MATH327: Statistical Physics

Friday, 16 February 2024

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Something to consider

The air in this room consists of $\sim 10^{25}$ molecules.

How can we explain its very smooth and stable large-scale behaviour?

Recap

Random walks

Law of diffusion $\Delta x \propto \sqrt{N}$

general result $\longleftrightarrow$ CLT

(Plan) Prob. spaces for many particles evolving in time

Constraint: Energy conserved (first law)

Spin system $E = -H(2n_+ - N)$

Example: $N \sim 10^{25}$ point particles (all mass m)

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

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

Instead treat time evolution as stochastic process

$$\omega_1 \to \omega_2 \to \omega_3 \to \cdots$$

micro-states ω_i

Statistical ensemble is set $\Omega = \{w_1, w_2, \dots\}$
of all micro-states
accessible through time evolution

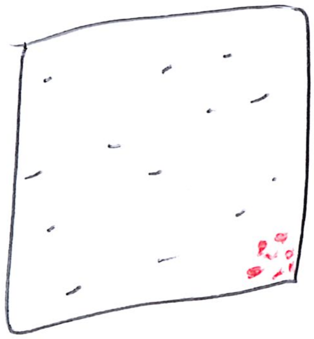
Each w_i has probability p_i of being adopted
→ probability space

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

Conserved quantities unchanged under time evolution
→ characterize statistical ensemble

Micro-canonical ensemble characterized by
conserved internal energy E and particle number N } implies isolation

Connect to physical intuition
Expect smooth behaviour, stable over time
└ equilibrium
(focus of this module)



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

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

Equilibrium is dynamic (not static)
System continues adopting different w_i

Emergence of stable behaviour is related to <u>entropy</u>

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

Equilibrium micro-canonical $\quad p_i = \frac{1}{M}$

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

$\boxed{\text{Boltzmann's Equation}}$

page 29

Stable equilibrium behaviour → depend on conserved quantities

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

↳ $\{E, N, M\}$ inter-related

<u>Spin system example</u>

N spins with $H=0$ → $E=0$ for all $M=2^N$ micro-states

What is entropy? $\quad S = \log M = N \log 2$

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

↳ $n_+ = n_- = \frac{N}{2}$

$$M = \binom{N}{n_+} = \binom{2n_+}{n_+} = \frac{(2n_+)!}{(n_+!)^2}$$

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

Suppose $N=8$ → $n_+ = n_- = 4$

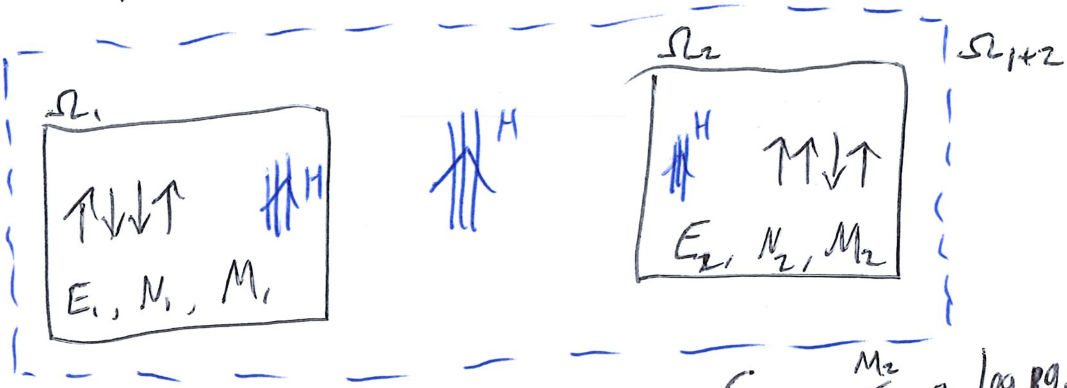
$$S = \log\left(\frac{8!}{4!\,4!}\right) = \log\left(\frac{\cancel{8}\cdot 7\cdot\cancel{6}\cdot 5}{\cancel{4}\cdot\cancel{3\cdot 2}}\right) = \log(70)$$

page 29

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

related to extensivity

Considering statistical independent subsystems



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

Analyze 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 $\rightarrow M_{1+2} = M_1 M_2$

$\llcorner p_i$ $\qquad \llcorner q_k$ each $\rightarrow$ probabilities $p_i q_k$

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

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

page 31

Extensive quantity adds up across independent subsystems

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

Intensive quantities independent of extent of system

temperature, density, ...

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

Suppose Ω_1 & Ω_2 independently in equilibrium

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

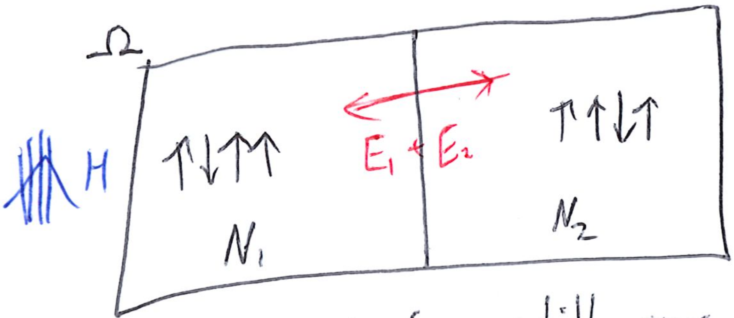
$$S_1 = \log M_1 \qquad S_2 = \log M_2$$

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

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

Now put subsystems in <u>thermal contact</u>, wait for equilibrium

exchange energy, not particles



Total $E = E_1 + E_2$ still conserved $\rightarrow$ Ω is micro-canonical

subsystems are <u>not</u>

How many micro-states M for overall Ω?

Use energy conservation: e_1 from N_1 spins, $E - e_1$ from N_2 spins $\Big\}$ $M_{e_1} = M^{(1)}_{e_1} M^{(2)}_{E-e_1}$

Case $e_1 = E_1$ accounts for all $M_{1+2} = \underbrace{M_1}_{M^{(1)}_{E_1}} \underbrace{M_2}_{M^{(2)}_{E_2}}$

$$\text{Overall } M = \sum_{e_1} M^{(1)}_{e_1} M^{(2)}_{E-e_1} = M_1 M_2 + \sum_{e_1 \neq E_1} M^{(1)}_{e_1} M^{(2)}_{E-e_1} \geq M_1 M_2$$

Equality when $\{E_1, E_2\}$ only possible distribution

Very special case!

Result: $S = \log M \geq \log(M_1 M_2) = S_{1+2}$
(therm. equil.)

Second Law of thermodynamics

When isolated (sub)systems in therm. equil.
brought into thermal contact
entropy $S \geq S_{1+2} = S_1 + S_2$ can never decrease
(increases except in very special cases)

More generically, entropy never decreases as time passes
(generically increase)

→ Finite-M system is in thermodynamic equilibrium
if its entropy is maximal

Holds for any stat. ensemble
→ derive micro-canonical $p_i = \frac{1}{M}$ → $\log M = S$

Maximize $S = -\sum_i p_i \log p_i$ with conserved E, N
and $\sum_i p_i = 1$

Use Lagrange multiplier

$$\bar{S}(\lambda) = S + \lambda\left(\sum_i p_i - 1\right) = -\sum_i p_i \log p_i + \lambda\left(\sum_i p_i - 1\right)$$

1) Maximizing $\bar{S}(\lambda)$ w.r.t. p_k

2) Impose $\sum_i p_i = 1$ → $\frac{\partial \bar{S}}{\partial \lambda} = 0$ & $\max \bar{S} \leftrightarrow \max S = \bar{S}(\lambda = 0)$

$$\frac{\partial S}{\partial p_k} = 0 = \frac{\partial}{\partial p_k}\left[-\sum_i p_i \log p_i + \lambda\left(\sum_i p_i - 1\right)\right]$$

$$= -\log p_k - \frac{p_k}{p_k} + \lambda$$

$$\log p_k = \lambda - 1 \rightarrow p_k = \exp(\lambda - 1) = \text{const.} = \frac{1}{M} \checkmark$$

page 34

$$S = \log M$$

Derived micro-canonical therm. equil. def.
from entropy maximization