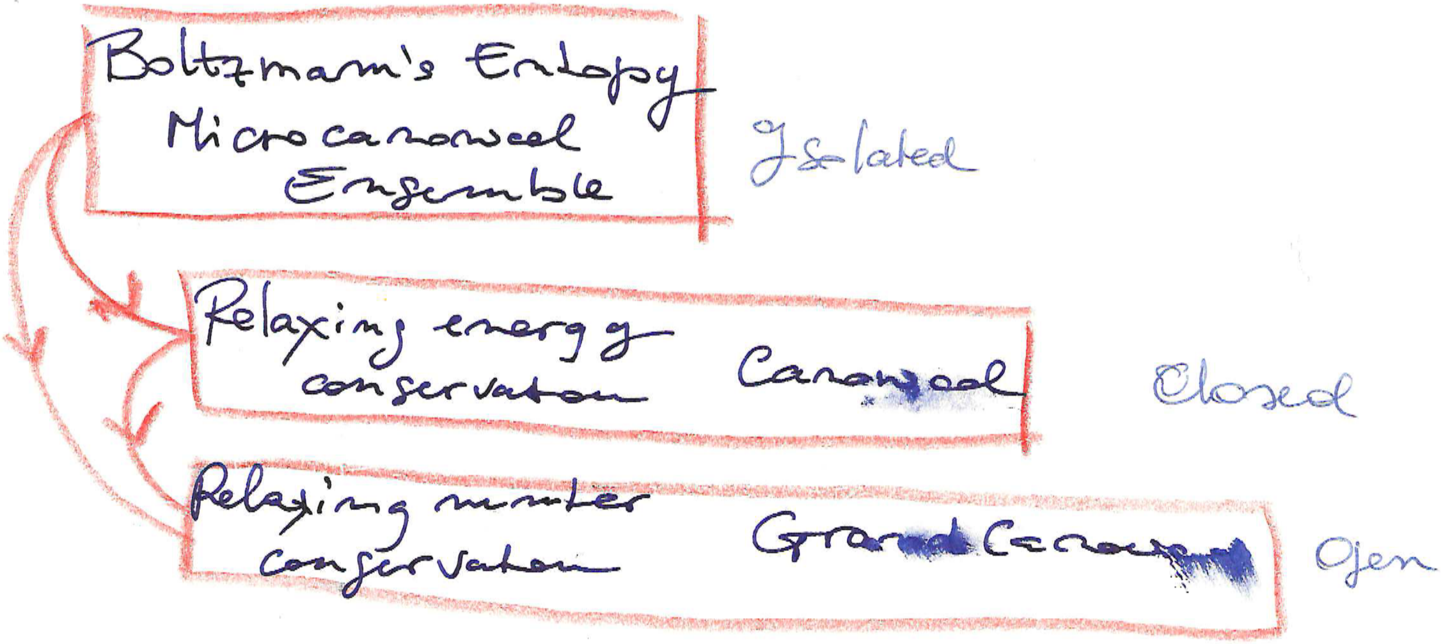
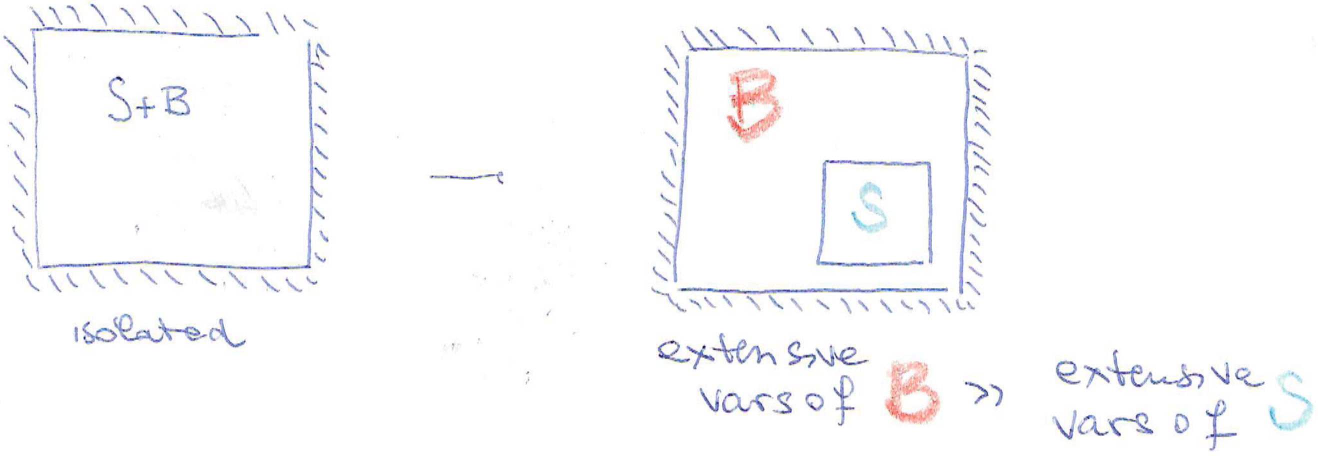
Gibbs Ensembles & Ensemble equivalence in thermodynamic limit



Microcanonical → Canonical

by tracing out "bath" degrees of freedom



$$\hat{\rho}^{(S)} = \operatorname{tr}_B \hat{\rho}^{(S+B)}$$

$$\rho^{(S)} = \frac{\boxed{\Delta \int \frac{d p_B^{3N_B}\, d q_B^{3N_B}}{N_B!\, h^{3N_B}} \delta(E-H)}}{} \; — \; W^{(S)} \qquad = \frac{W^{(S)}}{\operatorname{tr}_B W^{(S)}}$$

$W^{(s)}$ is the weight of a microscopic configuration of S

is traced over any allowable configuration of B

$$\underset{(B)}{\mathrm{tr}} \to \int \frac{d^{3N_B}p_B \, d^{3N_B}q_B}{N_B!\, h^{3N_B}} \to \int dX_B$$

measure of B scaled by appropriate dimensional h^{3N} permutations N_B

$$W^{(s)} = \int dX_B \, \delta(E - H_S - H_B - \cancel{H_{SB}})$$

short range interactions $\to H_S \sim N_S$ $\to H_B \sim N_B$

$$H_{SB} \sim \underbrace{\rho_B \mathcal{S} a}_{N_B^{int}} \underbrace{\rho_S a^3}_{N_S^{int}} = \overbrace{\rho_S \mathcal{S} a}^{N_S^{int}} \overbrace{\rho_B a^3}^{N_B^{int}}$$

~~if $\rho_S \sim \rho_B = \rho$~~

~~$H_{SB} \sim \rho^2 \mathcal{S} a \, a^3$~~

$$H_{SB} = \sum_i^{(S)} \sum_j^{(B)} V_{ij}$$

$\uparrow \rho_S \mathcal{S} a$ N_S^{int} $\quad \uparrow \rho_B a^3$ $N_B^{int}(1)$

$$= \sum_j^{(B)} \sum_i^{(S)} V_{ji}$$

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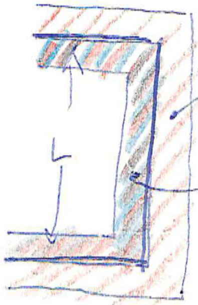


$N_B^{int} = \rho_B a \mathcal{S}$

$N_S^{int} = \rho_S a \mathcal{S}$

$$H_{SB} \sim \rho_S \mathcal{S} a \, \rho_B a^3 = N_S \left(\frac{a}{L}\right) \left(\frac{a}{e_B}\right)^3$$ finite

Macroscopic

Bath interparticle distance

$a \ll L$

introduce dummy integration

$$W^{(s)} = \Delta \int_0^E dE_S \int dX_B\, \delta(E - E_S - H_B)\, \delta(E_S - H_S)$$

$$Z_B(\underbrace{E-E_S}_{E_B}, \underbrace{V-V_S}_{V_B}, \underbrace{N-N_S}_{N_B})$$

Bath volumes and numbers of particles are fixed

⇒ approx the dependence of Z_B from E_S

$$Z_B(E-E_S) = e^{S_B(E-E_S)/k_B}$$ for $E \gg E_S$ (Bath $\gg$ Syste

$$S_B(E-E_S) = \underbrace{S_B(E)}_{O(N)} - \underbrace{\frac{\partial S_B}{\partial E}}_{\text{intensive}} \underbrace{E_S}_{O(N_S)} + \frac{1}{2} \cancel{\underbrace{\frac{\partial^2 S_B}{\partial E^2}}_{O(\frac{1}{N})} \underbrace{E_S^2}_{O(N_S^2)}} + O(E_S^3)$$

$$O(N) + O(N_S) + O\left(\cancel{N_S \frac{N_S}{N}}\right)$$

$$\left(\frac{\partial S_B}{\partial E}\right)_{E_S=0} = \frac{1}{T_B}$$ defs of bath temperature

$$W^{(s)} \cong e^{\frac{S_B(E)}{k_B}} \int_0^E dE_S\, e^{-\frac{E_S}{k_B T_B}}\, \delta(E_S - H_S)$$

$$W^{(s)} \propto e^{-\frac{H_S(p_S q_S)}{k_B T_B}}$$

System Hamiltonian

Bath temperature

Canonical partition function

we define

$$Z = \underset{B}{\mathrm{tr}}\, W^{(s)}$$

$$Z = \int \frac{d^{3N_s}p_s\, d^{3N_s}q_s}{N_s!\, h^{3N_s}}\, e^{-\frac{H_s}{k_B T_B}}$$

or simply forgetting the bath which ~~is~~ here appears only trough the temperature

$$\boxed{Z = \int \frac{d^{3N}p\, d^{3N}q}{N!\, h^{3N}}\, e^{-\beta H}} \qquad \beta = \frac{1}{k_B T}$$

thermodynamic potential is

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

this can be proved trough the steepest descent method

Let's express the canonical partition function as
dummy integrals

$$Z = \int \frac{d^{3N}p\, d^{3N}q}{N!\, h^{3N}}\, e^{-\beta H} = \frac{1}{\Delta}\int_0^\infty dE\, e^{-\beta E}\, \underbrace{\int \frac{d^{3N}p\, d^{3N}q}{N!\, h^{3N}}\, \Delta\, \delta(E-H)}_{Z_{micro}(E)}$$

$$Z = \int dE\, e^{-\beta E}\, Z_{micro}(E)$$

↑ this is the normalization ⇒

Distribution of Energies in the Canonical Ensemble

$$P(E) = \frac{e^{-\beta E} Z_{micro}(E)}{Z}$$

correctly normalized to 1

↳ is peaked sharply around a value $\bar{E}$ such that

$$e^{-\beta \bar{E}} Z_{micro}(\bar{E}) = e^{-\beta F(\bar{E})}$$

Helmholtz free energy

→ ensemble equivalence

Steepest Descent

$$\mathcal{I} = \int dx\, e^{-Nf(x)} \quad \text{for } N \to \infty$$

suppose that $\bar{x}$ is an extreme of f

such that

$$\frac{df}{dx}\Big|_{\bar{x}} = 0$$

Neglect and then check!

then

$$f(x) \simeq f(\bar{x}) + \frac{1}{2}\frac{d^2f}{dx}\Big|_{\bar{x}}(x-\bar{x})^2 + \boxed{\frac{1}{3!}\frac{d^3f}{dx}\Big|_{\bar{x}}(x-\bar{x})^3} + \dots$$

$$e^{-Nf} = e^{-Nf(\bar{x})}\, e^{-\frac{N}{2}\frac{d^2f}{dx}\big|_{\bar{x}}(x-\bar{x})^2}$$

$$\mathcal{I} = e^{-Nf(\bar{x})}\int dx\, e^{-\frac{N}{2}\frac{d^2f}{dx^2}\big|_{\bar{x}}(x-\bar{x})^2}$$

$$\hookrightarrow \sigma^2 = \frac{1}{N\frac{d^2f}{dx^2}\big|_{\bar{x}}}$$

suppose $\frac{d^2f}{d\bar{x}^2}\Big|_{\bar{x}} > 0$ and finite as $N \to \infty$

then $(x-\bar{x}) \sim 1/\sqrt{N}$

and the cubic term is of order

$$\frac{1}{3!}\boxed{\frac{d^3f}{dx^3}}\Big|_{\bar{x}} \quad 1/N^{3/2}$$

suppose finite as $N \to \infty$

while the quadratic term

$$\frac{1}{2!}\frac{d^2f}{dx^2}\frac{1}{N}$$

$$e^{-\beta E} \underset{\uparrow \text{ system}}{Z_{\text{micro}}(E)} = e^{-\beta[\underset{\nearrow}{E} - T\,\underset{\nearrow}{\overline{S(E)}}^{\,\text{system}}]}$$

extensive

therefore

$$Z_{\text{can}} = \int_0^\infty dE\; e^{-\beta[\underbrace{E - T\overset{\swarrow \text{ system entropy}}{S(E)}}_{\text{extensive}}]} = \int (d\varepsilon)\, N\, e^{-\beta N(\underset{\nearrow\ \varepsilon}{\frac{E}{N}} - \frac{S}{N}T)}$$

let's calculate integral with steepest descent

$$\bar{E}:\quad \frac{d}{dE}\left(E - TS(E)\right) = 0$$

$$1 - \underset{\swarrow\ \text{bath temperature}}{T}\,\underset{\searrow\ \text{System temperature}}{\frac{dS}{dE}} = 0 \qquad \Rightarrow \quad \bar{E} \text{ such that } T_B = T_S$$

fluctuations

$$\left.\frac{d^2}{dE^2}\left(E - TS(E)\right)\right|_{\bar{E}} = -T\left(\frac{\partial^2 S}{\partial E^2}\right)_{V,N\,\bar{E}} = -\underset{\nearrow\ \text{bath}}{T}\;\frac{\partial}{\partial E}\left(\frac{1}{\underset{/\ \text{system}}{T(E)}}\right)_{\bar{E}}$$

$$\frac{\partial}{\partial E}\,\frac{1}{T(E)} = -\frac{1}{T^2}\,\frac{\partial T}{\partial E} = -\frac{1}{T^2 C_V}$$

$$\left.\frac{d^2}{dE^2}\left(E - TS(E)\right)\right|_{\bar{E}} = -T\left(-\frac{1}{T^2 C_V}\right) = \frac{1}{TC_V}$$

$$Z_{\text{can}} = e^{-\beta[\bar{E} - TS(\bar{E})]}\;\underbrace{\underbrace{\int dE\; e^{-\frac{\beta}{2}\frac{1}{TC_V}(E-\bar{E})^2}}_{\text{fluctuations}}}_{\sqrt{2\pi\sigma_E^2}}$$

$$\boxed{\sigma_E^2 = k_B T^2 C_V}$$

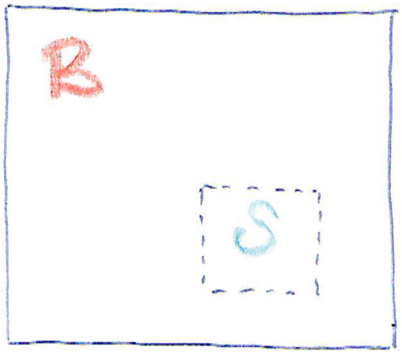
$$-\frac{1}{\beta}\ln Z_{con} = \underbrace{\bar{E} - TS(\bar{E})}_{\Theta(N)} + \underbrace{\xcancel{\frac{1}{2\beta}\ln 2\pi\sigma_E^2}}_{O\,\frac{1}{2}\ln N^2 = \ln N}$$

$$-\frac{1}{\beta}\ln Z_{con} = F_{termodin}$$

Microcanonical → Gran canonical

as the system is closed we get the canonical distribution function and partition function

We can generalise the procedure to include open systems



where now S can exchange particles with B

We can calculate the weight for a given configuration of N_S particles in system S and $N-N_S$ particles in ~~system~~ bath

$$W^{(N_S)} = \int_0^E dE_S \, Z_B(E-E_S, V-V_S, N-N_S) \, \delta(E_S - H_S)$$

where

$$Z_B(E-E_S, V-V_S, N-N_S) = \int \frac{d^{3N_B}p_B \, d^{3N}q_B}{N_B! \, h^{3N_B}} \, \delta(E-E_S-H_B)$$

to calculate the grand-canonical partition function we must trace $W^{(N_S)}$ but allowing a variable N_S (open system)

We must acount for indistinguishability of particles between bath & system therefore

$$\mathrm{tr}\, W^{(N_s)} = \boxed{\sum_{\{N_s\}}}\ \boxed{\frac{1}{N!\,\cancel{h^{3N}}}} \int \frac{d^{3N_s}p_s\, d^{3N_s}q_s}{h^{3N_s}}\ \boxed{N_B!\,\cancel{h^{3N_B}}}\ W^{(N_s)}$$

divide by the full N! permutations

multiply by the permutation of bath particles included in defs of $W^{(N_s)}$

sum of all possible configuration for N_s particle in system

Now

$$\sum_{\{N_s\}} f(N_s) = \sum_{0}^{N} {}_{N_s} \underbrace{\binom{N}{N_s}} f(N_s)$$

function that does not depend on the configuration but only on the total number

# of ways disregarding the order that N_s particles can be chosen from N

eq. 2 particles over 4

1 2 3 4

12	23	34
13	24	
14		

= 6

$$\binom{4}{2} = \frac{4!}{2!\,2!} = \frac{\overset{2}{\cancel{4}}\cdot 3\cdot \cancel{2}}{\cancel{2}\,\cancel{2}} = 6$$

$$\mathrm{tr}\, W^{(N_s)} = \sum_{N_s} \underbrace{\binom{N}{N_s}\frac{1}{N!}}\ N_B! \int \frac{d^{3N_s}p\, d^{3N_s}q}{h^{3N_s}\ \boxed{N_s!}}\ W^{(N_s)}$$

$$\frac{\cancel{N!}}{N_s!\,(N-\cancel{N_s})!}\ \frac{1}{N!}\ \cancel{N_B!}$$

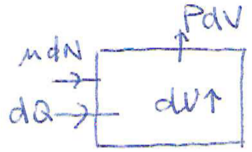
Now we must express $W^{(N_s)}$ by taking onto account that both Energy and Number of particle are now varables

$$W^{(N_s)} = \int_0 dE_s \, \overset{\swarrow \text{Microcanonical partition fu}}{Z_B}(E-E_s, V-V_s, N-N_s)\, \delta(E_s - H_s)$$

$$Z_B(E-E_s, N-N_s) = e^{\frac{S_B(E-E_s, N-N_s)}{k_B}}$$

$$S_B(E-E_s, N-N_s) = S_B(\vec{E}, \vec{N}) - \underset{\frac{1}{T_B}\nearrow}{\left(\frac{\partial S_B}{\partial E}\right)} E_s - \underset{-\frac{\mu_B}{T_B}\uparrow}{\left(\frac{\partial S_B}{\partial N}\right)} N_s + \cdots$$

$$\underset{\nearrow \; S(E,V,N)}{dS} = \frac{dU}{T} + \frac{P}{T} dV - \frac{\mu}{T} dN$$



$$W^{(N_s)} = \underbrace{e^{\frac{S_B(E,N)}{k_B}}}_{\text{proportionality factor}} \; e^{-\frac{H_s}{k_B T} + \frac{\mu}{k_B T} N_s}$$

$$\mathrm{tr}\, W^{(N_s)} = \underset{\uparrow \; \text{irrelevant}}{\text{const}} \; \Sigma_N \int \frac{dp_s^{3N_s} dq_s^{3N_s}}{h^{3N_s} N_s!} \, e^{-\beta(H_s - \mu N_s)}$$

$$\boxed{\rho^{(N_s)} = \frac{e^{-\beta(H_s - \mu N_s)}}{\Sigma \; e^{\beta\mu N_s} Z \quad (N_s)}}$$