MATH327: StatMech and Thermo

Wednesday, 26 February 2025

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Something to consider

What should we do with the sum $Z = \sum_i e^{-E_i/T}$

when E_i depends on continuously varying momenta?

Recap

Applications of canonical ensemble

Physics of information (spin system)

Today

Classical, non-relativistic, ideal gases → mixing entropy

"Gibbs paradox"

→ Not quantum

exactly know (x, y, z) and $\vec{p} = (p_x, p_y, p_z)$

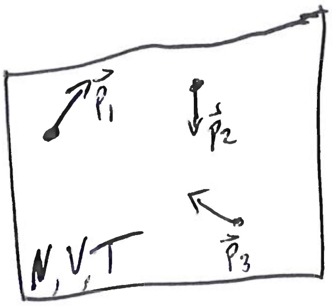
Non-rel. means slow vs. speed of light

$E_n = \frac{1}{2m} p_n^2$ for mass $m > 0$

inner product $p^2 = \vec{p} \cdot \vec{p} = p_x^2 + p_y^2 + p_z^2$

Ideal means no interactions between particles

$E_i = \frac{1}{2m} \sum_{n=1}^{N} p_n^2$ for ω_i



N particles in cubic box of volume $V = L^3$

T fixed by thermal reservoir

Start with partition function $Z = \sum_i e^{-E_i/T}$

problem

uncountable micro-states
depend of continuous $\{\vec{p}_n\}$

Need to regularize system
→ countable micro-states with well-defined Z
Then take limit of sums → integrals

Declare only possible momenta are
$\vec{p} = (p_x, p_y, p_z) = \hbar \frac{\pi}{L}(k_x, k_y, k_z)$ countable $k_{x,y,z} \in \mathbb{Z}$
Planck constant converts units ($\frac{1}{L}$ vs. p)

Countable energy levels for each particle
$E_k = \frac{p^2}{2m} = \frac{\hbar^2\pi^2}{2mL^2} k^2 = \varepsilon(k_x^2 + k_y^2 + k_z^2)$ $\varepsilon = \frac{\hbar^2\pi^2}{2mL^2}$

Lowest energies: $\boxed{\frac{E}{\varepsilon} = 0, 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, \ldots}$ $\vec{k}=(2,2,0)$ + perms, $\vec{k}=(2,1,1)$ + perms.

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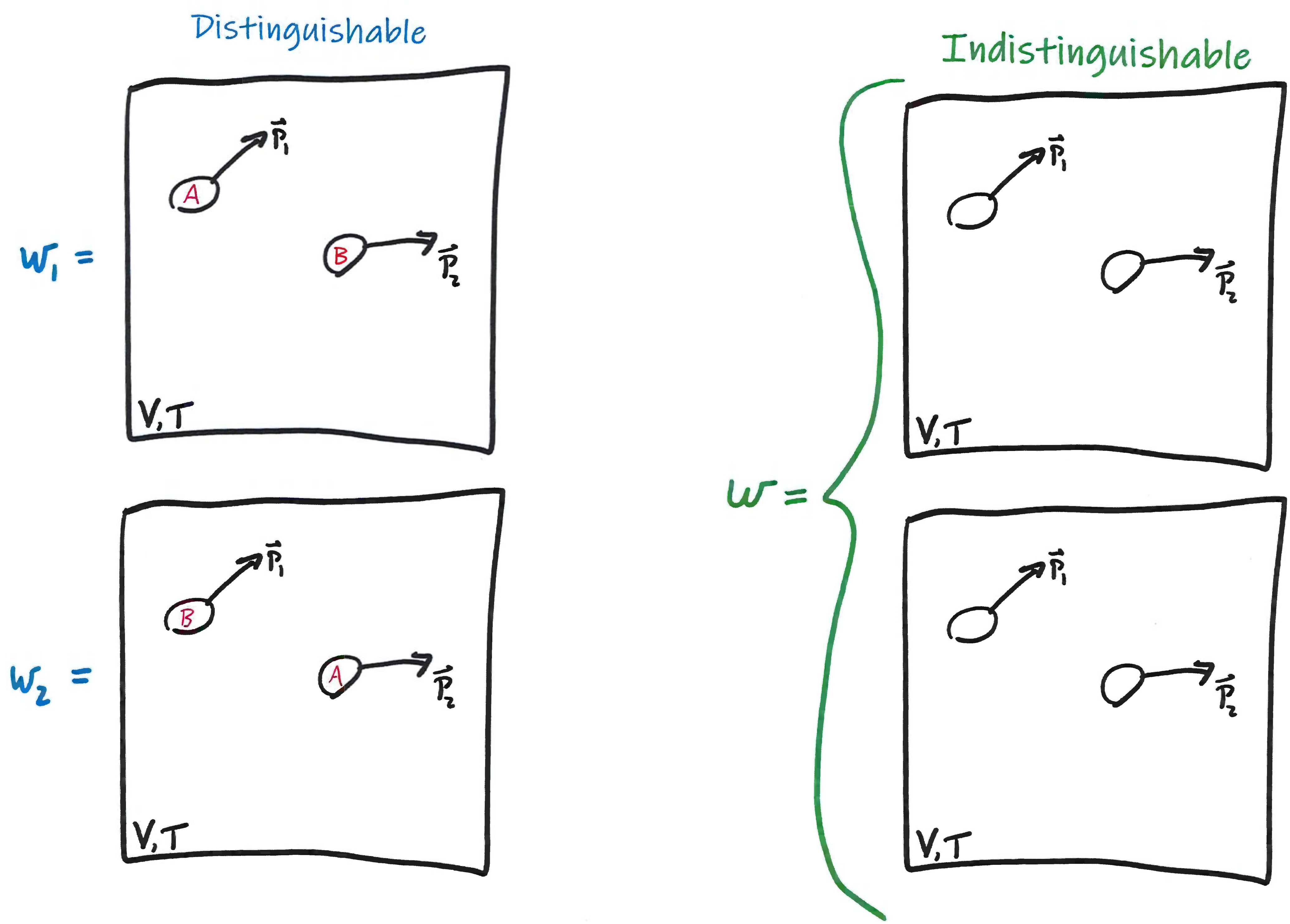
Not 7, 15, 23, 28, 31, ...

Unlike spin system, not evenly spaced
Quantum ~~phx~~ physics characterized by "quantized" energy
Here just ansatz to be removed...
... but can prep for quantum gases by restricting $k_{x,y,z} = 0, 1, 2, \ldots$

$\pm k_i \neq 0 \rightarrow$ same k^2 & E & $e^{-E/T}$
→ restriction changes Z by constant factor
doesn't affect p^2-dependent expectation values

$$\langle f(p^2)\rangle = \sum_i f(p^2)_i P_i = \frac{1}{Z}\sum_i f(p^2)\, e^{-E/T}$$


Distinguishable
$W_1 =$
A
B
$\vec{p}_1$
$\vec{p}_2$
V,T
$W_2 =$
B
A
$\vec{p}_1$
$\vec{p}_2$
V,T
Indistinguishable
$W =$
$\vec{p}_1$
$\vec{p}_2$
V,T
$\vec{p}_1$
$\vec{p}_2$
V,T

Consider single particle

$$Z_1 = \sum_i e^{-E_i/T} = \sum_{k_{x,y,z}=0}^{\infty} \exp\left[-\frac{\varepsilon}{T}\left(k_x^2 + k_y^2 + k_z^2\right)\right]$$

$$= \left(\sum_{k_i=0}^{\infty} \exp\left[\frac{-\hbar^2 \pi^2}{2mTL^2} k_i^2\right]\right)^3$$

Regularized ✓

Take limit of sum → integral

$$p_i = \frac{\hbar\pi}{L}\hat{k}_i$$

$$d\hat{k}_i = \frac{L}{\hbar\pi} dp_i$$

$$Z_1 \to \left(\int_0^{\infty} \exp\left[\frac{-\hbar^2\pi^2}{2mTL^2}\hat{k}_i^2\right] d\hat{k}_i\right)^3$$

continuous

$$\int_0^{\infty} \to \frac{1}{2}\int_{-\infty}^{\infty}$$

$$Z_1 = \left(\frac{L}{2\pi\hbar}\int_{-\infty}^{\infty} \exp\left[-\frac{p_i^2}{2mT}\right] dp_i\right)^3$$

gaussian $\sqrt{2\pi m T}$

$$Z_1 = \left(L\sqrt{\frac{mT}{2\pi\hbar^2}}\right)^3 = \left(\frac{L}{\lambda_{th}(T)}\right)^3$$

For convenience define $\lambda_{th}(T) = \sqrt{\frac{2\pi\hbar^2}{mT}} \ll L$

thermal de Broglie wavelength

Generalize to N dist'able particles

$$Z_D = Z_1^N = \left(\frac{mTL^2}{2\pi\hbar^2}\right)^{3N/2} = \left(\frac{L}{\lambda_{th}}\right)^{3N} = \left(\frac{V}{\lambda_{th}^3}\right)^N$$

Depends of volume V along with N and T

What about indist'able particles?

Can't be labelled

$N=2$ $(\vec{p}_1 \neq \vec{p}_2)$: 1 indist'able vs. 2 dist'able micro-states

$N=3$ $(\vec{p}_i \neq \vec{p}_k$ for $i \neq k$ – assumption)

1 indist'able w_i vs. $6=3!$ dist'able micro-states

$\vec{p}_1$	A	A	B	B	C	C
$\vec{p}_2$	B	C	A	C	A	B
$\vec{p}_3$	C	B	C	A	B	A

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General result $Z_I = \frac{1}{N!} Z_D = \frac{1}{N!} Z_1^N = \frac{1}{N!}\left(\frac{V}{\lambda_{th}^3}\right)^N$

$$= \frac{1}{N!}\left(\frac{mTL^2}{2\pi\hbar^2}\right)^{3N/2}$$

Helmholtz free energy

$$F_I = -T\log Z_I = T\log(N!) - \frac{3}{2}NT\log\left(\frac{mTL^2}{2\pi\hbar^2}\right)$$

Predict $\langle E\rangle_I = -T^2\frac{\partial}{\partial T}\left(\frac{F}{T}\right)$

$$= -T^2\frac{\partial}{\partial T}\left(-\frac{3}{2}N\log T + T\text{-indep.}\right)$$

$$= \frac{3}{2}NT$$

$$C_V = \frac{3}{2}N > 0$$

Sensible macroscopic relation emerges
from microscopic dynamics ✓

Entropy is $S_I = \frac{\langle E\rangle_I - F_I}{T} = \frac{3}{2}N + \frac{3}{2}N\log\left(\frac{L^2}{\lambda_{th}^2}\right) - \underbrace{\log(N!)}_{N\log N - N}$

$$\approx \frac{5}{2}N + N\log\left(\frac{V}{N\lambda_{th}^3}\right)$$

Depends on volume
information from locations

Dist'able case just drops $\log(N!)$

$$\left.\begin{aligned} F_D &= -\frac{3}{2}NT\log\left(\frac{mTL^2}{2\pi\hbar^2}\right) \\ \langle E\rangle_D &= \frac{3}{2}NT = \langle E\rangle_I \end{aligned}\right\} \quad S_D = \frac{3}{2}N + N\log\left(\frac{V}{\lambda_{th}^3}\right)$$

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$\langle E \rangle$ doesn't depend on information
because constant factor $\frac{1}{N!}$ in Z_I vs. Z_D
(unlike spin system)

S_I & S_D differ - which is larger

$$S_I - S_D = N - N\log N = -\log(N!) < 0$$

$S_I < S_D$ — extra info from dist'ability ✓

Note both S_D & S_I go negative if $\frac{V}{\lambda_{th}^3} \ll 1$

$$S = -\sum_i p_i \log p_i < 0 \quad \text{nonsensical}$$

Sign of assumptions breaking down $\quad mTL^2 \ll 2\pi\hbar^2$
↳ classical → quantum

Mixing

Remove wall, re-equilibrate, re-insert wall
Entropy must not decrease

$$\Omega_0 = \Omega_A \otimes \Omega_B \quad \longrightarrow \quad \Omega_C \quad \longrightarrow \quad \Omega_F = \Omega_A' \otimes \Omega_B'$$

$$S_0 = S_A + S_B \quad \longrightarrow \quad S_C \quad \longrightarrow \quad S_F = S_A' + S_B' \geq S_C \geq S_0$$

Consider 'indis'able case

$$\boxed{\begin{aligned} S_0 = S_A + S_B &= 2S_I(N, V, T) = 5N + 2N\log\left(\frac{V}{N\lambda_{th}^3}\right) \\ S_C = S_I(2N, 2V, T) &= 5N + 2N\log\left(\frac{\cancel{2}V}{\cancel{2}N\lambda_{th}^3}\right) = S_0 \end{aligned}}$$

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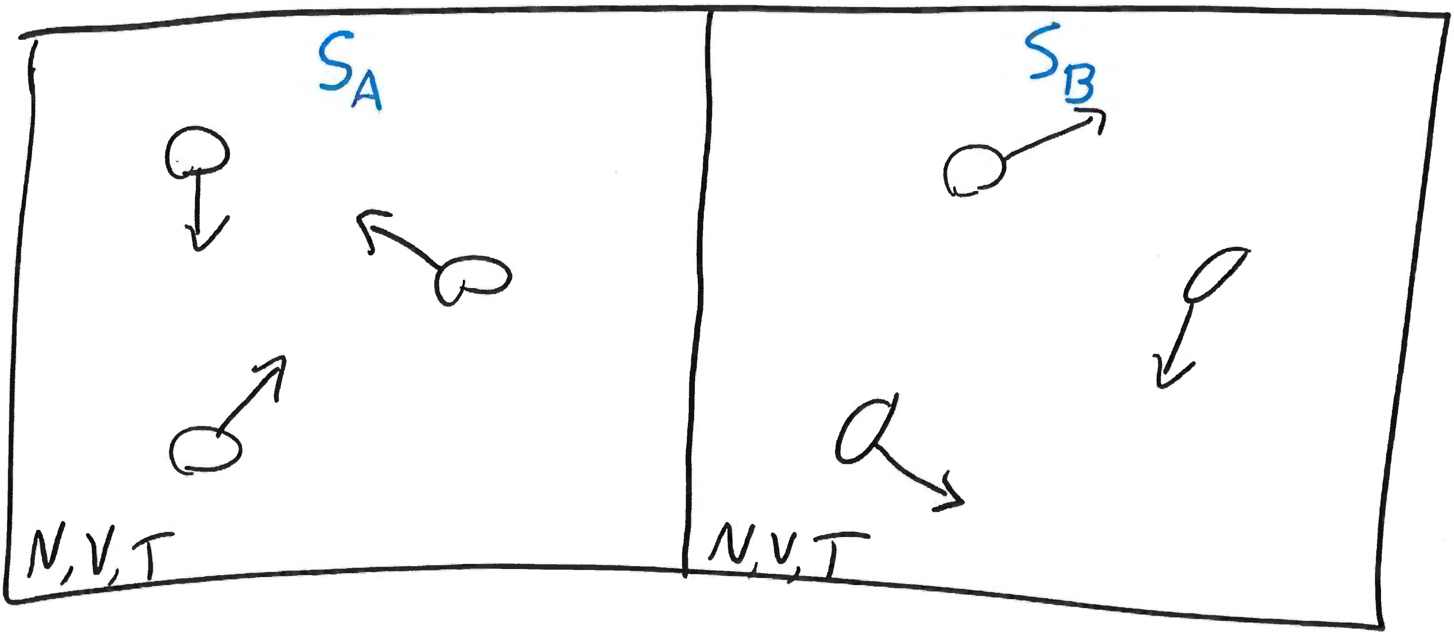
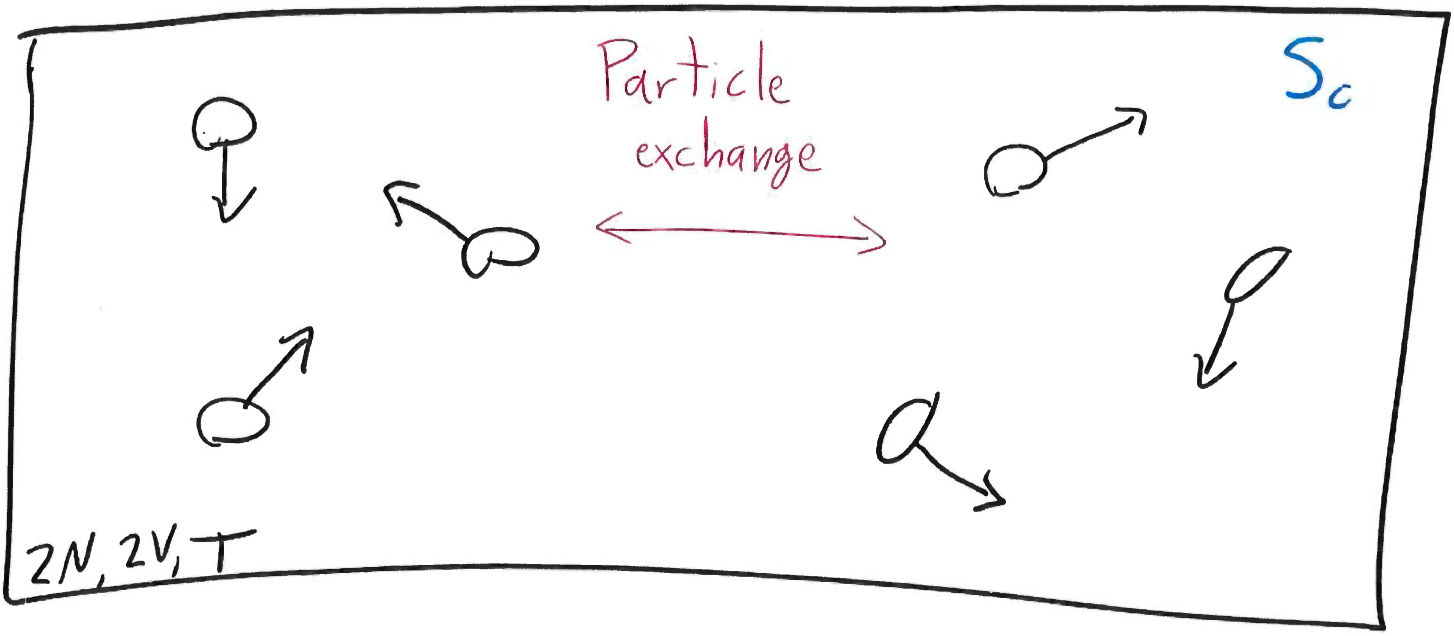
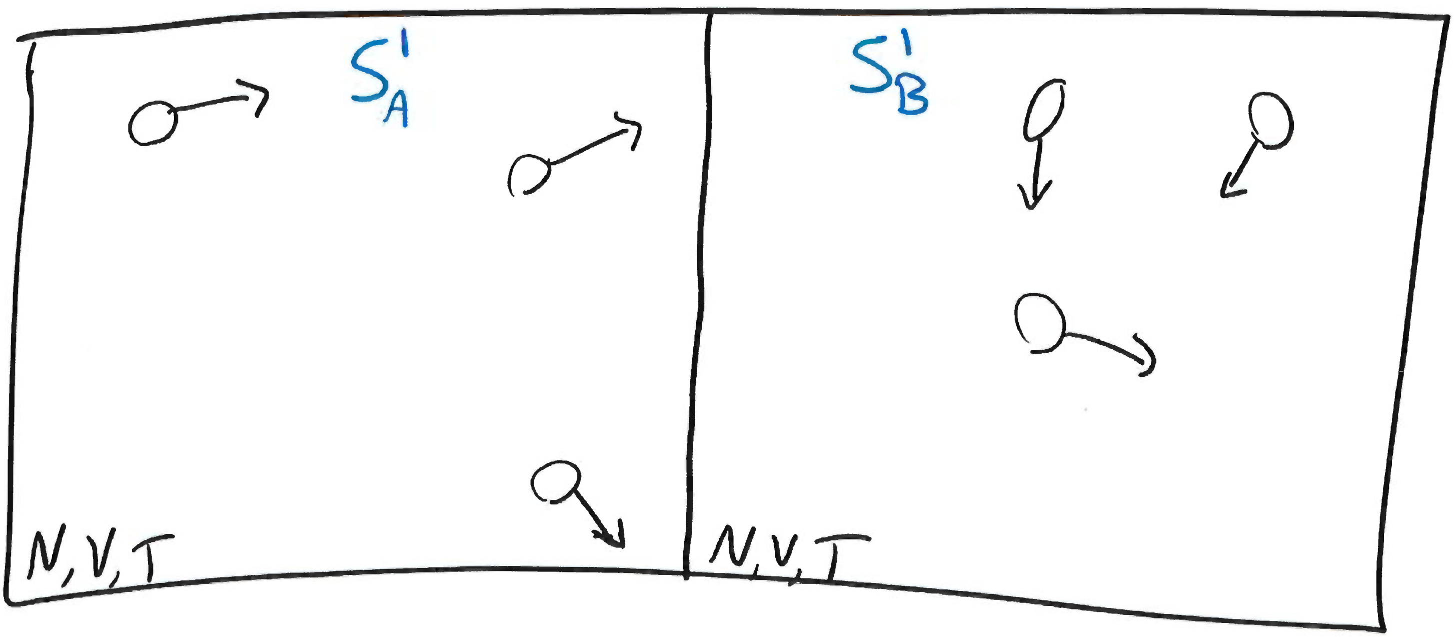
consistent w/second law ✓


S_A
S_B
N, V, T
N, V, T


Particle exchange
S_C
2N, 2V, T


S'_A
S'_B
N, V, T
N, V, T