MATH327: StatMech and Thermo

Thursday, 26 February 2026

H8 27 41

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 gases

Regularization $\rightarrow$ partition function for
continuous energies

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

Today

Dist'able vs. indist'able gas

Mixing & irreversibility

Control parameters $\rightarrow$ equation of state

Indist'able particles can't be labelled

$N=2 \quad (\vec{p}_1 \neq \vec{p}_2): 1$ th indist'able vs. 2 dist'able micro-states
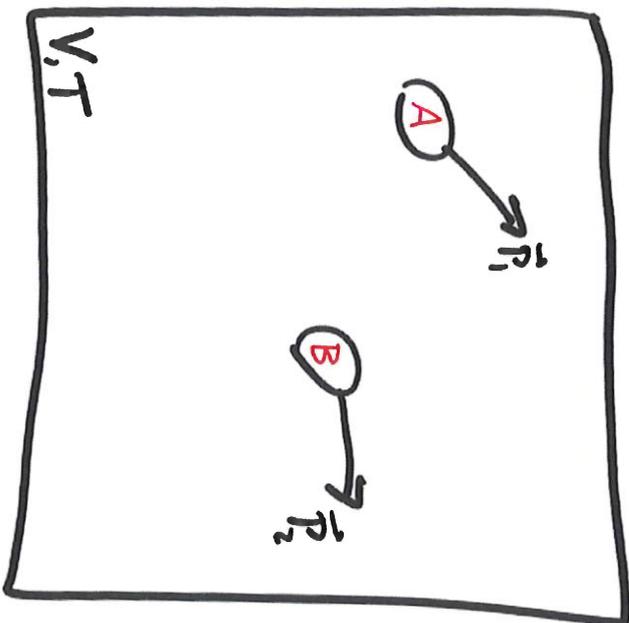
$N=3 \quad (\vec{p}_c \neq \vec{p}_k$ for $c \neq k): 1$ indist'able w

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

$6 = 3!$ dist'able w_i
from label

Distinguishable

$W_2 =$

$W_1 =$

V, T

V, T

V, T

V, T

A

B

B

A

$\vec{P_1}$

$\vec{P_2}$

$\vec{P_1}$

$\vec{P_2}$
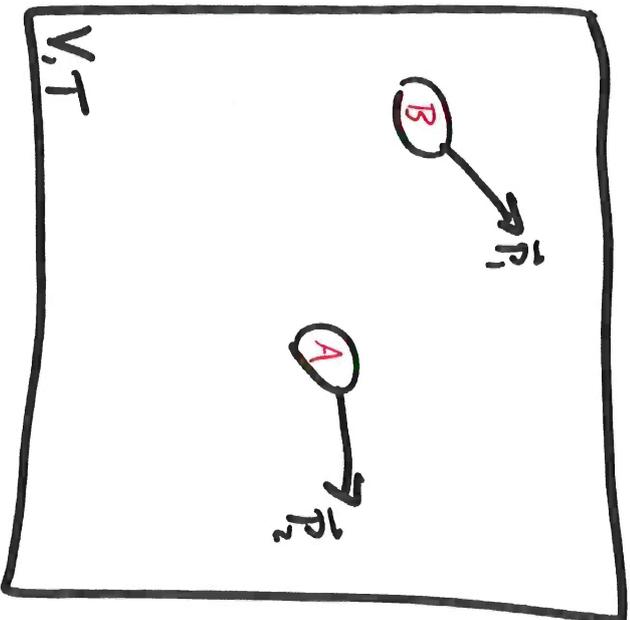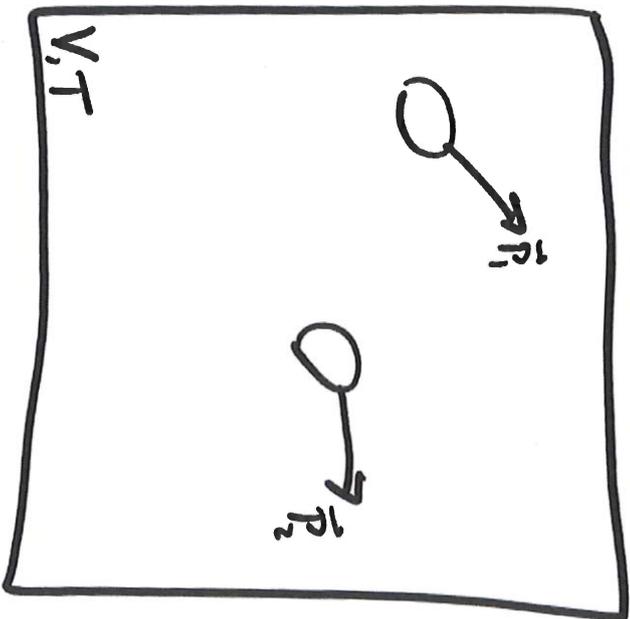
Indistinguishable

$W =$

V, T

V, T

$\vec{P_1}$

$\vec{P_2}$

$\vec{P_1}$

$\vec{P_2}$
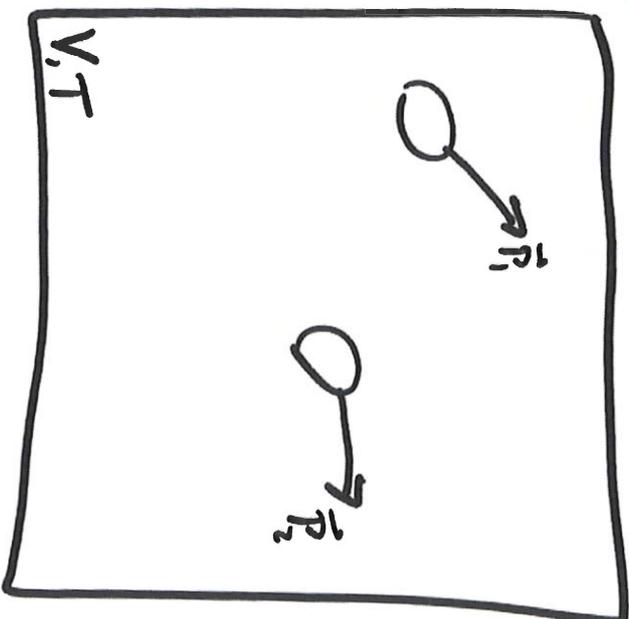
General result: $Z_I = \frac{1}{N!} Z_D = \frac{1}{N!} Z_1^N = \frac{1}{N!} \left(\frac{V}{\lambda_{th}^3} \right)^N = \frac{1}{N!} \left(\frac{mTL^2}{2\pi \hbar^2} \right)^{3N/2}$

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

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

Sensible macroscopic behaviour emerges
from microscopic dynamics

Entropy is $S_I = \frac{1}{T} \left(\langle E \rangle_I - F_I \right) = \frac{3}{2} N + \frac{3}{2} N \log \left(\frac{L^2}{\lambda_{th}^2} \right) - \log(N!)$

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

$N \log N - N$ (blue)

"occupied volume" $\qquad N \lambda_{th}^3 \ll V$ (blue)

Depends on volume — information from locations

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

$$F_D = -\frac{3}{2} NT \log \left(\frac{L^2}{\lambda_{th}^2} \right)$$

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

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

page 61

$\langle E \rangle$ doesn't depend on info.

because $Z_I \propto Z_D$

S_I & S_D differ — which is larger?

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

$$S_I < S_D \quad - \text{ extra info from dist'ability}$$

Note both $S_I, S_D < 0$ if $\frac{V}{\lambda_{th}^3} \ll 1$ $mTL^2 \ll 2\pi \hbar^2$

$$S = - \sum_{qi} P_i \log P_i < 0 \quad \text{nonsensical}$$

Sign of assumptions breaking down

↳ classical → quantum

Mixing

Remove wall, re-equilibrate, re-insert wall

Entropy must not decrease

$$\Omega_o = \Omega_A \otimes \Omega_B \qquad\qquad\qquad S_o = S_A + S_B$$

$$\downarrow \qquad\qquad\qquad\qquad\qquad \downarrow$$

$$\Omega_C \qquad\qquad\qquad\qquad\qquad S_C$$

$$\downarrow \qquad\qquad\qquad\qquad\qquad \downarrow$$

$$\Omega_F = \Omega_A' \otimes \Omega_B' \qquad\qquad\qquad S_F = S_A' + S_B'$$

Consider indist'able case

$$\boxed{\begin{aligned} S_o &= S_A + S_B = 2S_I(N, V, T) = 5N + 2N \log\left(\frac{V}{N\lambda_{th}^3}\right) \\ S_C &= S_I(2N, 2V, T) = 5N + 2N \log\left(\frac{2V}{2N \lambda_{th}^3}\right) = S_o \\ &\qquad\qquad \text{consistent w/ second law } \checkmark \end{aligned}}$$

Re-separate subsystems

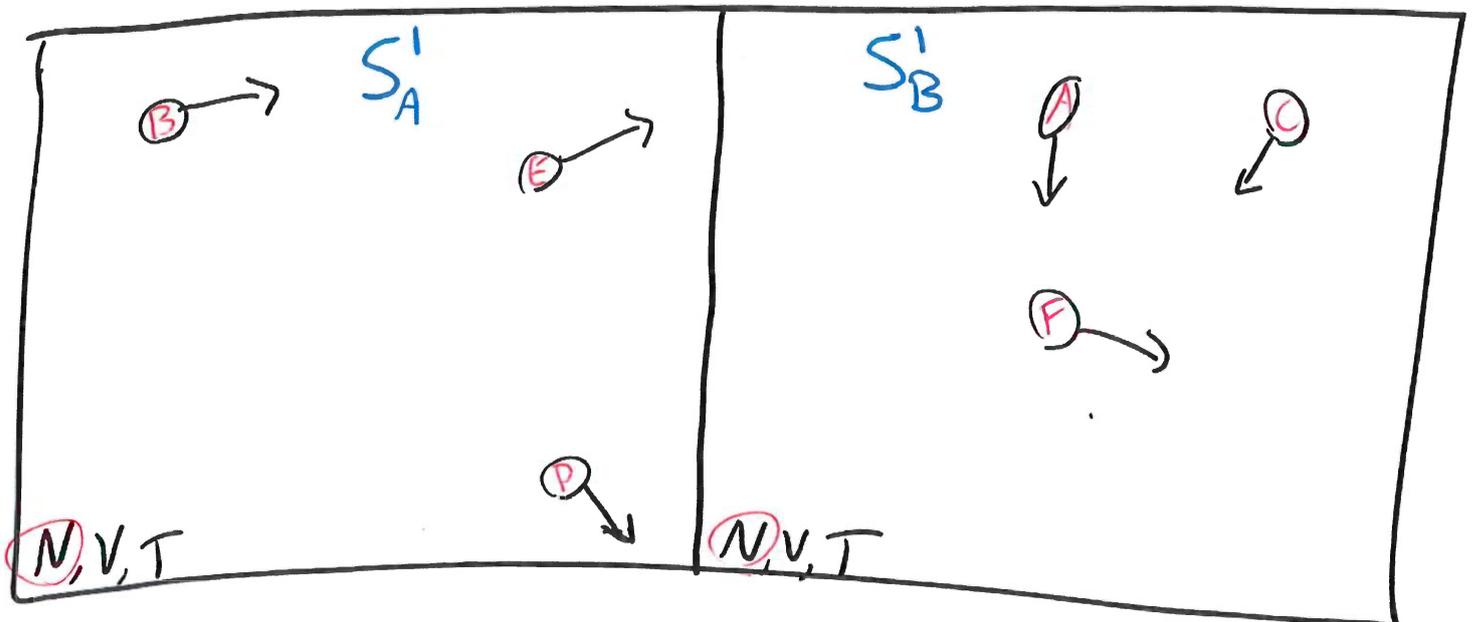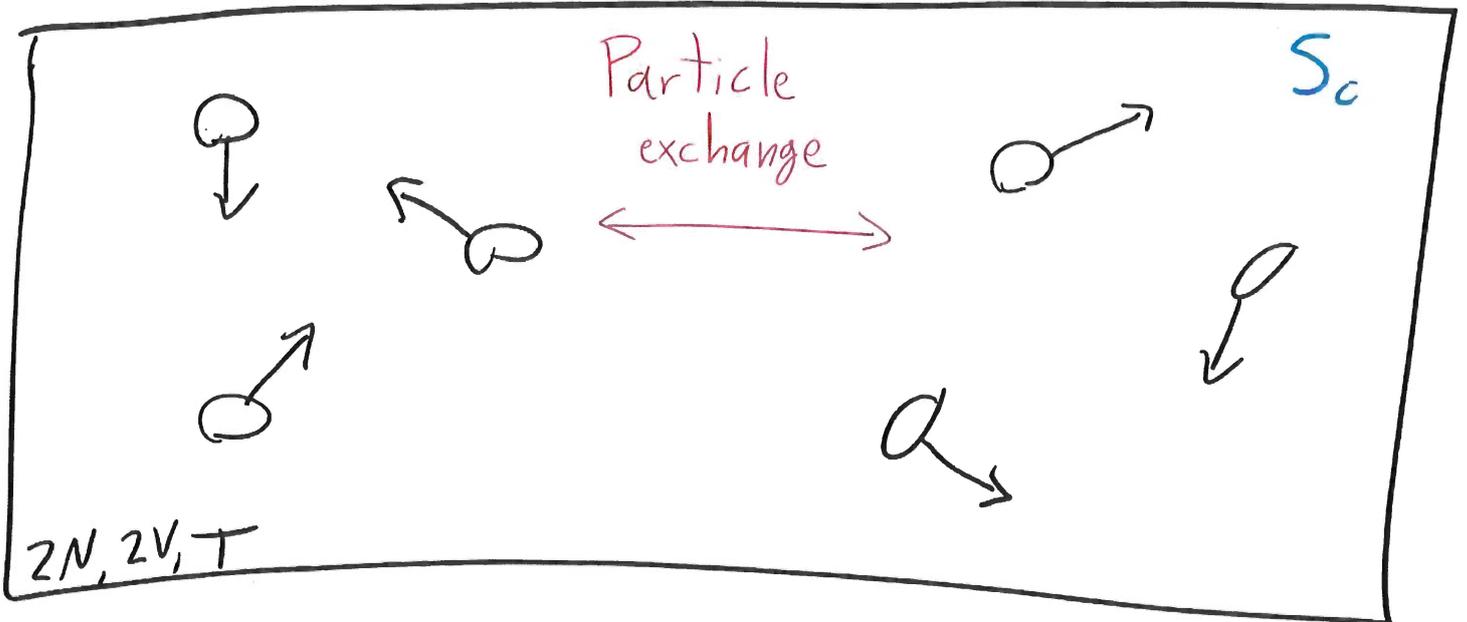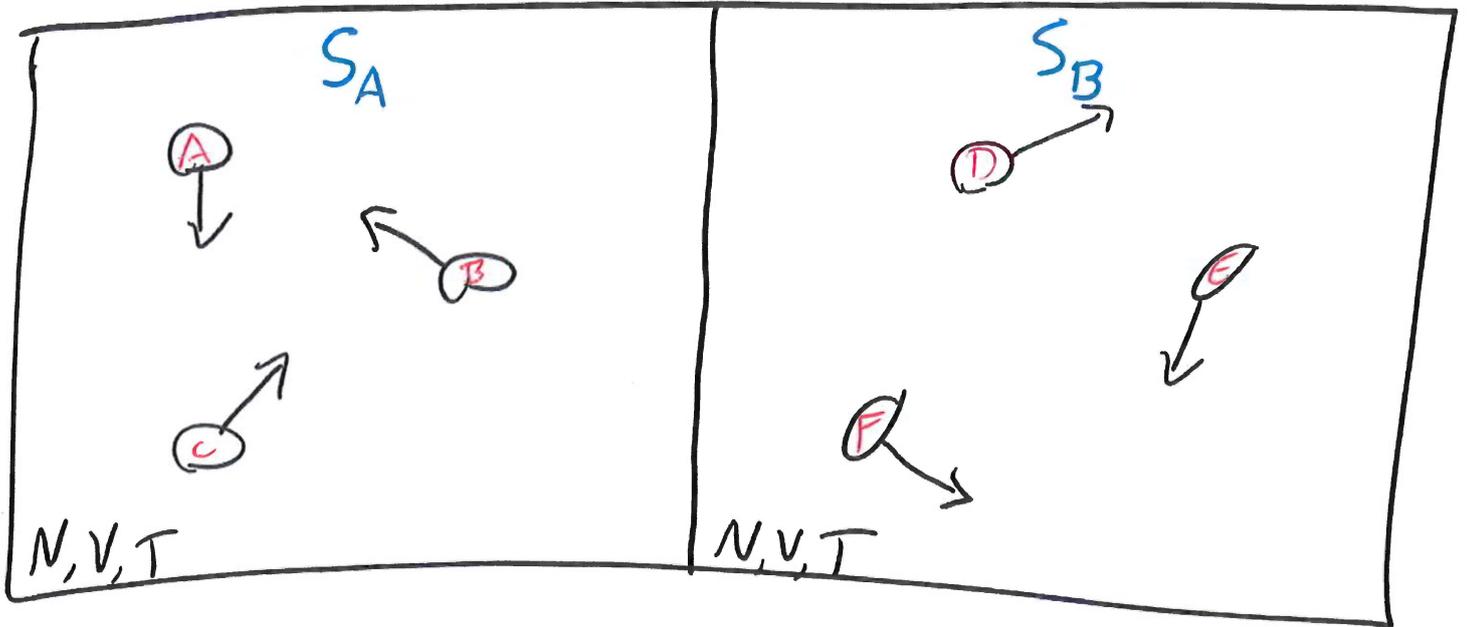Need to sum over micro-states from
all possible particles divisions
$$\{v, 2N-v\}$$

Each $Z_v = Z_I(v, V, T) \times Z_I(2N-v, V, T)$

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

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

$$Z_F = \sum_{v=0}^{2N} Z_v = \left(\frac{V}{\lambda_{th}^3}\right)^{\cancel{N}2N} \sum_v \frac{1}{v!\,(2N-v)!}$$

$$= \left(\frac{V}{\lambda_{th}^3}\right)^{2N} \sum_v \binom{2N}{v} \frac{1}{(2N)!}$$

Entropy $S_F = \frac{\partial}{\partial T}\left(T \log Z_F\right)$

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

$$+ \log\left[\sum_v \binom{2N}{v}\right]$$

complicated!

Simplify : Gibbs approximation

$N \gg 1 \rightarrow$ essentially all entropy from even division

$$N_A' = N_B' = N$$

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

No change in entropy — <u>reversible</u> process

Repeat for dist'able case

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

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

$$\Delta S_{mix} = S_c - S_o = 2N \log 2 > 0 \checkmark \qquad \text{mixing entropy}$$

If $S_F = 2S_D (N, V, T) < S_c$ then second law violated X

"Gibbs paradox"

Explanation: Dist'ability → more info than just $N_A' \approx N_B'$

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

→ Larger entropy $S_F = S_A' + S_B' > S_A + S_B$

Complicated calculations confirms $S_A' + S_B' \geqslant S_c$ ✓

~~strong~~ simpler case in tutorial

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

<u>Irreversible</u> process that increase entropy

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

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

In principle control experiments
measure response to changes

(canonically change $T_i \to T_F$
by connecting system to different reservoirs)

Vary one at a time: $C_V = \frac{\partial \langle E \rangle}{\partial T}\Big|_{N,V}$

micro-canonical $\frac{1}{T} = \frac{\partial S}{\partial E}\Big|_N$

<u>Pressure</u> $P = -\frac{\partial \langle E \rangle}{\partial V}\Big|_S$

changing volume with fixed entropy
("isentropic)

For ideal gas need constant entropy

S_D, S_I depend on $\dfrac{V}{\lambda_{th}^3} \propto VT^{3/2}$

$$VT^{3/2} = c^{3/2} \longrightarrow T = cV^{-2/3}$$

$$\langle E \rangle = \tfrac{3}{2}NT = \frac{3c}{2}\frac{N}{V^{2/3}}$$

$$P = -\frac{3c}{2} N \left(-\frac{2}{3} \frac{V^{-2/3}}{V} \right) = \frac{N}{V}\left(cV^{-2/3} \right) = \frac{NT}{V}$$

$PV = NT$ is $\underline{\text{ideal gas law}}$

$(P, V, T, P, \cdots)$

Equation of state (EoS) relating macroscopic properties

thermodynamic macro-state

Historically empirical observations
followed by mathematical explanation

Robert Boyle (1662) — change pressure with fixed N, T
Find $PV = \text{const.}$ ← "Boyle's law"

Fix N, P

$\dfrac{V}{T} = \text{const.}$

"Charles's law"

1787

Fix N, V

$\dfrac{P}{T} = \text{const.}$

"Gay-Lussac's law"
1802

Fix P, T

$\dfrac{V}{N} = \text{const.}$

"Avogadro's law"
1812

Combined into ideal gas law in 1830s

Derived from stat mech in 1850s

Mutual reinforcement of scientific progress
and Industrial Revolution (including engines)

Gay-Lussac

Lussac

Boyle

combined

ideal

$$\frac{PV}{TN} = k_{\mathrm{B}} = 1$$

Charles

Avogadro