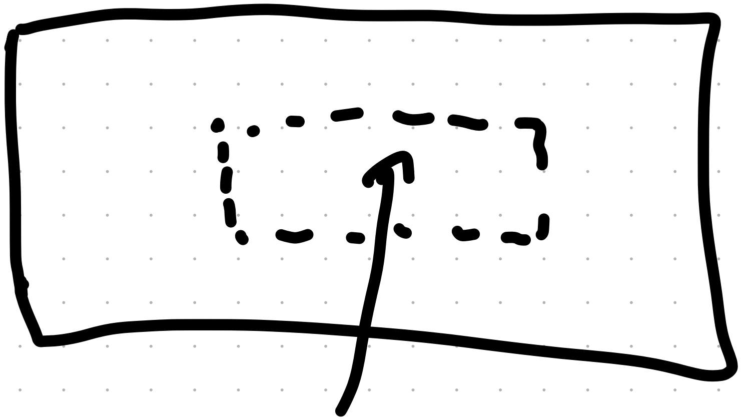
$P_{in} = P_{out}$ @ Equilibrium

$T_{in} = T_{out}$

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

$$S_{bath}(N_b, V_b, E_b) \approx S_{bath}(V_{tot}) + \underbrace{\left(\frac{\partial S}{\partial V_b}\right)}_{P/T} \underbrace{(V_b - V)}_{-V_{sys}} + \cdots$$

$$S \approx S(V) - \frac{PV}{T} \Rightarrow \Omega \propto e^{-PV/k_B T}$$



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

@ equilibrium

$\mu_{in} = \mu_{out}$

$\left(\frac{\partial G}{\partial N}\right)_{V,T}$

$\left(\frac{\partial G}{\partial N_\alpha}\right) = \mu_\alpha$, $\mu_\alpha^{in} = \mu_\alpha^{out}$ for all species α

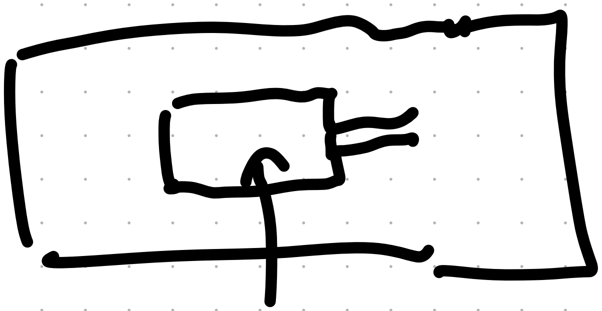
$$S_b(N_b, V_b, E_b) \approx S_b(N) + \underbrace{\left(\frac{\partial S}{\partial N_b}\right)}_{-\mu/T} \underbrace{(N_b - N)}_{-N_{sys}} + \cdots$$

$$\Omega_b \propto e^{+\mu N/k_B T}$$

$$S_b(N_b, V_b, \mathcal{E}_b) \approx S(N, V, \mathcal{E}) + \left(\frac{\partial S}{\partial N}\right)(N - N_b)$$

$$+ \left(\frac{\partial S}{\partial \mathcal{E}}\right)(\mathcal{E} - \mathcal{E}_b)$$

$$+ \left(\frac{\partial S}{\partial V}\right)(V - V_b) + \dots$$



Get N, $\underline{P}$, $\underline{T}$

$$\mathcal{E} = \mathcal{H}(x)$$

$$\Omega_b \propto e^{-PV/k_B T} \cdot e^{-\mathcal{E}/k_B T}$$

Prob in NPT is

μVT $\quad e^{-\mathcal{E}/k_B T + \mu N/k_B T}$

$$\left\{ \begin{array}{l} \mu PT \\ e^{-\beta(PV - \mathcal{E} + \mu N)} \end{array} \right.$$

Const N, P, T

$$\Delta(N,\underline{P},T) = C\int_0^\infty dV \int d\underline{X}\, \underbrace{e^{-\beta(\mathcal{H}(X)+PV)}}$$

$$C = \frac{1}{h^{3N} V_0}$$

$$= \frac{1}{V_0}\int_0^\infty dV\, \underline{e^{-\beta PV}}\; \underline{\underline{\Omega(N,V,T)}}$$

$$P(\underline{X},V) \propto e^{-\beta(PV+\mathcal{H}(X))} / \Delta$$

$$G = \underbrace{\mathcal{E} - TS}_{} + PV = \underbrace{A}_{} + PV$$

$$G = -k_B T \log \Delta(N,P,T)$$

[Isothermal Isobaric Ensemble

Grand Canonical (μ, V, T)

$$\mathcal{Z} = \sum_{N=0}^{\infty} \int dx\, e^{-\beta \mathcal{H}(x) + \beta \mu N}$$

Grand potential $\Omega(\underline{X}) = -k_B T \log \mathcal{Z}$

Remove constraint on N or V, can have fluctuations in N or V

N, P, T , V can vary

$\mathrm{Var}(V)$

$$\langle V\rangle = \underbrace{\left(\frac{\partial G}{\partial P}\right)_{N,T}} = -k_B T\left(\frac{\partial}{\partial P}\underbrace{\log\int dV\, e^{-\beta P V}\,\Omega(N,V,T)}\right)$$

$$= -k_B T\cdot\frac{1}{\Delta}\cdot\frac{\partial \Delta}{\partial P} = \frac{-k_B T}{\Delta}\cdot\int_{0}^{\infty} dV\,(-\beta V)\,e^{-\beta P V}\,\Omega$$

$$= \frac{1}{\Delta}\int_0^\infty dV\left[V e^{-\beta P V}\,\Omega(N,V,T)\right] = \langle V\rangle$$

$$\frac{\partial \langle V \rangle}{\partial P} = \frac{\partial}{\partial P}\left[\frac{1}{\Delta} \underbrace{\int dV\, e^{-\beta P V}\, \Omega(N,V,T)\, V}_{A} \right]$$

$$= \left[-\frac{1}{\Delta^2}\frac{\partial \Delta}{\partial P} \cdot A - \frac{1}{\Delta}\int dV\, (-\beta V)(V)\, e^{-\beta P V}\, \Omega(N,V,T) \right]$$

$$= -\beta \langle V \rangle \langle V \rangle + \beta \langle V^2 \rangle$$

$$= \beta\, \mathrm{Var}(V)$$

$$\omega \left[= \frac{\partial E}{\partial T} = \beta\, \mathrm{Var}(E) \right.$$

fluctuation-dissipation

Grand canonical (μ, V, T)

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{\beta\mu N} \Omega(N, V, T)$$

$$\langle N \rangle = \sum_{N=0}^{\infty} N \frac{e^{\beta\mu N} \Omega(N, V, T)}{\mathcal{Z}} = k_B T \frac{\partial \log \mathcal{Z}}{\partial \mu}$$

$$\underbrace{PV}_{\text{grand potential } (-PV)} = k_B T \log \mathcal{Z} = \underbrace{\langle N \rangle k_B T}_{\text{for ideal gas}}$$

for an ideal gas

$$Q(N,V,T) = \int d\vec{p}\, e^{-\beta p^2/2m} \cdot \frac{1}{N!\,h^{3N}}$$

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

IG

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

$$= \sum_{N=0}^{\infty} \left[\underbrace{e^{\beta\mu}\left(\frac{V}{\Lambda^3}\right)}_{\text{const}}\right]^N \cdot \frac{1}{N!} = \exp\left[e^{\beta\mu}\left(\frac{V}{\Lambda^3}\right)\right]$$

$$PV = +k_B T \log\left[\exp\left[e^{\beta\mu}\left(V/\Lambda^3\right)\right]\right]$$

$$= +k_B T\left[\underbrace{e^{\beta\mu}\left(V/\Lambda^3\right)}_{\langle N \rangle}\right] \leftarrow \text{check}$$

$$PV = \langle N \rangle k_B T$$

check

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \log \mathcal{Z}_1 = \frac{3}{2}\langle N \rangle k_B T$$

FDT

compressibility

$$\mathrm{Var}(V) = k_B T \frac{\partial \langle V \rangle}{\partial P}$$

N, P, T

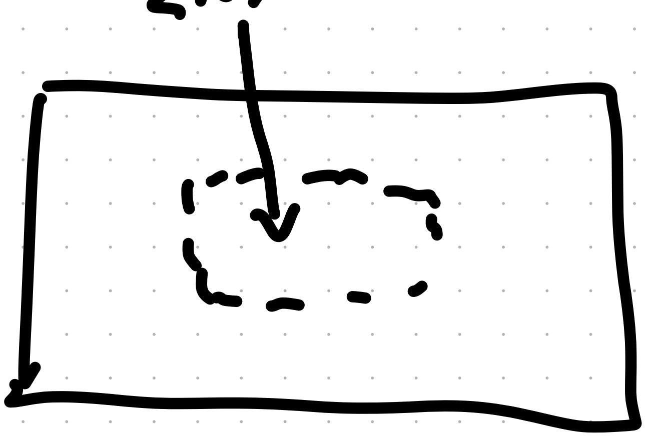
$$\mathrm{Var}(N) = k_B T \frac{\partial \langle N \rangle}{\partial \mu}$$

μ, V, T

$$= k_B T \cdot \frac{\langle N \rangle^2}{V} \underbrace{\kappa_T}_{\text{isothermal compressibility}}$$

volume change per atom

$\langle N \rangle$



μ, V, T