Gibbs paradox and quasi-static decomposition in small thermodynamic systems

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Part I
Background

Setup - Microscopic description -

$$\Gamma = (\boldsymbol{r}_1, \boldsymbol{r}_2, \cdots, \boldsymbol{r}_N, \boldsymbol{p}_1, \cdots, \boldsymbol{p}_N)$$

$$H_0(\Gamma) = \sum_{i=1}^{N} \frac{|\boldsymbol{p}_i|^2}{2m} + \sum_{i<j} V_{\mathrm{int}}(\boldsymbol{r}_i - \boldsymbol{r}_j)$$

Symmetry of permutations

$$H_0(\Gamma) = H_0(\sigma(\Gamma))$$

$$\sigma(\Gamma) = (\boldsymbol{r}_{\sigma(1)}, \boldsymbol{r}_{\sigma(2)}, \cdots, \boldsymbol{r}_{\sigma(N)}, \boldsymbol{p}_{\sigma(1)}, \cdots, \boldsymbol{p}_{\sigma(N)})$$

$$H(\Gamma; D, N, \kappa) = H_0(\Gamma) + \sum_{i=1}^{N} V_{\mathrm{wall}}(\boldsymbol{r}_i; D, \kappa)$$

Assumption : finite interaction length

$$V_{\mathrm{wall}}(\boldsymbol{r}; D, \kappa) = \frac{\kappa}{2}|d(\boldsymbol{r}, D)|^2$$

one-body potential confining in the region D

$$d(\boldsymbol{r}, D) = \inf_{\boldsymbol{r}' \in D} |\boldsymbol{r} - \boldsymbol{r}'|$$

Complete confinement $\kappa \to \infty$

Setup - Statistical mechanics-

Equilibrium distribution

$$\rho_\beta(\Gamma; D, N, \kappa) = \frac{1}{Z(T, D, N, \kappa)} \exp(-\beta H(\Gamma; D, N, \kappa))$$

Partition function

$$\beta = \frac{1}{k_{\mathrm{B}} T}$$

$$Z(T, D, N, \kappa) = \int d\Gamma \exp(-\beta H(\Gamma; D, N, \kappa))$$

$$Z(T, V, N) \equiv \lim_{\kappa \to \infty} Z(T, D, N, \kappa)$$

$$V = |D|$$

$$D \quad N$$

Question - Free energy -

$$F(T,V,N) = -\beta^{-1}\log\frac{Z(T,V,N)}{N!} + c_0 N$$

How to derive this formula?

Quantum statistical mechanics

$$S(T,V,N) \equiv -k_{\mathrm{B}}\mathrm{tr}[\hat{\rho}_\beta \log \hat{\rho}_\beta]$$

$$F(T,V,N) \equiv \langle H \rangle_\beta - TS(T,V,N)$$

classical limit

$$F(T,V,N) = -\beta^{-1}\left[\log \frac{Z(T,V,N)}{N!} + c_0 N\right]$$

$$c_0 = 3\log h$$

However,

$$S(T,V,N) \equiv -k_{\mathrm{B}} \int d\Gamma \rho_\beta \log \rho_\beta$$

$$F(T,V,N) \equiv \langle H \rangle_\beta - TS(T,V,N)$$

↓

$$F(T,V,N) = -\beta^{-1} \log Z(T,V,N)$$

$\log N!$ **is missing**

violation of the extensivity of the free energy (in the thermodynamic limit)

Some textbooks claim

$N!$ comes from quantum mechanics

If you think it, I recommend you to concentrate on my talk!

Standard "interpretation"

Quantum mechanics: each particle **cannot be distinguished**;
the density matrix is always symmetric wrt the permutation of the label

Classical mechanics: each particle **can be distinguished**;
= the distribution is not necessarily symmetric wrt the permutation of the label

⇒**"macroscopically" indistinguishable**
= there are no thermodynamic ways to distinguish particle labels

⇒ Subtract log ["the number of degenerated states"]

$$S(T,V,N) \equiv -k_{\rm B} \int d\Gamma \rho_\beta \log \rho_\beta - k_{\rm B} \log N!$$

I am not satisfied with this explanation.

The interpretation should be given after the formulation is completed

Express the concept “macroscopic indistinguishability” in terms of mathematical words

Problem

How to define **the free energy** (or entropy) for given

microscopic description (**Hamiltonian**)

and

statistical description (**canonical ensemble**)

The free energy should be defined by **thermodynamic relations**

Part II
Basic issues

T dependence of the free energy

$$E = \frac{\partial(\beta F)}{\partial \beta}$$ Gibbs-Helmholz relation

$$E = \langle H \rangle_\beta = -\frac{\partial \log Z(T,V,N)}{\partial \beta}$$ Canonical ensemble

$$\Rightarrow \quad \frac{\partial}{\partial \beta}[\beta F + \log Z] = 0$$

V dependence of the free energy

$$p = -\frac{\partial F}{\partial V}$$

Fundamental relation in thermodynamics

$$p = -\left\langle \frac{\partial H}{\partial V} \right\rangle_\beta = \beta^{-1} \frac{\partial \log Z(T, V, N)}{\partial V}$$

Canonical ensemble

$$\Rightarrow \quad \frac{\partial}{\partial V}\left[\beta F + \log Z\right] = 0$$

The form of free energy

$$\frac{\partial}{\partial\beta}[\beta F + \log Z] = 0 \qquad \frac{\partial}{\partial V}[\beta F + \log Z] = 0$$

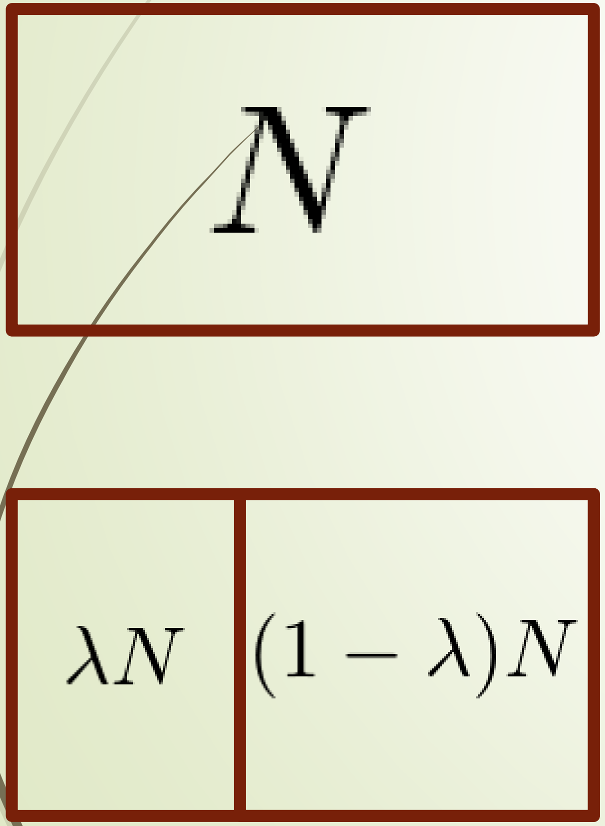
$$F(T,V,N) = -k_{\mathrm{B}}T[\log Z(T,V,N) - \phi(N)]$$

$\phi(N)$ not determined yet

Answer: $\phi(N) = \log N! - c_0 N$

How to determine $\phi(N)$

We consider a process in which a particle number is changed, and apply the formula “free energy change = quasi-static work”



Example:

Inserting the separating wall

$$(V,N) \to \{(\lambda V, \lambda N), ((1-\lambda)V, (1-\lambda)N)\}$$

for any $0 \le \lambda \le 1$ such that $\lambda N \in \mathbb{N}$

An assumption in thermodynamics

The quasi-static work decomposing the system should be zero

$$W_{\rm qs}[T;(V,N)\to\{(\lambda V,\lambda N),((1-\lambda)V,(1-\lambda)N)\}]=0 \qquad \star$$

for any $0\le\lambda\le 1$ such that $\lambda N\in\mathbb{N}$

$$F(\lambda V,\lambda N)+F((1-\lambda)V,(1-\lambda)N)-F(V,N)=0$$

$$\Rightarrow \quad \phi(N)=N\log N+c_1 N$$

which is different from $\phi(N)=\log N!-c_0 N$

Possible interpretation

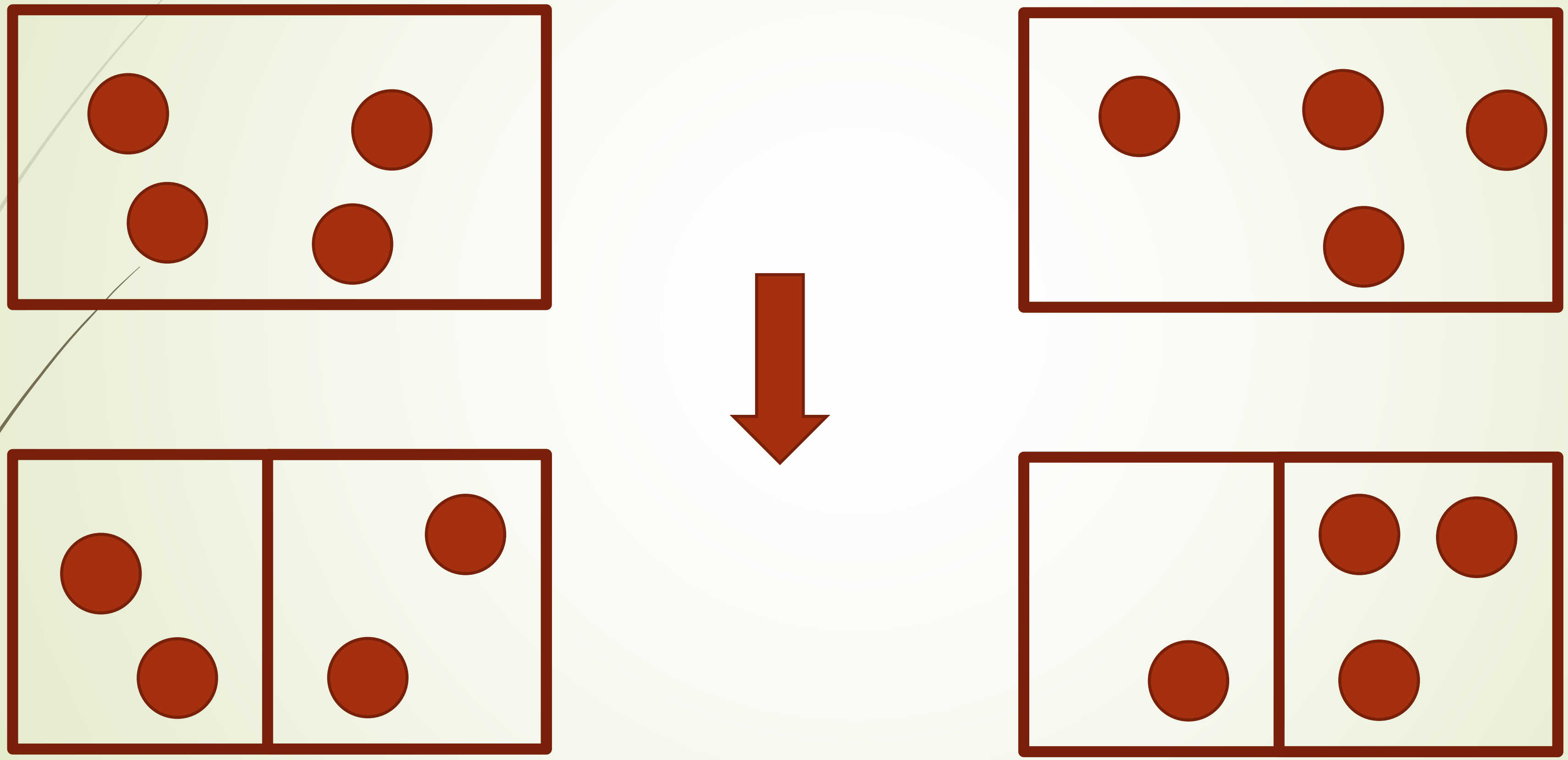
$$W_{\mathrm{qs}}[T;(V,N)\to\{(\lambda V,\lambda N),((1-\lambda)V,(1-\lambda)N)\}]=0 \quad \star \quad ?$$
$$0\le\lambda\le1$$

is valid only in the thermodynamic limit

➡ $$\phi(N)=N\log N+c_1N+o(N)$$

consistent with $$\phi(N)=\log N!-c_0N$$

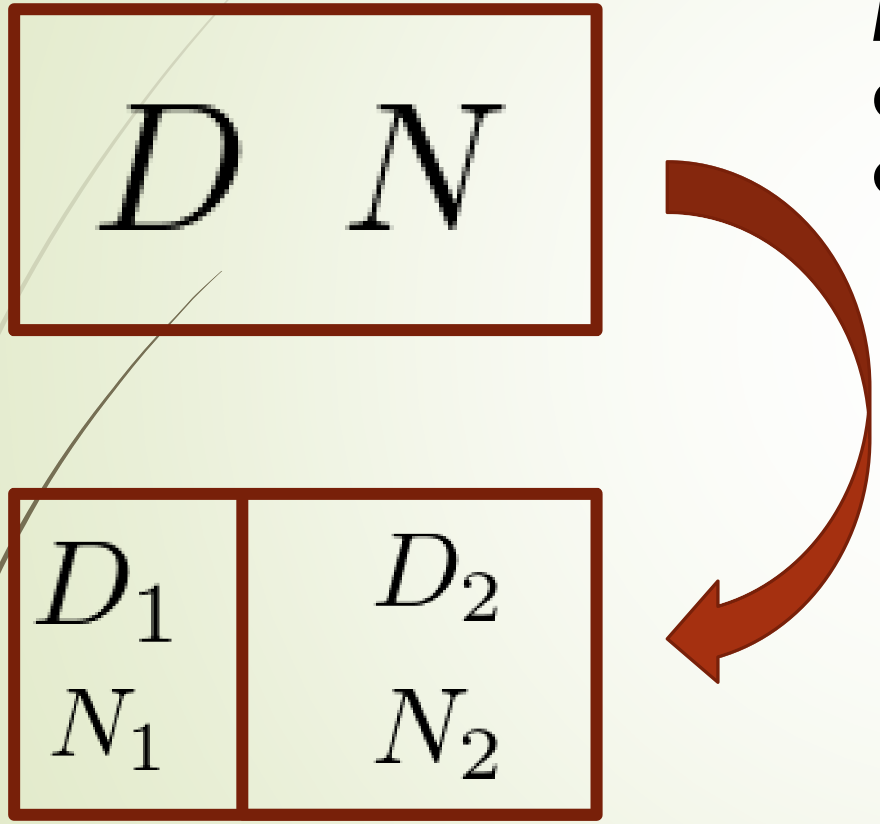
Small thermodynamic systems



Just inserting the separating wall

cannot fix the number partition precisely.

Measurement-and-feedback



Measure the particle number in the region; and insert the separation wall (depending on the measurement result)

Free energy difference:

$$F(V_1, N_1) + F(V_2, N_2) - F(V, N)$$
$$= -\beta^{-1}\left[\log\left(\frac{N!}{N_1!N_2!}Z(V_1, N_1)Z(V_2, N_2)\right) - \log Z(V, N)\right]$$

$$\phi(N) = \log N! - c_0 N$$

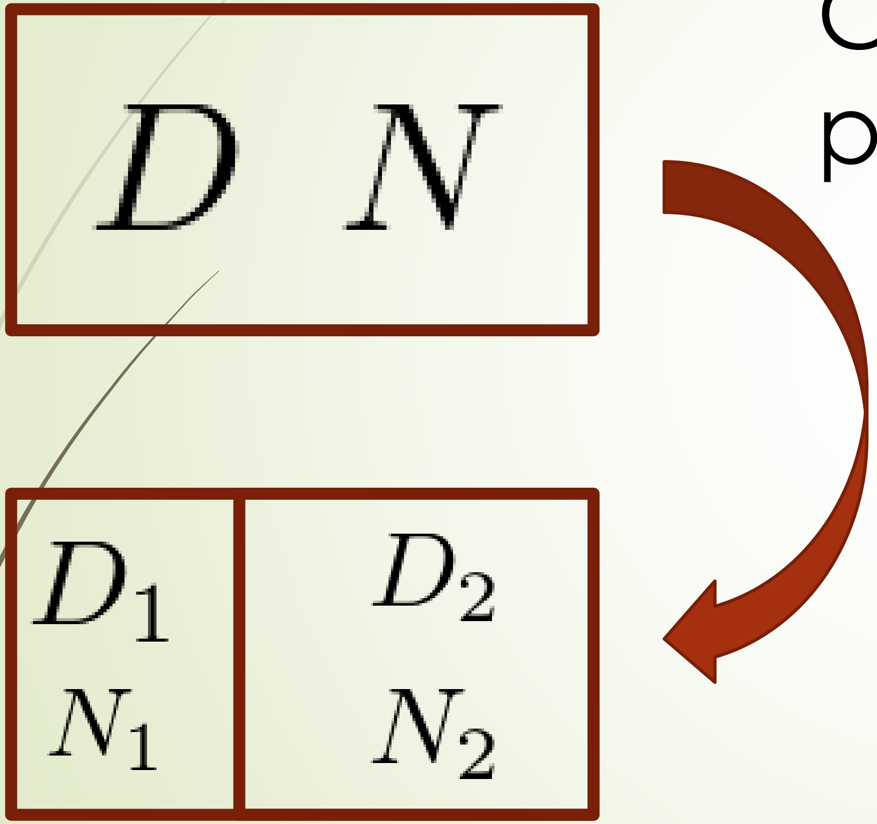
A. Yoshida and N. Nakagawa, Phys. Rev. Res. 2022

Although this result is very nice,
I am not satisfied with this explanation

Our motivation

We want to determine the free energy from quasi-static work within thermodynamics (without using information thermodynamics)

Question - quasi-static decomposition-



Construct a quasi-static process without measurement

$$D_1 \cap D_2 = \phi$$

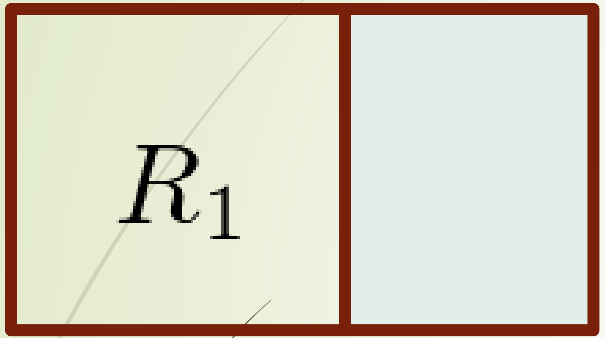
$$D_1 \cup D_2 = D$$

$$N_1 + N_2 = N$$

Separate two regions beyond the interaction length (not explicitly written below)

Part III
One solution

Special Confining potential



$$V(\Gamma; R_1) = 0$$

The number of particles in R_1 is equal to or greater than N_1

The potential should be symmetric wrt permutations of particle labels

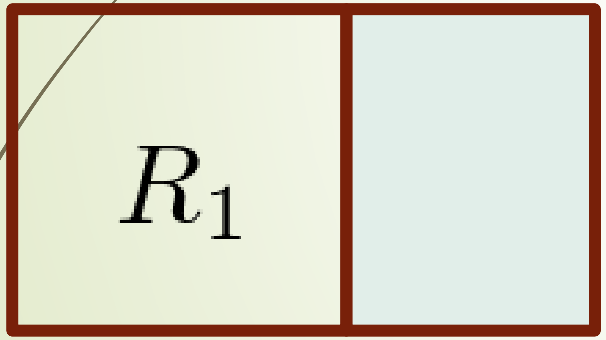
Number controlling potential

$$V(\Gamma; R_1) = \min_{\sigma \in P_N} \sum_{i=1}^{N_1} V_{\mathrm{wall}}(\boldsymbol{r}_{\sigma(i)}; R_1)$$

$$V_{\mathrm{wall}}(\boldsymbol{r}; D, \kappa) = \frac{\kappa}{2} |d(\boldsymbol{r}, D)|^2$$

$$d(\boldsymbol{r}, D) = \inf_{\boldsymbol{r}' \in D} |\boldsymbol{r} - \boldsymbol{r}'|$$

$$V(\Gamma; R_1) = 0$$

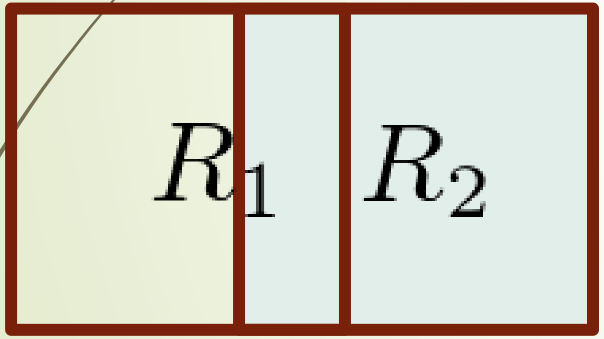


The number of particles in R_1 is equal to or greater than N_1

Number controlling potential II

$$V_{\rm con}(\Gamma; R_1, R_2) \equiv \min_{\sigma \in P_N} \left[\sum_{i=1}^{N_1} V_{\rm wall}(\boldsymbol{r}_{\sigma(i)}; R_1) + \sum_{i=N_1+1}^{N} V_{\rm wall}(\boldsymbol{r}_{\sigma(i)}; R_2) \right]$$

$$R_1 \cup R_2 = D$$

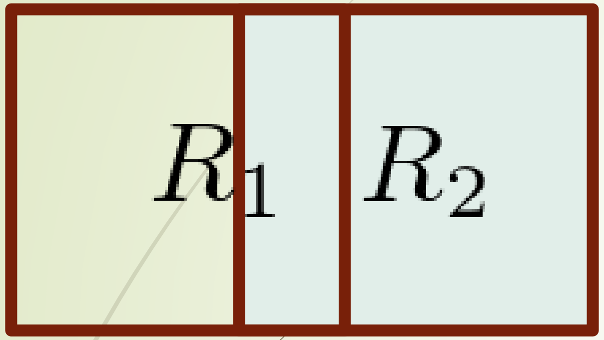


$$V_{\rm con}(\Gamma; R_1, R_2) = 0$$

The number of particles in R_1 (R_2) is equal to or greater than N_1 (N_2)

All particles are in D

Quasi-static decomposition



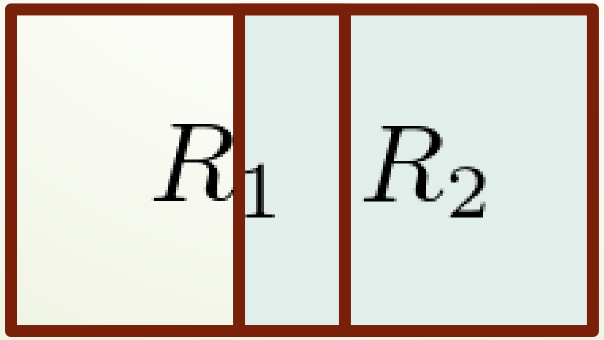
$$\tilde{H}(\Gamma; R_1, R_2) \equiv H_0(\Gamma) + V_{\rm con}(\Gamma; R_1, R_2)$$

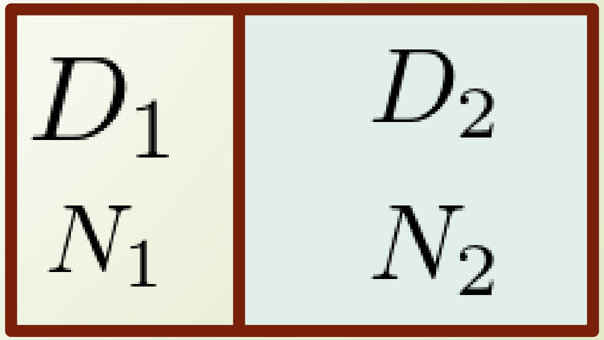
$$\tilde{Z}(R_1, R_2) = \int d\Gamma \exp(-\beta \tilde{H}(\Gamma; R_1, R_2))$$

T is ignored in the argument here and hereafter

$$D_1 \cap D_2 = \phi \quad D_1 \cup D_2 = D$$

$$(R_1, R_2) : (D, D) \to (D_1, D_2)$$





Quasi-static work

$$D_1 \cap D_2 = \phi \quad D_1 \cup D_2 = D \qquad (R_1, R_2) : (D, D) \to (D_1, D_2)$$

$$W(D \to D_1 \cup D_2; \kappa) = -\beta^{-1}[\log \tilde{Z}(D_1, D_2) - \log \tilde{Z}(D, D)]$$

$$\lim_{\kappa \to \infty} \tilde{Z}(D, D) = Z(V, N)$$

To calculate $\tilde{Z}(D_1, D_2)$

$$\tilde{H}(\Gamma; R_1, R_2) \equiv H_0(\Gamma) + V_{\rm con}(\Gamma; R_1, R_2)$$

$$\tilde{Z}(R_1, R_2) = \int d\Gamma \exp(-\beta \tilde{H}(\Gamma; R_1, R_2))$$

Preparation

$$\lim_{\kappa\to\infty} \tilde{Z}(D_1, D_2) = \int d\Gamma \exp(-\beta H_0(\Gamma)) \prod_{i=1}^{N_1} \chi(\boldsymbol{r}_{\sigma_\Gamma(i)} \in D_1) \prod_{i=N_1+1}^{N} \chi(\boldsymbol{r}_{\sigma_\Gamma(i)} \in D_2) \heartsuit$$

For Γ satisfying $V_{\mathrm{con}}(\Gamma; D_1, D_2) = 0$ $\quad \Gamma \mapsto \sigma_\Gamma \in G_{N_1}$

$$G_{N_1} = \{\sigma \in P_N | \sigma(1) < \sigma(2) \cdots < \sigma(N_1); \sigma(N_1+1) < \sigma(N_1+2) \cdots < \sigma(N)\}$$

The set of particle labels when N particles are separated into N_1 and N_2

RHS of $\heartsuit$: Insert $\displaystyle\sum_{\sigma \in G_{N_1}} \delta(\sigma, \sigma_\Gamma) = 1$

Calculation

RHS of ♥ : $$\sum_{\sigma \in G_{N_1}} \int d\Gamma \exp(-\beta H_0(\Gamma)) \prod_{i=1}^{N_1} \chi(\boldsymbol{r}_{\sigma(i)} \in D_1) \prod_{i=N_1+1}^{N} \chi(\boldsymbol{r}_{\sigma(i)} \in D_2)$$

$$H_0(\Gamma) = H_0(\sigma(\Gamma))$$ **Symmetry for permutation of particle labels**

$$\sum_{\sigma \in G_{N_1}} \int d\Gamma \exp(-\beta H_0(\Gamma)) \prod_{i=1}^{N_1} \chi(\boldsymbol{r}_{(i)} \in D_1) \prod_{i=N_1+1}^{N} \chi(\boldsymbol{r}_{(i)} \in D_2)$$

$$= |G_{N_1}| Z(V_1, N_1) Z(V_2, N_2)$$

$$= \frac{N!}{N_1! N_2!} Z(V_1, N_1) Z(V_2, N_2)$$

Summary of calculation

Quasi-static work :

$$F(V_1, N_1) + F(V_2, N_2) - F(V, N)$$

$$= -\beta^{-1}\left[\log\left(\frac{N!}{N_1!N_2!}Z(V_1, N_1)Z(V_2, N_2)\right) - \log Z(V, N)\right]$$

$$\Rightarrow \quad \phi(N) = \log N! - c_0 N$$

Part IV
Remarks

Information thermodynamics

Quasi-static work corresponding to the free energy change from the measurement-and-feedback

J. M. Horowitz and J. M. R. Parrondo, New. J. Phys. 13 123019 (2011).

↓

written in sentences, but not explicitly constructed

We give an explicit construction of such quasi-static work

Explicit presentation of the protocol by Horowitz and Parrondo, and discussion of the relevance with the N! problem)

H. Tasaki, https://arxiv.org/abs/2206.05513

Binary mixtures

Permutation symmetry holds only in the same particle type

Semi-permeable wall for each particle type

=thermodynamic distinguishablity

$$F(V, N_A, N_B) = -\beta^{-1} \log \frac{Z(V, N_A, N_B)}{N_A! N_B!} + c_A N_A + c_B N_B$$

Numerically efficient computation via non-equilibrium relations

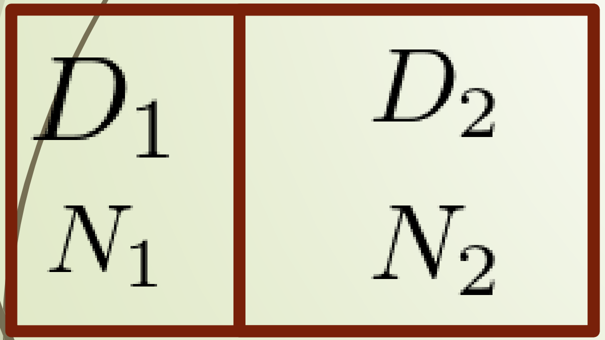
A. Yoshida and N. Nakagawa, Phys. Rev. Res. 2022

Previous work: composite system

“Partition function” of the composite system

$$Z_{\text{comp}}(V_1, N_1, V_2, N_2) = \frac{N!}{N_1! N_2!} Z(V_1, N_1) Z(V_2, N_2)$$

Warren, 1998; Frenkel 2014



If the LHS is defined from the normalization constant of the canonical ensemble, the confining potential (fixing the particle numbers) should be specified

$\Rightarrow$ our result is necessary

Previous work: large deviation

$$p(\hat{N}_1; V, N) = \frac{1}{\tilde{Z}(V,N)} \exp(-\beta[F(V_1, \hat{N}_1) + F(V - V_1, N - \hat{N}_1)])$$

The free energy is defined by this fluctuation relation

Swenden, 2006

D_1	D_2
N_1	N_2

The system of non-interacting particles is OK

Macroscopic systems are OK

How to formulate finite system of interacting particles ?

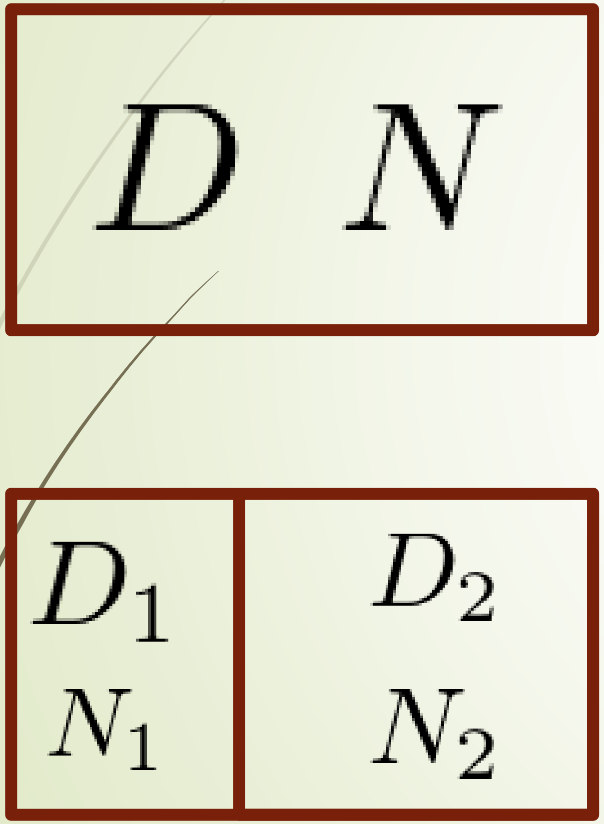
Previous work: Absolute irreversibility

- **Free energy based on non-equilibrium processes (Jarzynski eq)**
- **If the reversed path is singular ⇒ modified-Jarzynski eq**

  (Murashita-Funo-Ueda, 2014)
- **Modified Jarzynski equality for free mixing processes**
- **Difference between the same type and the different type**
- **Gibbs factorial (Murashita, Ueda, PRL, 2017)**

  The system of non-interacting particles is OK, but no proof is presentd for general cases

Summary



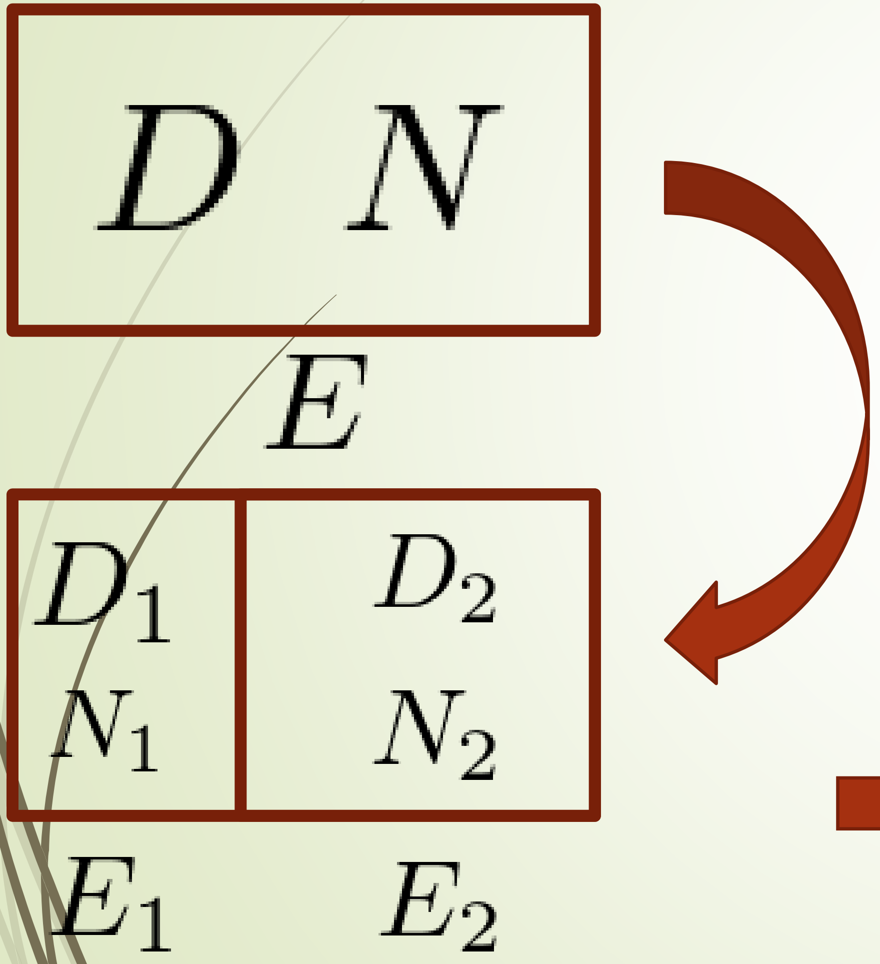
We construct a quasi-static decomposition process for small thermodynamic systems

"Quasi-static work = free energy difference " leads to the N! factor of the formula:

$$F(T,V,N) = -\beta^{-1}\left[\log \frac{Z(T,V,N)}{N!} + c_0 N\right]$$

See https://arxiv.org/abs/2205.05863

Thermally isolated systems



Hamiltonian systems (isolated)

$$\Omega(E,\mathcal{C}) \equiv \int d\Gamma \theta(E - H(\Gamma;\mathcal{C}))$$

Ergodic adiabatic theorem to our process

$$\frac{N!}{N_1!N_2!}\Omega(E_1,V_1,N_1)\Omega(E_2,V_2,N_2) = \Omega(E,V,N)$$

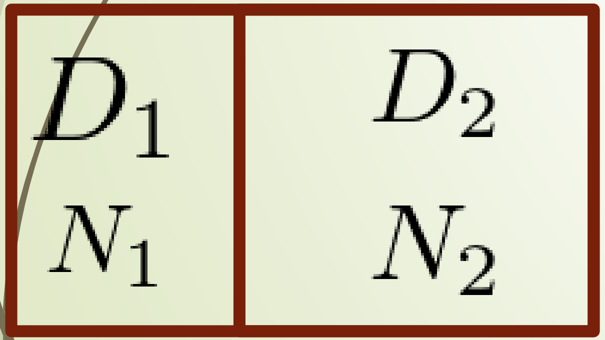
Entropy = adiabatic invariant

$$S(E,V,N) = c_1 \log \frac{\Omega(E,V,N)}{N!} + c_2 N$$

Quantum systems

$$Z^{\mathrm{QM}}(\mathcal{C}) = \mathrm{Tr}(\exp(-\beta \hat{\mathrm{H}}(\mathcal{C})))$$

$$Z^{\mathrm{QM}}_{\mathrm{comp}}(V_1, N_1, V_2, N_2) = Z^{\mathrm{QM}}(V_1, N_1) Z^{\mathrm{QM}}(V_2, N_2)$$



$$F(V, N) = -k_{\mathrm{B}} T [\log Z^{\mathrm{QM}}(V, N) - c_0 N]$$

Generalization

$H(\Gamma;\mathcal{C})$ Hamiltonian with a system condition $\mathcal{C}$

$$F(T,\mathcal{C}_1) - F(T,\mathcal{C}_0) = W_{\mathrm{qs}}(T;\mathcal{C}_0 \to \mathcal{C}_1)$$

$$F(T,\mathcal{C}_1) - F(T,\mathcal{C}_0) = -\beta^{-1}[\log Z(T,\mathcal{C}_1) - \log Z(T,\mathcal{C}_0)$$

$$Z(T,\mathcal{C}) = \int d\Gamma \exp(-\beta H(\Gamma;\mathcal{C}))$$