MATH327: StatMech and Thermo

Thursday, 5 February 2026

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Something to consider

How can we apply the framework of probability spaces
to analyse the $\sim 10^{25}$ molecules that compose the air in this room?

Recap

Random walks $\rightarrow$ law of diffusion $\Delta x \propto \sqrt{N}$

Connection to CLT

Today

Tutorial wrap-up

Diffusion wrap-up

Micro-canonical ensemble and equilibrium

Tutorial "random walk" has $P_W = \binom{N}{W} P_{win}^{W} P_{lose}^{N-W}$ $\quad l = 5$

$$= \frac{N!}{W!(N-W)!} \frac{18^W 19^{N-W}}{37^N}$$

CLT needs $\mu = (+5)\frac{18}{37} + (-5)\frac{19}{37} = -\frac{5}{37}$

$$\langle x_i^2 \rangle = 25$$

$$\sigma^2 = 25 - \frac{25}{37^2} = 25\left(1 - \frac{1}{37^2}\right) \approx 24.98$$

$$\rightarrow p(g) \approx \frac{1}{\sqrt{49{,}96\,\pi N}} \exp\left[-\frac{(g+0{,}135\,N)^2}{49{,}96\,N}\right]$$

Numerically integrate to find probabilities, $N=5$

$G_w = -25, -15, \dots, 15, 25$ $\qquad \Delta G = 10$

Key result

Law of diffusion $\longleftrightarrow$ central limit theorem

$\Delta x \propto \sqrt{N} \propto \sqrt{t}$ $\qquad p(x) \approx \frac{1}{\sqrt{2\pi D^2 t}} \exp\left[\frac{-(x - v_{dr} t)^2}{2D^2 t}\right]$

Both hold whenever single-step μ and σ^2 finite

μ: $\frac{v_{dr} \cdot t}{N}$ $\qquad \sigma^2$: $\frac{D^2 t}{N}$

Compare diffusion vs. drift $(v_{dr} \neq 0)$

$$\left.\begin{aligned} \Delta x &\propto \sqrt{t} \\ \langle x \rangle &\propto t \end{aligned}\right\} \quad \boxed{\frac{\Delta x}{\langle x \rangle} \propto \frac{1}{\sqrt{t}} \rightarrow 0 \quad \text{as } t \propto N \rightarrow \infty}$$

page 23

Relative fluctuations become negligible compared to non-zero drift

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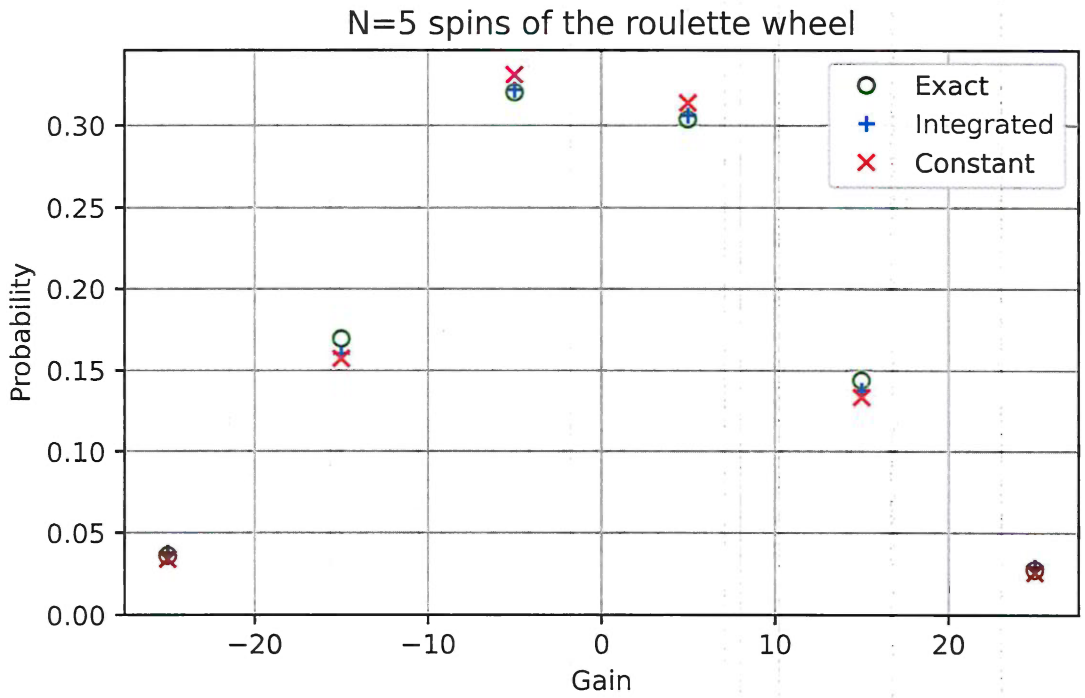
Statistical ensembles

Idea: Prob. space observe many particles evolving in time subject to constraints

ε

Time $t_1, t_2, t_3, \dots \rightarrow$ states $w_1, w_2, w_3, \dots$

"micro-states"



N=5 spins of the roulette wheel
Exact
Integrated
Constant
Probability
0.00
0.05
0.10
0.15
0.20
0.25
0.30
−20
−10
0
10
20
Gain

Powerful example: Spin system

Particles just point up $\uparrow \sim +1$ or down $\downarrow \sim -1$

Motivation from magnetic molecules, many uses

Example configuration of $N=8$ spins fixed in a line

$\uparrow\downarrow\uparrow\uparrow\uparrow\downarrow\uparrow\uparrow$

page 26 In total $2\cdot 2\cdot 2\cdots 2 = 2^N \to 256$ configurations

All 256 micro-states have $N=8$ spins

$\to N$ is a conserved quantity, same for all w_i

Also conserved: Internal energy of isolated ("closed") system.

$E(w_i) = E(w_j)$ for all i,j

Historically empirical observation

$\to$ "First law of thermodynamics"

Equivalently changing E of system Ω

$\to$ equal & opposite change in E of its surroundings

Spin system energy from "magnetic field" $H > 0$

H

$\uparrow$ $\delta E = -H$ n_+

$\downarrow$ $\delta E = H$ $n_- = N - n_+$

Internal energy $E = (-H)n_+ + H(N - n_+) = -H(2n_+ - N)$

$E(\uparrow\downarrow\uparrow\uparrow\uparrow\downarrow\uparrow\uparrow) = -H(12-8) = -4H$

With conservation $N=8$ and $E=-4H$

what fraction of micro-states are allowed?

page 27 $\dfrac{\text{allowed}}{\text{total}} = \dfrac{1}{256}\begin{pmatrix}8\\6\end{pmatrix} = \dfrac{8\cdot 7/2}{256} = \dfrac{28}{256} = \dfrac{7}{64} \approx 11\%$

Another example: $N \sim 10^{25}$ point particles of mass m

$$E = \frac{m}{2} \sum_{n=1}^{N} \vec{v}_n^{\,2} = \frac{1}{2m} \sum_n \vec{p}_n^{\,2}$$

Conserved energy $\rightarrow$ constrain accessible momenta

Don't work with $\sim 10^{25}$ time-evolution equations

Instead treat time evolution as stochastic process

$$w_1 \rightarrow w_2 \rightarrow w_3 \ldots$$

A <u>statistical ensemble</u> is set $\Omega = \{w_1, w_2, \ldots\}$ of all micro-states accessible through time evolution

Each w_i has probability $p_i > 0$ of being adopted
$\rightarrow$ prob. space

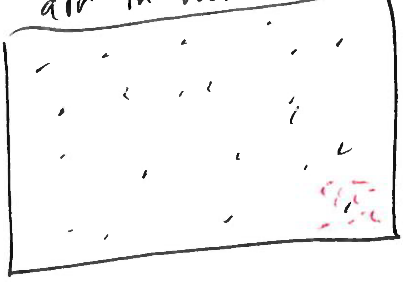
$\sum_i p_i = 1$ so that system in some micro-state at any time

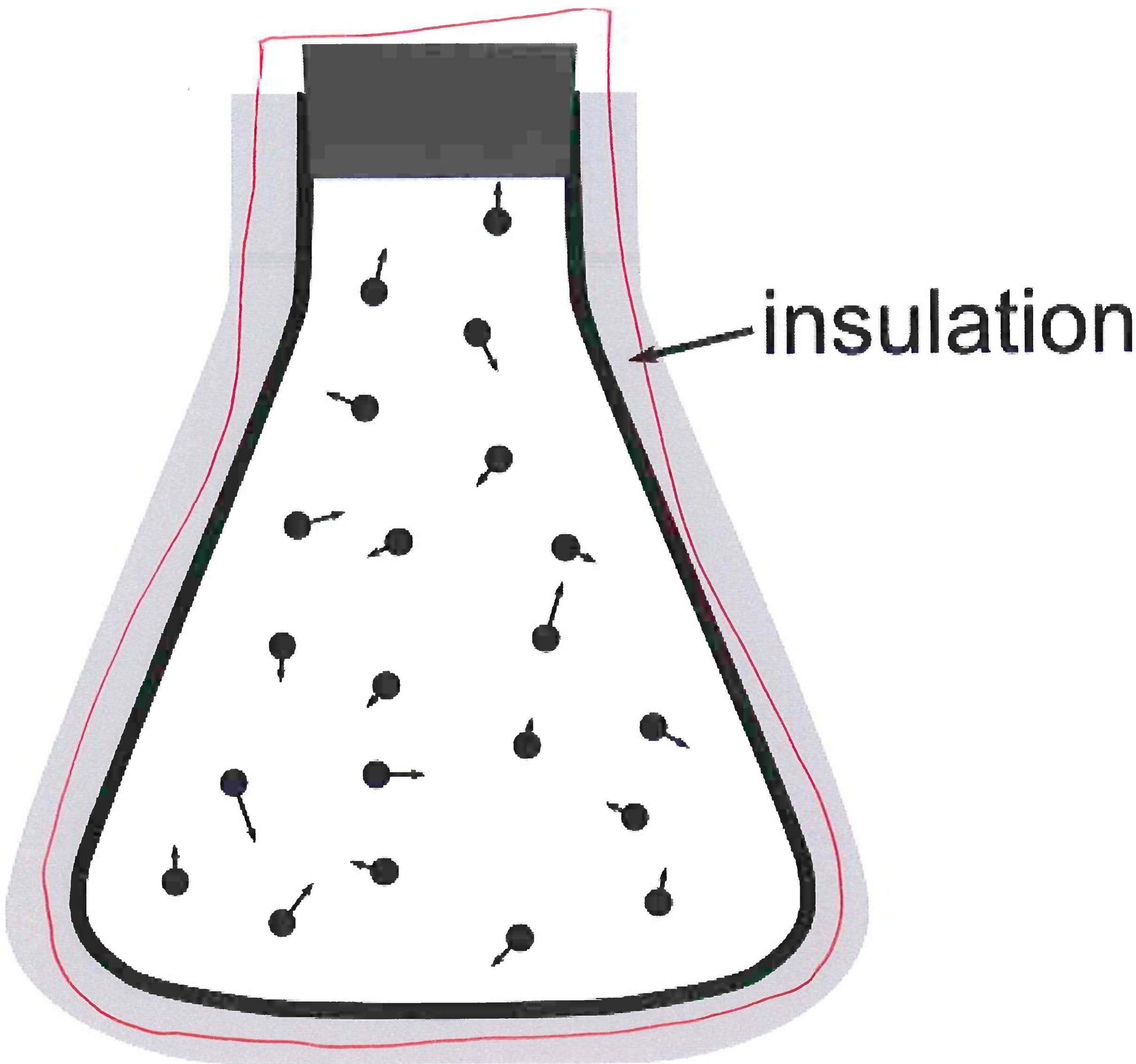
Conserved quantities unchanged under time evolution
$\rightarrow$ characterize statistical ensemble

<u>Micro-canonical</u> ensemble characterized by conserved internal energy E and particle number N $\Big\}$ imply isolation

From physical experience we expect smooth behaviour stable over time
"equilibrium"
(focus of this module)

air in room





Microcanonical
(const. N E)

A micro-canonical system Ω with M micro-states w_i is in thermodynamic equilibrium if and only if all probabilities p_i are equal

Finite $M \rightarrow p_i = \frac{1}{M}$ $\qquad \sum_i p_i = M\left(\frac{1}{M}\right) = 1$ ✓

Therm. equil. is dynamic – not static

System continues adopting different w_i

Emergence of stable behaviour related to entropy

Definition: For any stat. ensemble with countable M micro-states the entropy is $S = -\sum_{i=1}^{M} p_i \log p_i$

For micro-canonical in therm. equil.

$p_i = \frac{1}{M}$

$$\boxed{S = -\underbrace{\cancel{\sum_i}}_{\cancel{M}} \left(\frac{1}{\cancel{M}}\right) \log\left(\frac{1}{M}\right) = -\log\left(\frac{1}{M}\right) = \log M \quad \text{Boltzmann's Equation}}$$

page 29

Stable behaviour in therm. equil.

→ depend on conserved quanties

$S(E, N)$ for micro-canonical

E, N, M inter-related

Spin system example

What is entropy when $H = 0 \rightarrow E = 0$ for all w_i?

$$\boxed{S = \log M = \log 2^N = N \log 2}$$

page 29

What is $S(E=0, N)$ when $H>0$?

$\rightarrow n_+ = n_- = N/2$

$$S = \log M = \log \binom{N}{n_+} = \log \binom{2n_+}{n_+} = \log\left[\frac{(2n_+)!}{n_+!\ n_+!}\right]$$

$$= \log[(2n_+)!] - 2\log(n_+!)$$

Set $N=8 \rightarrow n_+ = n_- = 4$

$$S = \log\left(\frac{8!}{4!\ 4!}\right) = \log\left(\frac{8\cdot 7\cdot 6\cdot 5}{4\cdot 3\cdot 2}\right) = \log(70)$$

page 27

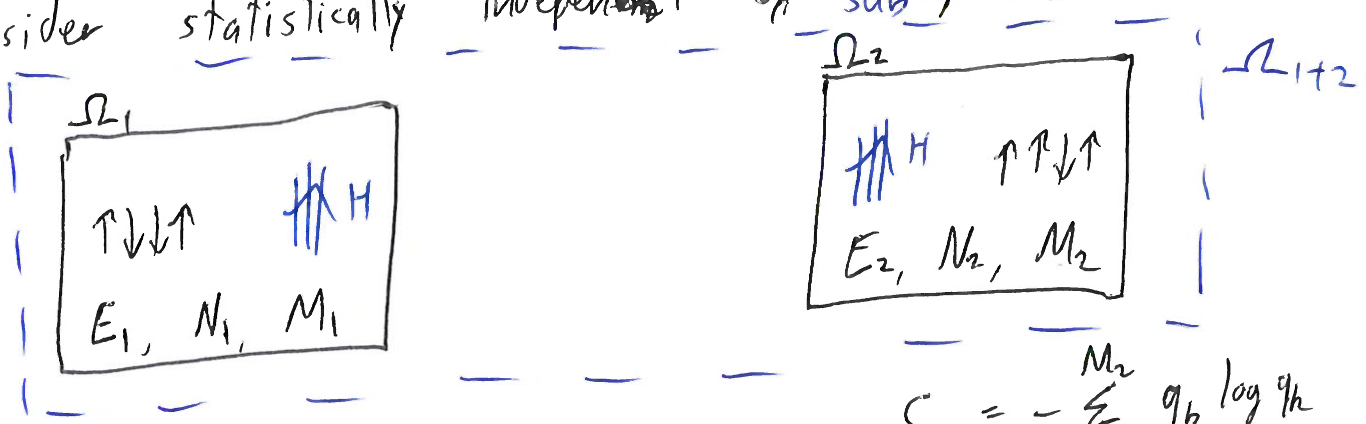
$M = 70$ for $E=0,\ N=8$

vs. 28 for $E = -4H$

IF $M \to \infty$ then $\log M = S \to \infty$

Related to property of <u>extensivity</u>

Consider statistically indepen~~den~~t ~~sy~~ sub systems



$$S_1 = -\sum_{i=1}^{M_1} p_i \log p_i \qquad S_2 = -\sum_{k=1}^{M_2} q_k \log q_k$$

Analyse as combined system Ω_{1+2}

What is $S_{1+2} = -\sum_{j=1}^{M_{1+2}} (\cdots)$?