MATH327: Statistical Physics

Monday, 13 February 2023

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Something to consider

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

How can we analyze this through the framework of probability spaces?

What sort of large-scale behaviour should we expect to predict?

Recap

Random walk – generic tool to model stochastic processes

Drift velocity $v_{dr} = \frac{N\mu}{t} = \frac{\mu}{\Delta t}$

Diffusion constant $D = \sqrt{\frac{N\sigma^2}{t}} = \sqrt{\frac{\sigma^2}{\Delta t}}$

Law of diffusion $\Delta x = D\sqrt{t}$

Related to central limit theorem

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

Spin systems & statistical ensembles

First law of thermodynamics = conservation of energy

Plan

Micro-canonical ensemble

Thermodynamical equilibrium

Entropy

Second law

Spin system

Energy as interaction between spin external magnetic field $H > 0$

$H \uparrow\uparrow\uparrow$

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

$E = -H$ $\qquad$ $E = H$

n_+ $\qquad$ $n_- = N - n_+$

Total energy $E = (-H)\, n_+ + (H)\, n_- = -H(2n_+ - N)$

$E(\uparrow\downarrow\uparrow\uparrow\uparrow\downarrow\uparrow\uparrow) = -H(2 \cdot 6 - 8) = -4H < 0$

With energy $E = -4H$ conserved

what ~~qu~~ fraction of states are allowed?

page 27

$$\text{Fraction} = \frac{\#\text{ allowed}}{\#\text{ total}} = \frac{\binom{8}{6}}{2^8} = \frac{8 \cdot 7/2}{256} = \frac{28}{256} = \frac{7}{64} \sim 11\%$$

Energy ~~and~~ of $N \sim 10^{25}$ point particles

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

Practically impossible solve $\sim 10^{25}$ time-evolution equations

or even specify $\sim 10^{25}$ initial conditions

Instead treat time evolution as stochastic process

$$w_1 \rightarrow w_2 \rightarrow w_3 \rightarrow \dots$$

$\llcorner$ w_i is micro-states

Statistical ensemble is set of all micro-states

$\Omega = \{w_1, w_2, \dots\}$

accessible through time evolution

Each micro-state w_i has probability p_i of being adopted

$\rightarrow$ probability space

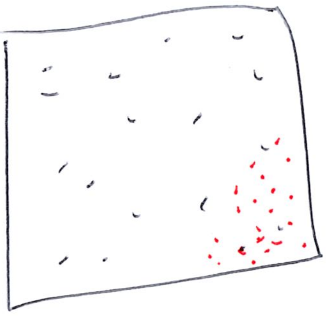
$\sum_i p_i = 1$ → system must be in some micro-state at any time

Conserved quantities unchanged under time evolution
→ characterize statistical ensemble

Micro-canonical ensemble characterized by
conserved (internal) energy E
and conserved particle number N

Energy conservation implies isolation!

Physical intuition: Expect steady, smooth, stable behaviour
equilibrium
Focus of this ~~s~~ module



Consider micro-canonical system Ω
M micro-states w_i
Thermodynamic equilibrium if and only if
all probabilities p_i equal

Finite M → $p_i = \frac{1}{M}$ so $\sum_{i=1}^{M} p_i = M\left(\frac{1}{M}\right) = 1$

Equilibrium system continues adopting different micro-states
"steady" not "static", equilibrium is dynamic

Emergence of steady behaviour related to entropy

Consider statistical ensemble Ω with countable $\underset{M}{\#}$ of micro-states

Entropy is $S = -\sum_{i=1}^{M} P_i \log P_i$

Specialize to micro-canonical ensemble in <u>equilibrium</u>

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

page 29

Boltzmann's equation

Micro-canonical → conserved E, N

In equilibrium, derived quantities like entropy steady & stable even though system dynamically adopts different micro-states

→ Entropy function of conserved quantities, $S(E,N)$

$\{E, N, M\}$ inter-related

<u>Spin system examples</u>

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

$$S = \log M = \log 2^N = N \log 2$$

Turn on magnetic field $H>0$

Now <u>$E=0$</u> only if $n_+ = n_-$

What is entropy? $S = \log M$

$$M = \binom{N}{n_+} \qquad N = n_+ + n_- = \underline{2n_+}$$

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

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

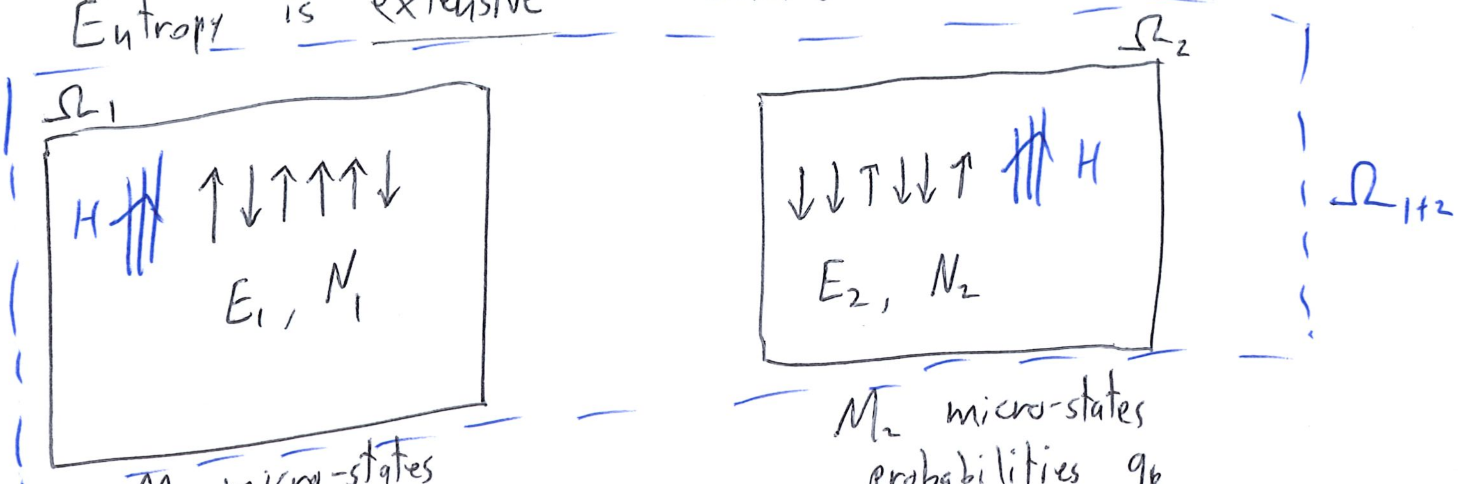
Suppose $N=8 \rightarrow n_+ = n_- = 4$

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

page 29

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

Entropy is extensive – consider two isolated systems



M_1 micro-states
probabilities p_i
$S_1 = -\sum_{i=1}^{M_1} p_i \log p_i$

M_2 micro-states
probabilities q_k
$S_2 = -\sum_{k=1}^{M_2} q_k \log q_k$

Analyze as combined system Ω_{1+2}
How many micro-states M_{1+2}?

Isolated subsystems statistically independent
M_2 micro-states for each $w_i \longrightarrow M_{1+2} = M_1 M_2$
$p_i \longrightarrow$ probabilities $p_i q_k$
q_k

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

Entropy $S_{1+2} = -\sum_{ik} p_i q_k \log(p_i q_k) = -\sum_{ik} p_i q_k (\log p_i + \log q_k)$

$= -\sum_i p_i \log p_i \underbrace{\sum_k q_k}_{1} - \underbrace{\sum_i p_i}_{1} \sum_k q_k \log q_k$

page 31

$= S_1 + S_2$

Extensive entropy $S_{1+2} = S_1 + S_2$ for independent subsystems
energy $E_{1+2} = E_1 + E_2$ particle # $N_{1+2} = N_1 + N_2$

Intensive quantities independent of extent of system (temperature density)

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

Suppose each subsystem independently in therm. equil.

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

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

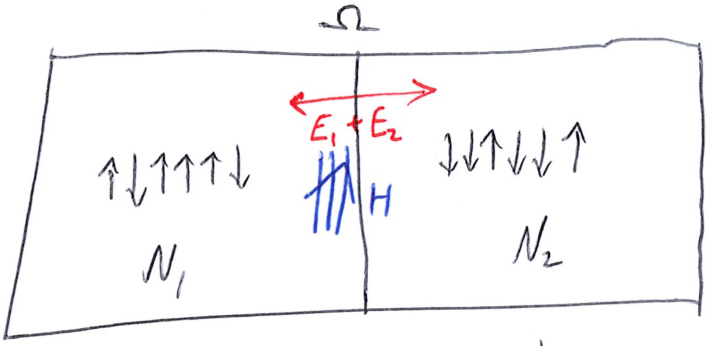
$p_i q_k = \frac{1}{M_1 M_2} = \frac{1}{M_{1+2}}$ → also in equilibrium

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

Thermal contact

Allow two subsystems to exchange energy (not particles)

Wait for equilibrium



Ω is <u>not</u> Ω_{1+2}

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

subsystems are <u>not</u>

What is total # of micro-states M for overall Ω

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

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

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 only for extremely special case that $\{E_1, E_2\}$ only possible energy distribution

$M \geq M_1 M_2 \rightarrow S = \log(M) \geq \log(M_1 M_2) = S_{1+2}$

(at therm. equil.)

Second law of thermodynamics

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

More generally, entropy never decreases as time passes
and generically increases

Provides more general definition of thermodynamic equilibrium
System is in therm. equil. if its entropy is maximal

Holds for micro-canonical and other ensembles
↳ Can recover earlier definition

Need to maximize $S = -\sum_i p_i \log p_i$
requiring conserved E, N and $\sum_i p_i = 1$

Use Lagrange multiplier

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

Maximize $\bar{S}(\lambda)$ and then impose $\sum_i p_i = 1$

then $\frac{\partial \bar{S}}{\partial \lambda} = 0$

→ maximum $\bar{S}$ corresponds to max. of $S = \bar{S}(\lambda = 0)$

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

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

$\log p_k = \lambda - 1$

$p_k = e^{\lambda - 1} = \text{const.}$
$= 1/M$ ✓

page 34