MATH327: StatMech and Thermo

Monday, 10 February 2025

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Something to consider

A micro-canonical system in thermodynamic equilibrium
adopts all possible micro-states with equal probability.

How can this explain the smooth and stable distribution
of the $\sim 10^{25}$ molecules that compose the air in this room?

<u>Recap</u>

Random walks, diffusion, CLT

Statistical ensembles

↳ Stochastically sample micro-states ω_i w/probability p_i

Micro-canonical ensemble – conserve E, N "first law"

Thermodynamic equilibrium

↳ Micro-canonical all p_i equal

<u>Today</u>

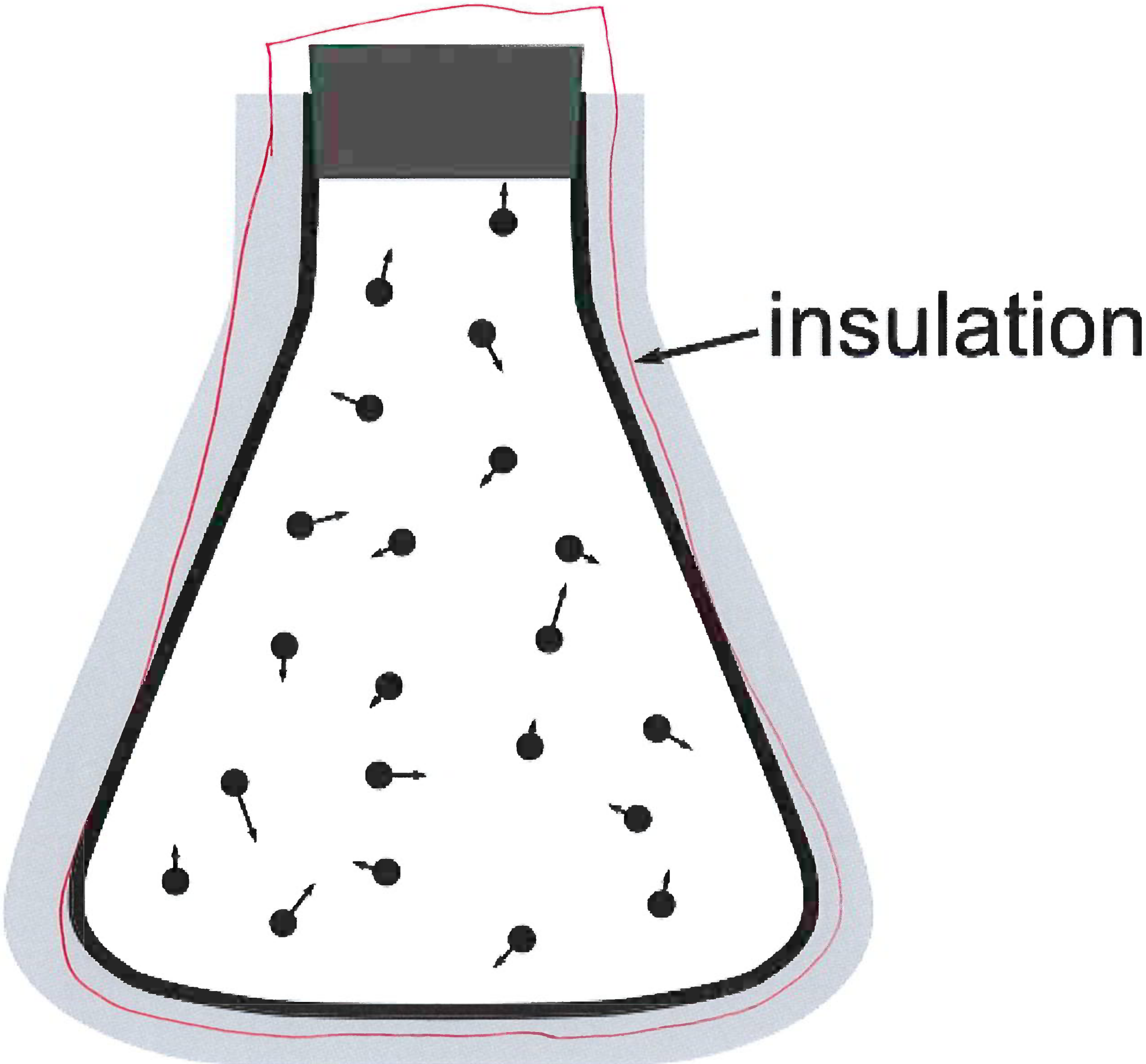
Therm. equil. → entropy

second law?

Note equilibrium is dynamic – not static

System continues adopting different ω_i

Emergence of stable behaviour related to entropy



Microcanonical
(const. N E)

commons.wikimedia.org/wiki/File:Statistical_Ensembles.png

Definition: For <u>any</u> statistical ensemble with countable # of micro-states <u>entropy</u> is $S = -\sum_{i=1}^{M} p_i \log p_i$

For micro-canonical in therm. equil.

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

$$\boxed{S = -\sum_i^{M} \frac{1}{M} \log\left(\frac{1}{M}\right) = -\log\left(\frac{1}{M}\right) = \log M}$$

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Boltzmann's Equation

Stable behaviour in therm. equil.

→ depend on conserved quantities

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

↳ E, N, M inter-related

<u>Spin system example</u>

N spins with $H=0 \rightarrow E=0$ for all $\overbrace{\text{micro-states}}^{2^N = M}$

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

What is $S(E=0, N)$ when $H>0$? page 29

$n_+ = n_- = \frac{N}{2}$

$$S = \log M = \log \binom{N}{N/2} = \log\left(\frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!}\right)$$

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

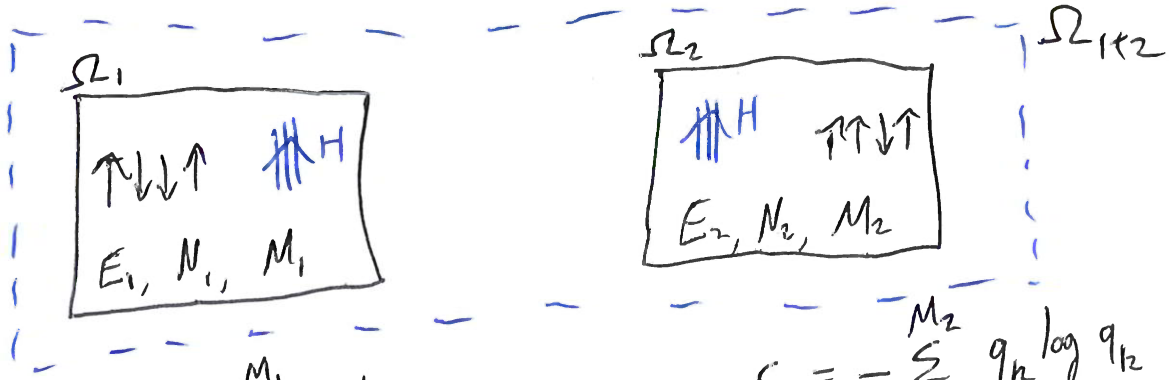
Set $N=8 \rightarrow n_+ = n_- = 4$

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

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

related to <u>extensivity</u>

Consider statistically independent subsystems



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

Analyse as combined system Ω_{1+2}

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

For each $w_i \in \Omega_1$, M_2 micro-states from Ω_2
$\quad\ \llcorner p_i \qquad\qquad\qquad \llcorner q_k$ each

$\therefore\ M_{1+2} = M_1 M_2$ micro-states w/prob. $p_i q_k$

Sanity check: $\displaystyle\sum_{M_{1+2}} p_i q_k = \sum_{i=1}^{M_1}\sum_{k=1}^{M_2} p_i q_k = \Big(\underbrace{\sum_{i=1}^{M_1} p_i}_{1}\Big)\Big(\underbrace{\sum_{k=1}^{M_2} q_k}_{1}\Big) = 1$ ✓

Entropy

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$$\boxed{\begin{aligned} S_{1+2} &= -\sum_{i,k} p_i q_k \log(p_i q_k) = -\sum_{i,k} p_i q_k \left(\log p_i + \log q_k\right) \\ &= -\sum_i p_i \log p_i \Big(\underbrace{\sum_k q_k}_{1}\Big) - \Big(\underbrace{\sum_i p_i}_{1}\Big) \sum_k q_k \log q_k = S_1 + S_2 \end{aligned}}$$

<u>Extensive</u> quantity adds up across independent subsystems

$S_{1+2} = S_1 + S_2 \qquad E_{1+2} = E_1 + E_2 \qquad N_{1+2} = N_1 + N_2$

Intensive quantity independent of extent of system

temperature, pressure, density

$M_{1+2} = M_1 M_2$ neither intensive nor extensive

Suppose Ω_1 & Ω_2 independently in therm. equil.

$$p_i = \frac{1}{M_1} \qquad q_k = \frac{1}{M_2}$$

$$S_1 = \log M_1 \qquad S_2 = \log M_2$$

$$p_i q_k = \frac{1}{M_1} \cdot \frac{1}{M_2} = \frac{1}{M_{1+2}} \longrightarrow \text{also in equilibrium}$$

$$S_{1+2} = \log M_{1+2} = \log(M_1 M_2) = \log M_1 + \log M_2 = S_1 + S_2 \quad \checkmark$$

On Weds: Put in <u>thermal contact</u>, wait for equilibrate

exchange energy, not particles