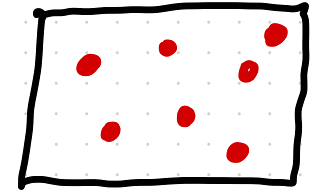
Setup and motivation

large or small

- classical system of N identical particles $j = 1, 2, \dots, N$

Λ



$$\begin{cases} \text{positions } \mathbf{r}_1, \dots, \mathbf{r}_N \in \Lambda \subset \mathbb{R}^3 \\ \text{momenta } \mathbf{p}_1, \dots, \mathbf{p}_N \in \mathbb{R}^3 \end{cases}$$

box

$$\begin{cases} \mathbb{R} = (\mathbf{r}_1, \dots, \mathbf{r}_N) \in \Lambda^N \\ \mathbb{P} = (\mathbf{p}_1, \dots, \mathbf{p}_N) \in \mathbb{R}^{3N} \end{cases}$$

- equilibrium state

$H(\mathbb{R}, \mathbb{P})$ standard Hamiltonian $H(\mathbb{R},\mathbb{P}) = \sum_{j=1}^{N} \left(\frac{|\mathbf{p}_j|^2}{2m} + u(\mathbf{r}_j) \right) + \frac{1}{2} \sum_{j \neq k} v(\mathbf{r}_j - \mathbf{r}_k)$

equlibrium expectation

$$\langle \cdots \rangle_{\beta, H} = \frac{1}{Z(\beta, H)} \int d\mathbb{R}\, d\mathbb{P} \, (\cdots) \, e^{-\beta H(\mathbb{R}, \mathbb{P})},$$

partition function

$$Z(\beta, H) = \int d\mathbb{R}\, d\mathbb{P}\, e^{-\beta H(\mathbb{R}, \mathbb{P})}$$

- the standard expression for the Helmholtz free energy

$$F(\beta, H) = -\beta^{-1} \log \frac{Z(\beta, H)}{C^N N!}$$

$C > 0$ constant (usually $C = h^3$)

why? $\Rightarrow$ any physical reasoning??

$\Big($ quantum system $-\beta^{-1} \log \mathrm{Tr}\, e^{-\beta \hat{H}} \simeq -\beta^{-1} \log \dfrac{Z(\beta, H)}{h^{3N} N!}$ BUT why $F = -\beta^{-1} \log \mathrm{Tr}\, e^{-\beta \hat{H}}$?? $\Big)$

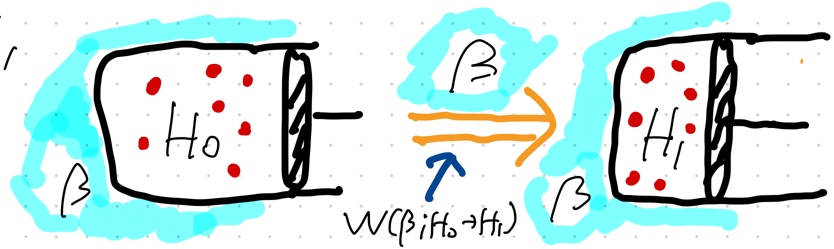
properties of $Z(\beta, H)$

- energy expectation value

$$\langle H \rangle_{\beta,H} = -\frac{\partial}{\partial \beta} \log Z(\beta, H)$$

- quasi-static work

a quasi-static isothermal process in which the Hamiltonian is changed slowly from H_0 to H_1



the work done by the external angent who controls the Hamiltonian

$$W(\beta; H_0 \to H_1) = \frac{1}{\beta} \log Z(\beta, H_0) - \frac{1}{\beta} \log Z(\beta, H_1)$$

$$\left(\text{special case} \quad P(\beta, H) = \frac{1}{\beta} \frac{\partial}{\partial V} \log Z(\beta, H) \right)$$

Standard premises for $F(\beta, H)$ → thermodynamics

P-1 Gibbs-Helmholtz relation $\langle H \rangle_{\beta, H} = \frac{\partial}{\partial \beta} \{ \beta F(\beta, H) \}$

$$F(\beta, H) = -\frac{1}{\beta} \log[\Phi \, Z(\beta, H)] \text{ with } \Phi \text{ independent of } \beta$$

P-2 minimum work principle $W(\beta; H_0 \to H_1) = F(\beta, H_1) - F(\beta, H_0)$

$$F(\beta, H) = -\frac{1}{\beta} \log[\Phi \, Z(\beta, H)] \text{ with } \Phi \text{ independent of } H$$

▷ from these two premices $\boxed{F(\beta, H) = -\frac{1}{\beta} \log[\Phi(N) \, Z(\beta, H)]}$

$\Phi(N)$ is arbitrary → statistical mechanics is useful with any $\Phi(N)$

are there any physical premises that fix $\Phi(N)$??

P-3 extensivity $F_{TD}[T; \lambda V, \lambda N] = \lambda F_{TD}[T; V, N]$ implies

$$\Phi(N) = (C'N)^{-N} \sim \frac{1}{(C'e)^N N!}$$

only for $N \gg 1$

the Sasa-Hiura-Nakagawa-Yoshida (SHNY) process and the third premise

(i) the SHNY process

specified and fixed N_L and N_R

quasi-static isothermal proces

NOT a standard equilbrium

P-3′ refined minimum work principle

$$W_{SHNY} = F(\beta, N_L, H_L) + F(\beta, N_R, H_R) - F(\beta, N, H_0) \quad (*)$$

(ii) the result from an explicit construction — see below

$$W_{SHNY} = \frac{1}{\beta}\log\frac{Z_0(\beta)}{N!} - \left\{\frac{1}{\beta}\log\frac{Z_L(\beta)}{N_L!} + \frac{1}{\beta}\log\frac{Z_R(\beta)}{N_R!}\right\} \quad (**)$$

$$Z_0(\beta) = \int d\mathbb{R}\, d\mathbb{P}\, e^{-\beta H_0}$$

$$Z_L(\beta) = \int d\mathbb{R}_L\, d\mathbb{P}_L\, e^{-\beta H_L}$$

$$Z_R(\beta) = \int d\mathbb{R}_R\, d\mathbb{P}_R\, e^{-\beta H_R}$$

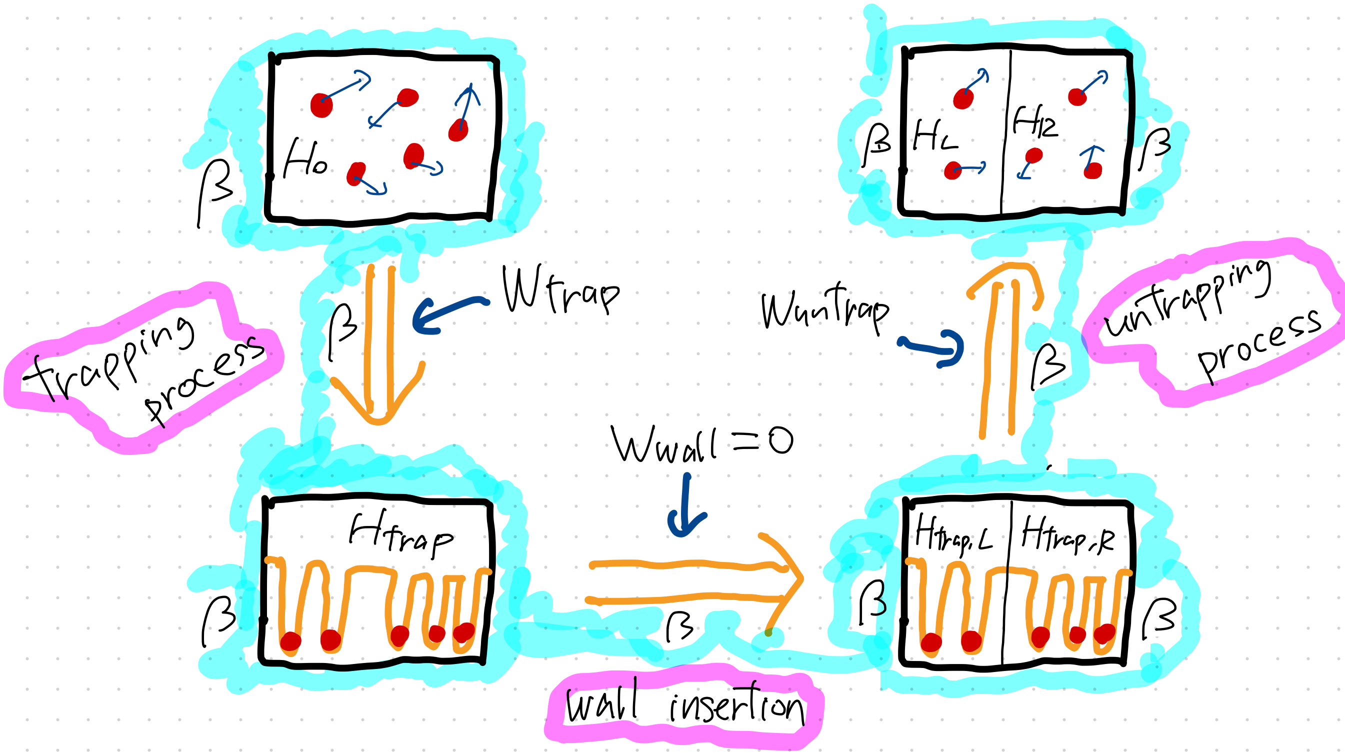
from (*) and (**)

$$\boxed{F(\beta, N, H) = -\frac{1}{\beta}\log\frac{Z(\beta, H)}{C^N N!}}$$

desired N dependent factor!!

Construction of a SHINY process

Horowitz, Parrondo 2011



W_{trap}, W_{untrap} can be evaluated from the standard relation

$$W(\beta; H_{init} \to H_{fin}) = \frac{1}{\beta}\log Z(\beta, H_{init}) - \frac{1}{\beta}\log Z(\beta; H_{fin})$$

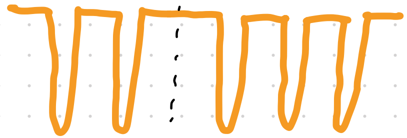
Construction of a SHiNY process

▷ Trapping Hamiltonian

$$H_{trap}(\mathbb{R},\mathbb{P}) = \sum_{j=1}^{N}\left(\frac{\|\mathbb{p}_j\|^2}{2m} + U_{trap}(\mathbb{r}_j)\right) + \frac{1}{2}\sum_{\substack{j,k=1\\(j\neq k)}}^{N} V_{rep}(|\mathbb{r}_j-\mathbb{r}_k|)$$

short range repulsion

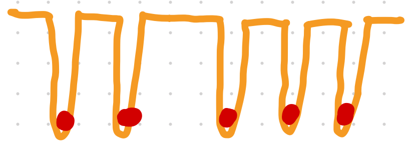
$U_{trap}(\mathbb{r})$



N_L deep minima in Λ_L

N_R deep minima in Λ_R

equlibrium state



$$Z_{trap}(\beta) = \int d\mathbb{R}\, d\mathbb{P}\, e^{-\beta H_{trap}(\mathbb{R},\mathbb{P})}$$
$$\simeq N!\,(z(\beta))^N$$

Trapping process

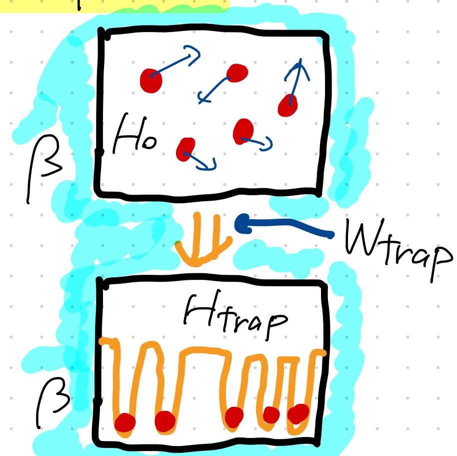
$$H_\alpha(\mathbb{R},\mathbb{P}) = (1-\alpha)H_0(\mathbb{R},\mathbb{P}) + \alpha H_{trap}(\mathbb{R},\mathbb{P}) \qquad \alpha\in[0,1]$$

start from H_0 and change α slowly from 0 to 1,
(the system is in touch with heat bath at β)

quasi-static isothrmal process

$$W_{trap} = \frac{1}{\beta}\log Z_0(\beta) - \frac{1}{\beta}\log Z_{trap}(\beta)$$
$$= \frac{1}{\beta}\log\frac{Z_0(\beta)}{N!} - \frac{N}{\beta}\log z(\beta)$$

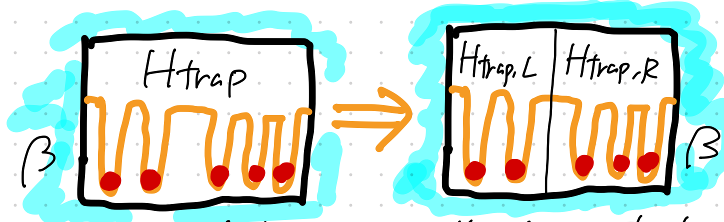
standard relation see p.2



Wall-insertion process

divde Λ into Λ_L and Λ_R by a thin wall

$$W_{wall} = 0$$



the state essentially does not change

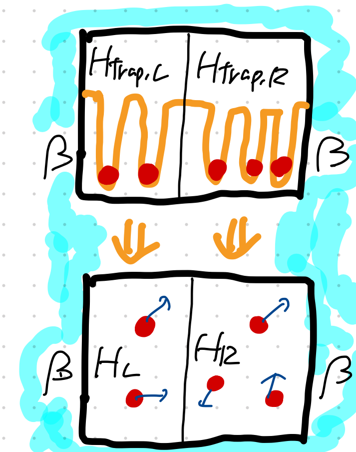
untrapping process

the opposite of trapping

$$H_{trap,L} \to H_L, \quad H_{trap,R} \to H_R$$

$$W_{untrap,L} = \frac{N_L}{\beta} \log \mathfrak{z}(\beta) - \frac{1}{\beta} \log \frac{Z_L(\beta)}{N_L!}$$

$$W_{untrap,R} = \frac{N_R}{\beta} \log \mathfrak{z}(\beta) - \frac{1}{\beta} \log \frac{Z_R(\beta)}{N_R!}$$



∴ the total work needed for the SHNY process

$$W_{SHNY} = W_{trap} + W_{wall} + W_{untrap,L} + W_{untrap,R}$$

$$= \frac{1}{\beta} \log \frac{Z_0(\beta)}{N!} - \frac{N}{\beta} \log \mathfrak{z}(\beta) + \frac{N_L}{\beta} \log \mathfrak{z}(\beta) - \frac{1}{\beta} \log \frac{Z_L(\beta)}{N_L!} + \frac{N_R}{\beta} \log \mathfrak{z}(\beta) - \frac{1}{\beta} \log \frac{Z_R(\beta)}{N_R!}$$

$$= \frac{1}{\beta} \log \frac{Z_0(\beta)}{N!} - \frac{1}{\beta} \log \frac{Z_L(\beta)}{N_L!} - \frac{1}{\beta} \log \frac{Z_R(\beta)}{N_R!}$$

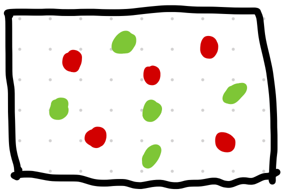
⟸ the desired relation

FAQs

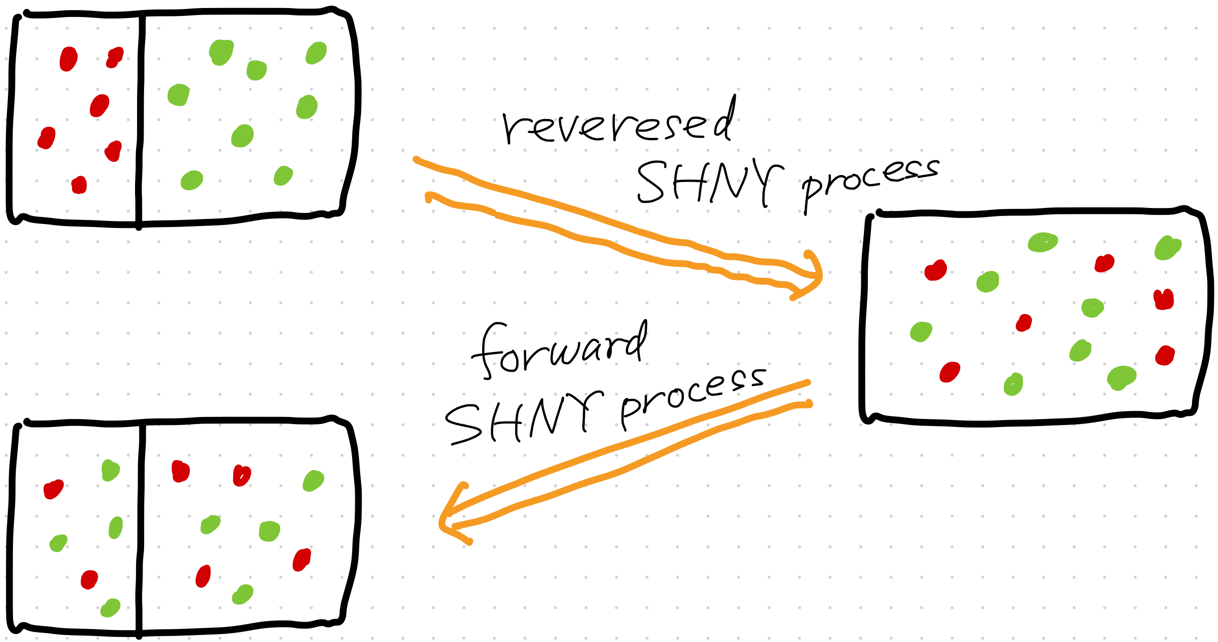
▷ What does it precisely mean that classical particles are identical

- only dynamical properties — the same mass, the same potential, the same interactions, ..
  ↕ quantum case — the basic symmetry of the Hilbert space.
- the identity guarantees that the wall insertion process is reversible.

▷ What happens if the particles are identical but distinguishable?



- nothing changes if we simply ignore the colors and analyze quasi-static work → $\boxed{\text{The same factor } N!}$
- there may be potentials or interactions that distinguish the colors
  ↓
  the particles are no longer identical!


reveresed
SHNY process
forward
SHNY process