# MATH327: StatMech and Thermo

Monday, 3 March 2025

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**Something to consider**

We can describe the air in this room, and the air in the hall, as ideal gases governed by the canonical ensemble.

What should we expect to happen if we open or close the door that separates them?

Recap

Classical ideal gas

Canonical partition funcs, for continuous energies

$$Z_I = \frac{1}{N!} Z_D = \frac{1}{N!} Z_1^N = \frac{1}{N!}\left(\frac{V}{\lambda_{th}^3}\right)^N \qquad \lambda_{th} = \sqrt{\frac{2\pi\hbar^2}{mT}}$$

Predict $\langle E \rangle_I = \langle E \rangle_D = \frac{3}{2} NT$

$$S_I = \frac{\cancel{3}\,5}{2} N + N \log\left(\frac{V}{N\lambda_{th}^3}\right) < S_D = \frac{\cancel{5}\,3}{2} N + N \log\left(\frac{V}{\cancel{N}\lambda_{th}^3}\right)$$

corrected after lecture - sorry!

Today

Finish mixing vs. second law

(so far $S_C = S_A + S_B$ for indist'able)

Equation of state

Re-separate systems

Need to sum over all possible particle divisions

$\{\nu, 2N-\nu\}$

Each $Z_\nu = Z_I(\nu, V, T) \times Z_I(2N-\nu, V, T)$

$$= \frac{1}{\nu!\,(2N-\nu)!} \cancel{\left(\frac{V}{\lambda_{th}^3}\right)^{\nu}} \left(\frac{V}{\lambda_{th}^3}\right)^{2N-\cancel{\nu}}$$

$$Z_F = \sum_{\nu=0}^{2N} Z_\nu = \sum_\nu \left(\frac{V}{\lambda_{th}^3}\right)^{2N} \frac{1}{\nu!\,(2N-\nu)!} = \left(\frac{V}{\lambda_{th}^3}\right)^{2N} \sum_\nu \binom{2N}{\nu} \frac{1}{(2N)!}$$

Entropy $S_F = \frac{\partial}{\partial T}(T \log Z)$

$$= 2N \frac{\partial}{\partial T}\left(T \log\left(\frac{V}{\lambda_{th}^3(T)}\right)\right) - \log[(2N)!] + \log\left[\sum_\nu \binom{2N}{\nu}\right]$$

complicated!

Simplify: Gibbs approximation

$N \gg 1 \to$ essentially all entropy from even distribution

$N_A' = N_B' = N$

$S_F = 2S_I(N, V, T) = S_A + S_B = S_C$

No change in entropy — reversible process

Repeat for dist'able case

$S_0 = S_A + S_B = 2S_D(N, V, T) = 3N + 2N \log\left(\frac{V}{\lambda_{th}^3}\right)$

$S_C = S_D(2N, 2V, T) = 3N + 2N \log\left(\frac{2V}{\lambda_{th}^3}\right)$

$\Delta S_{mix} = S_C - S_0 = 2N \log 2 > 0$ ✓     mixing entropy

$S_F = 2S_D(N, V, T) = S_0 < S_C$

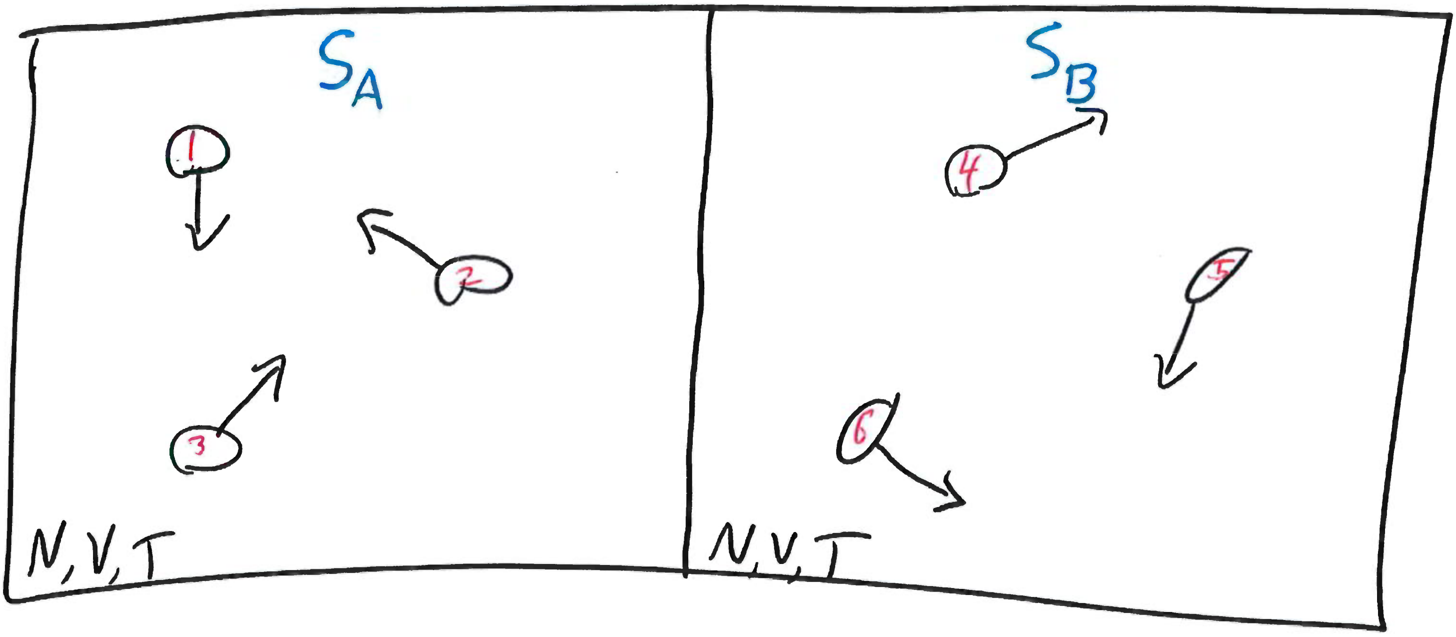
Would violate second law ✗

"Gibbs paradox"

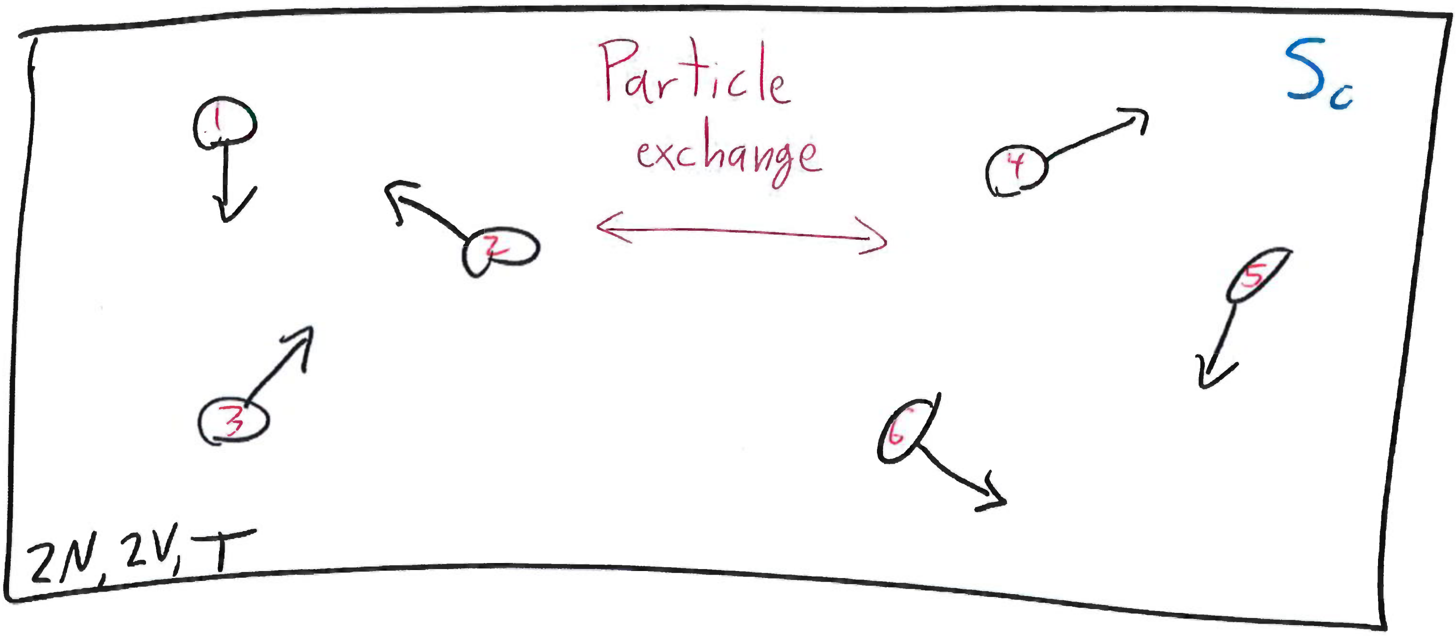
Explanation

Dist'ability → more info than just $N_A'$, $N_B'$

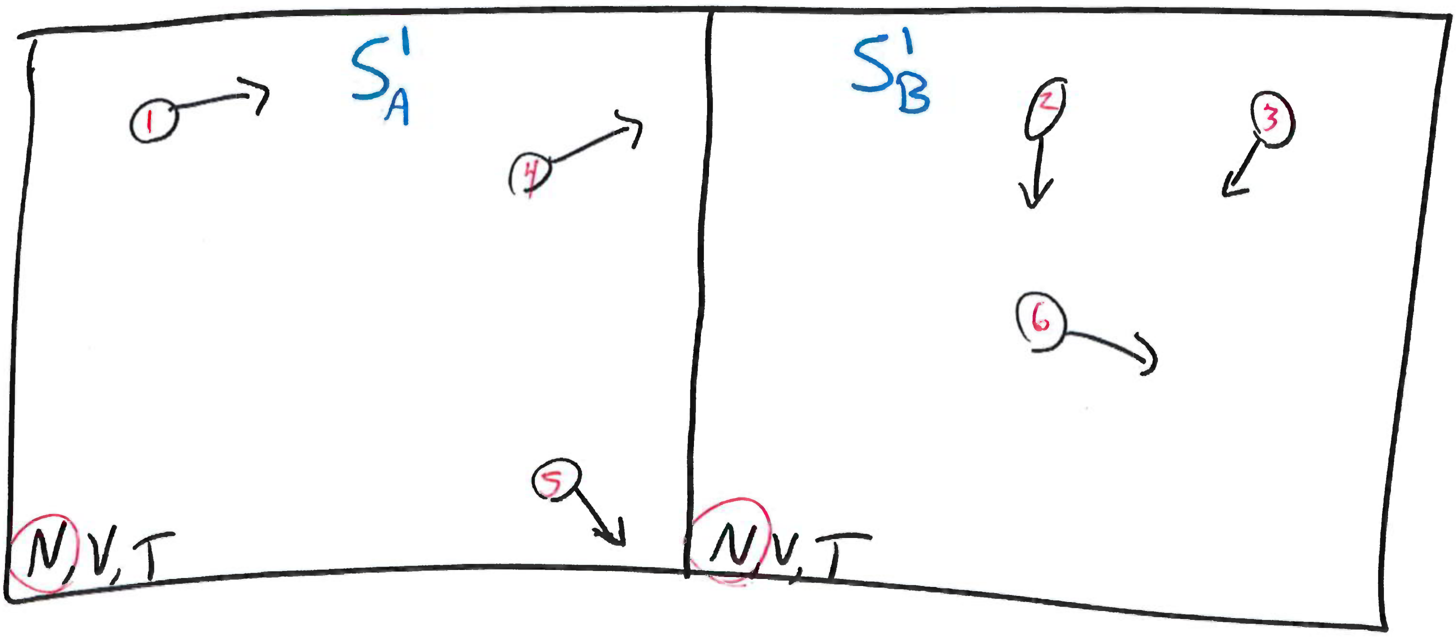
Many more micro-state with different labels in addition to $\Omega_A \otimes \Omega_B$



S_A
S_B
1
2
3
4
5
6
N, V, T
N, V, T

Particle exchange
S_c
1
2
3
4
5
6
2N, 2V, T

S'_A
S'_B
1
4
5
2
3
6
N, V, T
N, V, T

$\rightarrow$ larger entropy $S_A' + S_B' > S_A + S_B$

Complicated calculation confirms $S_A' + S_B' \geq S_C$

simpler case in tutorial

Result: For dist'able particles, practically impossible to return to original system

Irreversible process that increases entropy

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$$Z_D, Z_I \propto \left(\frac{V}{\lambda_{th}^3}\right)^N \propto \left(V T^{3/2}\right)^N$$

V and T are <u>control parameters</u> (like H in spin systems)

In principle control experimentally

measure response to changes

(canonically change $T_i \rightarrow T_f$

by connecting system to different reservoir)

Vary one at a time: $C_V = \left.\frac{\partial \langle E \rangle}{\partial T}\right|_V$

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_N$$