MATH327: Statistical Physics

Monday, 6 March 2023

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Something to consider

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

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

Recap

Applications of the canonical ensemble

Classical ideal gas

Regulate to get partition as integral over continuous momenta

Derive energies & entropies dist'able vs. indist'able

$\langle E\rangle_D = \langle E\rangle_I = \frac{3}{2}NT$ (also V-indep.)

No dependence on information (labeling)

Unlike spin system (because ideal gas $\frac{1}{N!}$ same for all indist. micro-states)

Entropies differ

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

Which is larger? $S_I - S_D = N - N\log N = -\log(N!) < 0$ $N \gg 1$

S_o $S_I < S_D$ reflects extra info from dist'ability

Entropies depend on $V\lambda_{th}^{-3} = \left(L/\lambda_{th}\right)^3 \gg 1$

$\lfloor$ can think of λ_{th}^3 as "occupied volume"

$\lambda_{th}^3 \gtrsim V \rightarrow S<0$

Nonsense since $S = -\sum_i p_i \log p_i \quad 0 \le p_i \le 1$

Classical assumption break down

$$\lambda_{th}^2 = \frac{\hbar^2 \pi^2}{2mT}$$

low temperatures

$\hbar^2 \pi^2 \gtrsim 2mTL^2$

<u>Mixing</u>

What happens to entropy when two canonical systems combined and then re-separated

$$\Omega_A + \Omega_B \rightarrow \Omega_C \rightarrow \Omega_A' + \Omega_B'$$

$$S_A + S_B \rightarrow S_C \rightarrow S_A' + S_B'$$

First consider indist'able particles

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

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

$S_A + S_B = S_C$ consistent with second law

Re-separating systems

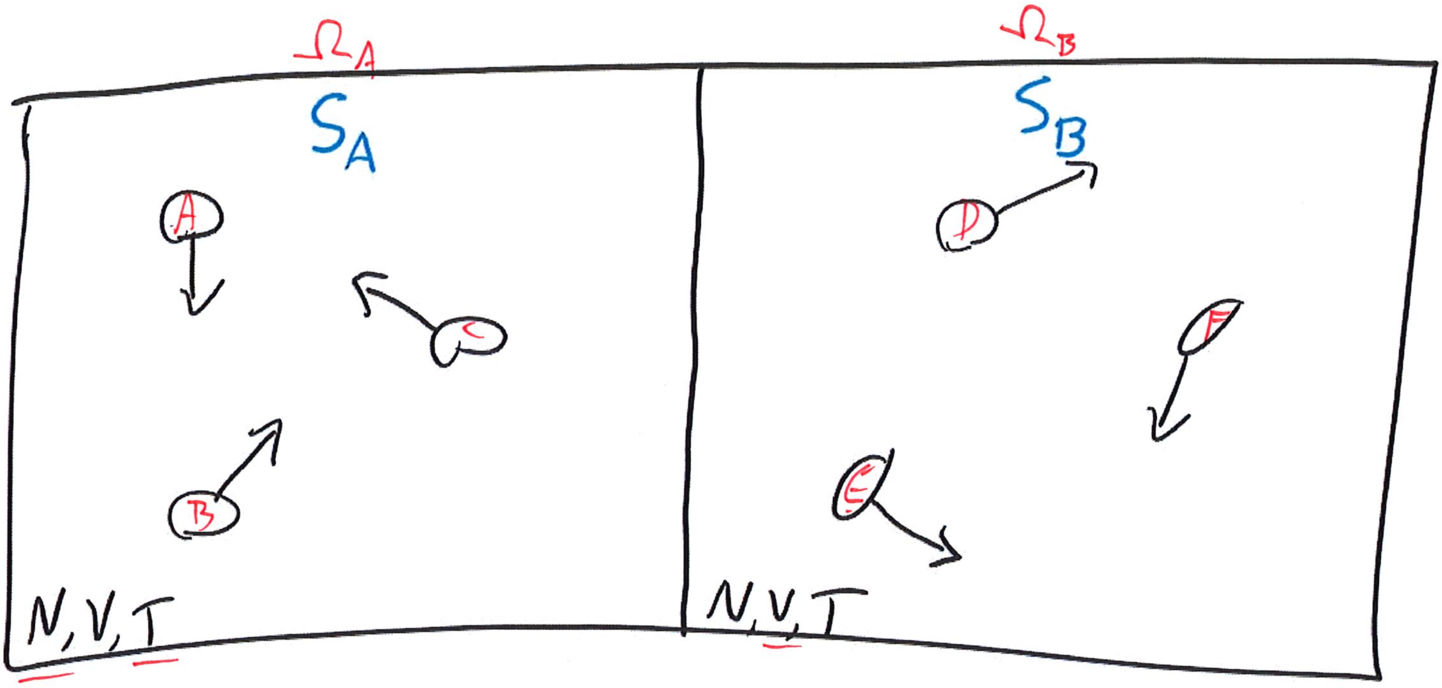
Need to <u>sum</u> over all possible particle divisions $\{\nu, 2N-\nu\}$

when computing partition func. $\rightarrow$ entropy

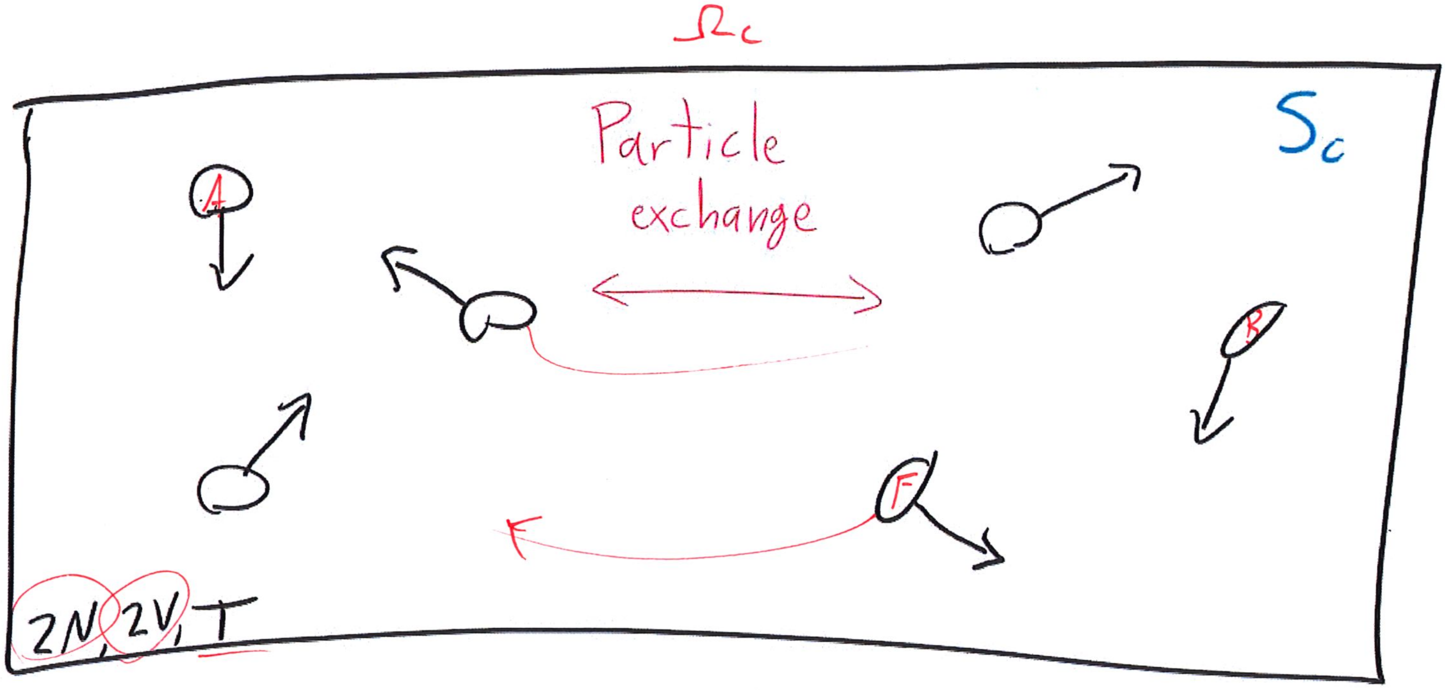
Z is product of $Z_A'(\nu) \times Z_B'(2N-\nu)$

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

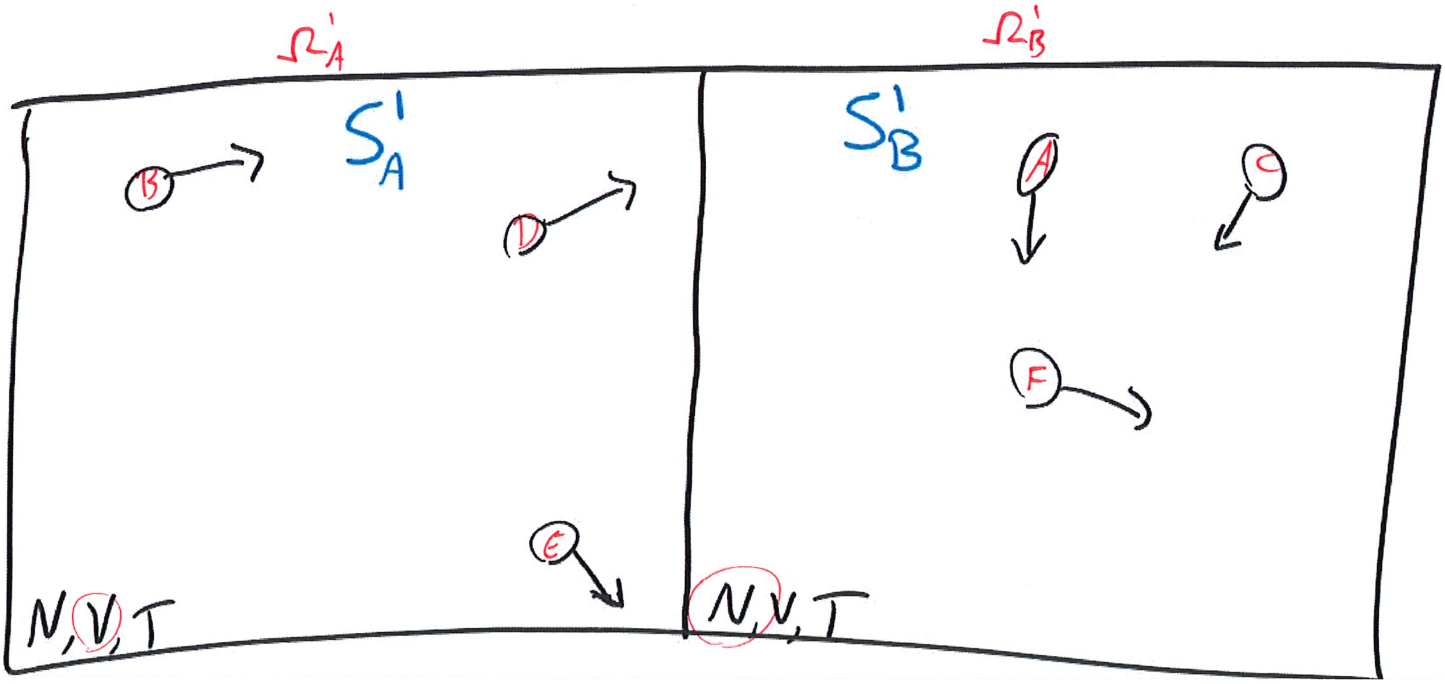
$$= \frac{1}{\nu!}\left(\frac{V}{\lambda_{th}^3}\right)^\nu \times \frac{1}{(2N-\nu)!}\left(\frac{V}{\lambda_{th}^3}\right)^{2N-\nu} = \frac{1}{\nu!(2N-\nu)!}\left(\frac{V}{\lambda_{th}^3}\right)^{2N}$$



Ω_A
Ω_B
S_A
S_B
A
B
C
D
E
F
N, V, T
N, V, T



Ω_C
Particle exchange
S_C
A
F
2N, 2V, T



Ω'_A
Ω'_B
S'_A
S'_B
B
D
E
A
C
F
N, V, T
N, V, T

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

$$\binom{2N}{\nu} = \frac{(2N)!}{\nu!\,(2N-\nu)!}$$

Entropy $S' = S_A' + S_B' = \frac{\partial}{\partial T}\left(T \log Z'\right)$

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

From tutorial, almost all entropy from even division $N_A = N_B = N \gg 1$

This approximation means $S_A' + S_B' = S_C = S_A + S_B$

Nothing dramatic from opening door or closing it (reversible process)

What about dist'able particles?

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

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

$\Delta S_{mix} = S_C - (S_A + S_B) = 2N \log 2 > 0$

Mixing entropy consistent with second law $S_C > S_A + S_B$

$N_A' = N_B' = N \rightarrow S_B' + S_A' = S_A + S_B < S_C$

violates second law

so-called "Gibbs paradox"

Dist'able particles $\rightarrow$ more info than just N_A', N_B'

Many more micro-states with different labels

compared to $\Omega_A + \Omega_B$

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

Corrected calculation confirms $S_A^1 + S_B^1 \geq S_C$

simplified case in tutorial

Little chance of getting back to original (dist'able) system

Irreversible process — increases entropy

Recall partition function $Z_I = \frac{1}{N!}\left(\frac{V}{\lambda_{th}^3}\right)^N$

Volume is <u>control parameter</u> coming from energies E_i

Similarly H is control parameter for spin systems

Can control in experiment

observe response to changes

To disentangle behaviour, others control params need to be fixed

Examples: $\frac{1}{T} = \frac{\partial S}{\partial E}\Big|_N$ $\quad C_V = \frac{\partial \langle E \rangle}{\partial T}\Big|_V$

Response of energy to change in volume with fixed entropy (isentropic)

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

For ideal gases, S depends on $V\lambda_{th}^{-3} \propto VT^{3/2}$

constant entropy requires $VT^{3/2} = \text{const.}$

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

$$\langle E \rangle = \frac{3}{2}NT = \frac{3c}{2}NV^{-2/3}$$

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

Rearrange <u>$PV = NT$</u>

Ideal gas law

↳ Example of <u>equation of state</u> (EoS)

↳ macro-state

thermodynamic state

EoS are relations between macroscopic properties
pressure, volume, temperature, internal energy

Historically EoS empirically observed before mathematical derivation
Robert Boyle 1660s
change pressure of gas with fixed T and N
find $PV = \text{const.}$ "Boyle's law"

Similar relations

Fix N and P
$\frac{V}{T} = \text{const.}$
"Charles's law"
1787

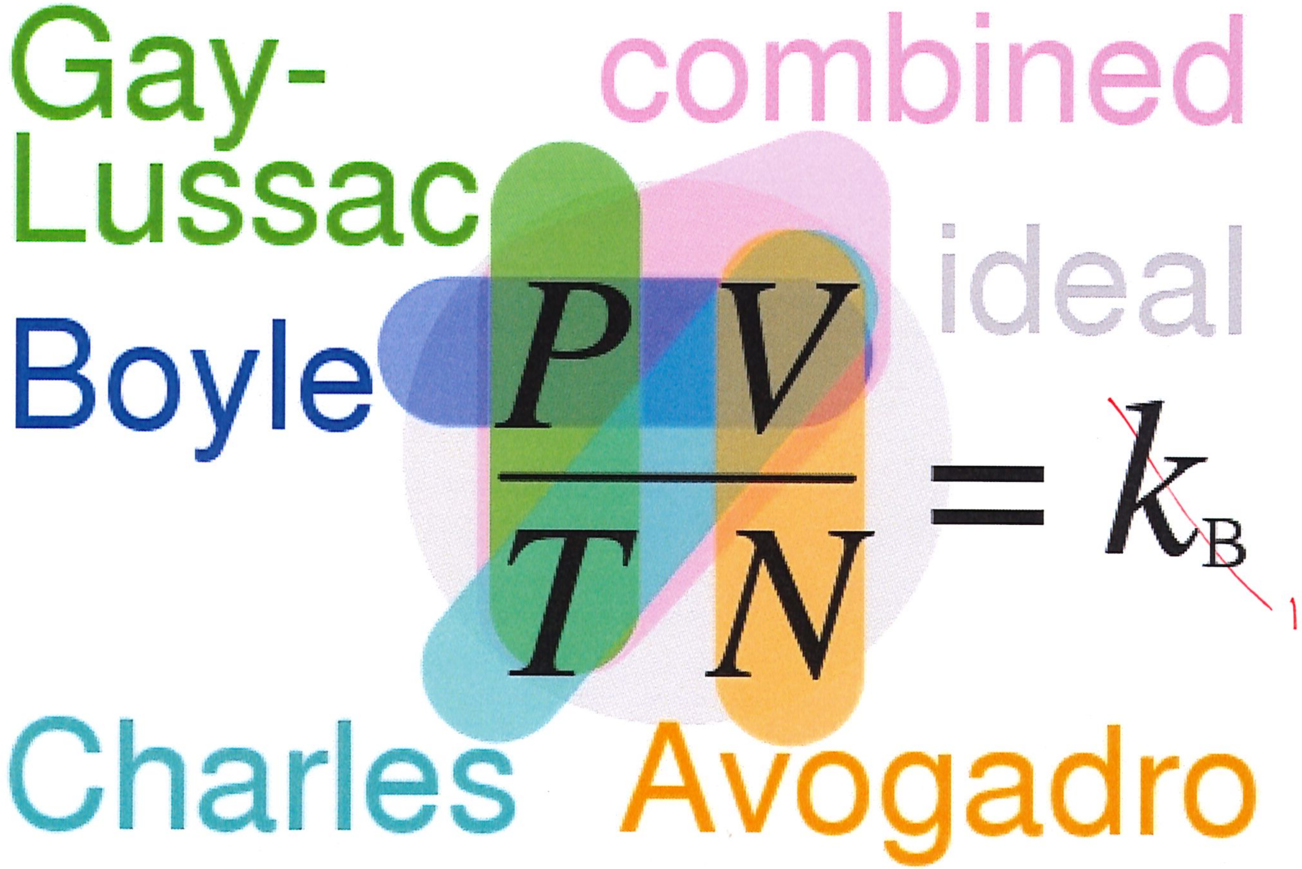
Fix N and V
$\frac{P}{T} = \text{const.}$
"Gay-Lussac's law"
1802

Fix P & T
$\frac{V}{N} = \text{const.}$
"Avogadro's law"
1812

Combined into ideal gas law in 1830s (Clapeyron)
Derive from statistical physics in 1850s (Krönig, Clausius)
Major progress during Industrial Revolution not coincidence
Virtuous cycle of maths insight & industrial applications
including engines

Connect pressure $P = \frac{-\partial \langle E \rangle}{\partial V}\Big|_S$ to mechanical process
Related to work done by force $\vec{F}(\vec{r})$
that changes energy of object
by displacing it by $d\vec{r}$

Infinitesimal $W = dE = \vec{F} \cdot d\vec{r}$ (inner product)
Generalizes to $W = \underbrace{\Delta E}_{E_f - E_i} = \int \vec{F} \cdot d\vec{r}$ (line integral)



commons.wikimedia.org/wiki/File:Ideal_gas_law_relationships.svg

Example: Single object falling due to gravity $\vec{F} = (0, 0, -mg)$

Start at rest $(E_0 = 0)$ at height h

Final energy $E_f = W = \int \vec{F} \cdot d\vec{r} = -mg \int_h^0 dz = mgh > 0$

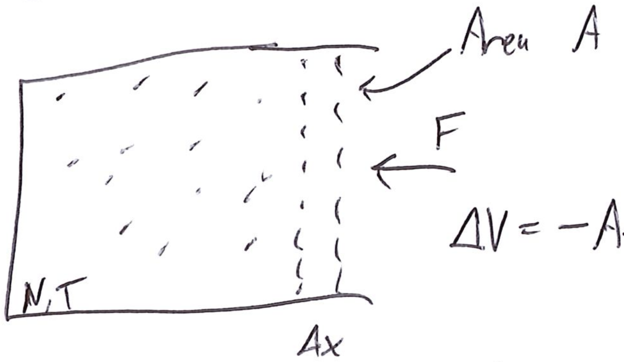
$$\frac{p_z^2}{2m} = mgh \rightarrow p_z = -m\sqrt{2gh}$$

For statistical systems with $N \gg 1$

work is change in internal energy due to a force

$\downarrow$ changes volume

Illustration



$\Delta V = -A\Delta x$ (isentropic)

Work $W = F\Delta x = \Delta\langle E\rangle \neq 0$

Energy increases by $F\Delta x$

due to volume decreasing, $\Delta V = -A\Delta x$

$$P = -\frac{\partial\langle E\rangle}{\partial V}\bigg|_S = \frac{-F\Delta x}{-A\Delta x} = \frac{F}{A}$$

Pressure is force per unit area

on surface of container holding gas