MATH327: StatMech and Thermo

Thursday, 12 February 2026

42 28 58

Something to consider

A micro-canonical system has to be isolated from the rest of the world to ensure its internal energy is conserved.

How can we arrange to observe a system while still obeying conservation of energy (the first law)?

Recap

Extensivity

Second law $\to$ generalized therm. equil.

Today

Temperature

Spin system

Heat exchange

Canonical ensemble

Micro-canonical temperature $T(E,N)$

Like entropy a derived quantity stable in therm. equil.

Definition (in therm. equil.): $\frac{1}{T} = \frac{\partial S}{\partial E}\Big|_N = \frac{\partial}{\partial E} \log M\Big|_N$

If we add energy

large increase in entropy $\to$ small T

and vice versa

Example: Spin system, $E = -H(2n_+ - N)$ $H>0$

Different (conserved) E means different n_+, M, S, T

Lowest energy: $\uparrow\uparrow\cdots\uparrow$ $n_+ = N$ $n_- = 0$

$E_0 = -NH$ $M(E_0) = 1 = \binom{N}{0}$

Next-lowest: $\uparrow\uparrow\cdots\uparrow\downarrow$ $n_+ = N-1$ $n_- = 1$

$\uparrow\downarrow\uparrow\cdots\uparrow\uparrow$ $E_1 = -H(N-2)$ $M(E_1) = N = \binom{N}{1}$

page 35

In general $M(E_{n_-}) = \binom{N}{n_-} = \dfrac{N!}{n_-!\underbrace{(N-n_-)!}_{n_+!}} = \binom{N}{n_+}$

Need derivative of $S = \log M$

need n_+, n_- in terms of $\{E, N\}$

need differentiable approx. to $n_+!$, $N!$

System is random walk in energy space

Each spin is step of $\pm H$ in E $H>0$

$\rightarrow$ ± 1 in $x = \dfrac{-E}{H} = 2n_+ - N$

Same ~~to~~ one-dim'l walk as before, with $p = q = \frac{1}{2}$

All 2^N walks = spin configs equally likely

$M(E_{n_-}) = 2^N P_{n_+}$ $P_{n_+} = \dfrac{1}{2^N}\binom{N}{n_+}$

Approx. P_{n_+} for $N \gg 1$ using CLT

$$p(x) \approx \frac{1}{\sqrt{2\pi N\sigma^2}} \exp\left[-\frac{(x - N\mu)^2}{2N\sigma^2}\right] = \frac{1}{\sqrt{2\pi N}} \exp\left(\frac{-x^2}{2N}\right)$$

$\mu = 2p - 1 = 0$

$\sigma^2 = 4pq = 1$

Integrate distribution using constant approx.

$$P_{n_+} \approx p(2n_+ - N)\,\underbrace{\Delta n_+}_{1} = \frac{1}{\sqrt{2\pi N}} \exp\left(\frac{-E^2}{2NH^2}\right)$$

$$M(E) = \frac{2^N}{\sqrt{2\pi N}} \exp\left(\frac{-E^2}{2NH^2}\right)$$

page 36

$$\boxed{\frac{1}{T} = \frac{\partial}{\partial E} \log M = \frac{\partial}{\partial E}\left(\frac{-E^2}{2NH^2} + E\text{-indep.}\right) = \frac{-E}{NH^2}}$$

Temperature $T = \frac{-NH^2}{E}$ for $N \gg 1$, $H > 0$

Unexpected features:

T divergent if $E \to 0$ $\quad n_+ \approx n_-$

T negative if $E > 0$ $\quad n_+ < n_-$

↳ Adding energy reduces number of micro-states

Definition: Natural systems have $T > 0$

Spin system is natural when $E < 0$ $\quad n_+ > n_-$

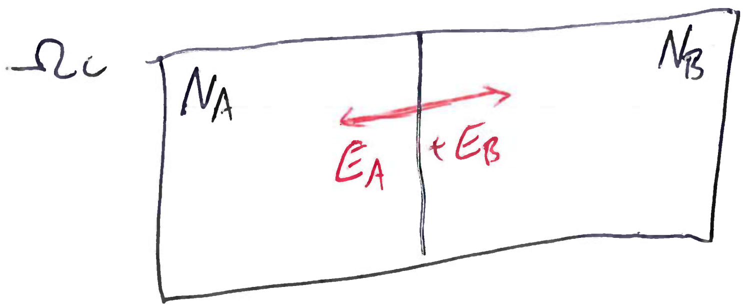
Minimum (natural) $T_{min} = H > 0$ for minimum $E_0 = -NH$

Adding energy increases M, S, T until $n_- \approx n_+$

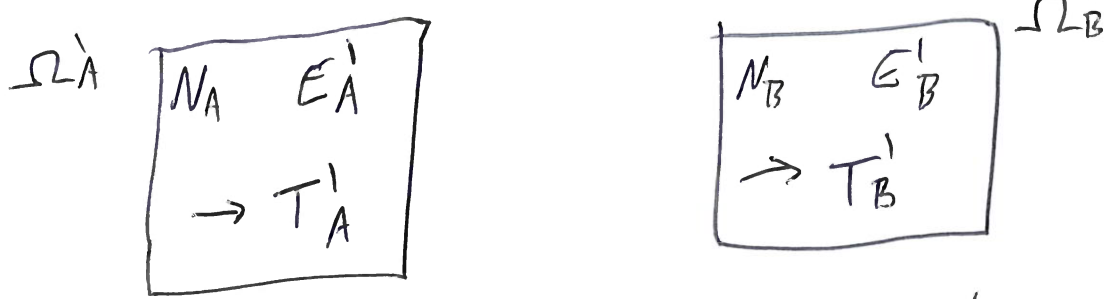
More general analysis: Heat exchange

1) Two isolated micro-canonical subsystems

2) Put in thermal contact



3) Re-isolate the subsystems



Check expectation that energy flow from hotter to colder system

$$E_s' = E_s + \Delta E_s \qquad \Delta E_A = -\Delta E_B$$

$s = A, B$

Taylor expand

$$\boxed{\begin{aligned} S(E_s') &= S(E_s + \Delta E_s) \\ &= S(E_s) + \left.\frac{\partial S}{\partial E_s}\right|_{E_s} \Delta E_s + \mathcal{O}(\Delta E_s^2) \\ &\approx S(E_s) + \frac{\Delta E_s}{T_s} \end{aligned}}$$

page 38

Second law: $S(E_A) + S(E_B) \leq S(E_A + E_B) \leq S(E_A') + S(E_B')$

$$\boxed{\begin{aligned} &\cancel{S(E_A)} + \cancel{S(E_B)} \leq \cancel{S(E_A)} + \frac{\Delta E_A}{T_A} + \cancel{S(E_B)} + \frac{\Delta E_B}{T_B} \\ &\frac{\Delta E_A}{T_A} - \frac{\Delta E_A}{T_B} = \Delta E_A \left(\frac{1}{T_A} - \frac{1}{T_B} \right) \geq 0 \end{aligned}}$$

page 38

$T_A > T_B \rightarrow \Delta E_A < 0$

Energy flow from hotter Ω_A to colder Ω_B

(reducing T_A') (increase T_B')

$T_A < T_B \rightarrow \Delta E_A > 0$ " Ω_B " Ω_A

Special case $T_A = T_B \rightarrow \Delta E_A = 0$ $T_S' = T$

Complete isolation required by micro-~~sys~~ canonical ensemble is unrealistic

More practical: Canonical ensemble

characterized by fixed T and conserved N

T fixed by thermal contact with large external "reservoir" ("heat bath")

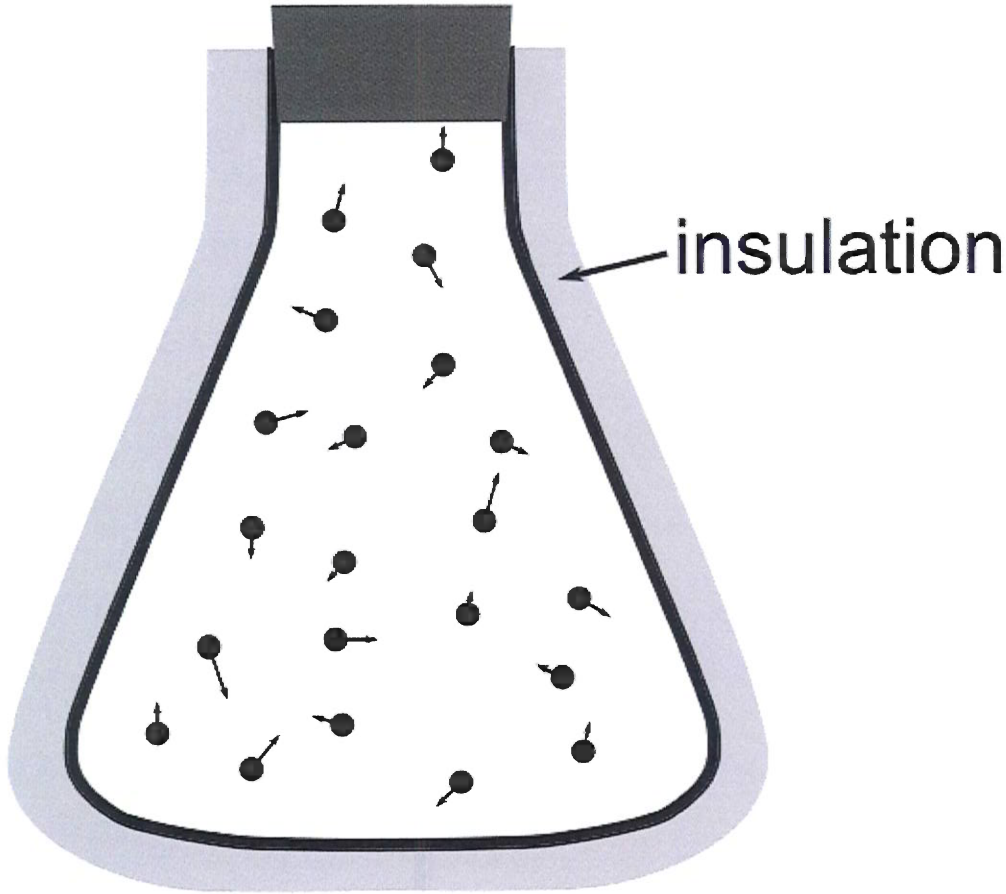
System + reservoir remains micro-canonical

$\Omega \otimes \Omega_{res} = \Omega_{tot}$ with conserved $E_{tot} = E + E_{res}$

E can fluctuates without change intensive T

Need to show details of Ω_{res} don't matter

$\rightarrow$ can consider Ω ~~on~~ its own commons.wikimedia.org/wiki/File:Statistical_Ensembles.png



Microcanonical
(const. N E)

Canonical
(const. N T)

Sensible ansatz for Ω_{res} from <u>replica trick</u>

Let Ω_{res} be $R-1 \gg 1$ replicas of Ω

all in therm. equil. and thermal contact

$$E_{tot} = E + E_{res} = \sum_{r=1}^{R} E_r$$

Micro-states $w_i \in \Omega$ have non-conserved E_i $i=1, \dots, M$

<u>Occupation number</u> n_i is number of replicas adopting w_i

$$\sum_{i=1}^{M} n_i = R$$

$$\sum_i n_i E_i = E_{tot}$$

$$\sum_i \frac{n_i}{R} = 1 = \sum_i p_i$$

occupation probability

System + reservoir Ω_{tot} fully specified by $\{n_i\}$ or $\{p_i\}$

It has $\frac{1}{T} = \left.\frac{\partial S_{tot}}{\partial E_{tot}}\right|_{N_{tot}} = \left.\frac{\partial}{\partial E_{tot}} \log M_{tot}\right|_{N_{tot}}$

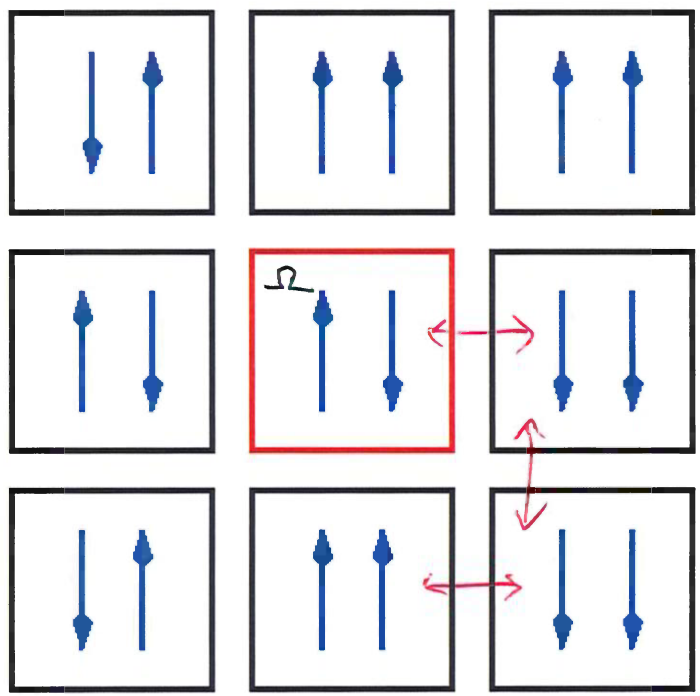
M_{tot} counts ways of arranging R replicas into set $\{n_i\}$

$$M_{tot} = \binom{R}{n_1}\binom{R-n_1}{n_2}\binom{R-n_1-n_2}{n_3} \cdots$$

$$= \left(\frac{R!}{n_1!\,\cancel{(R-n_1)!}}\right)\left(\frac{\cancel{(R-n_1)!}}{n_2!\,\cancel{(R-n_1-n_2)!}}\right)\left(\frac{\cancel{(R-n_1-n_2)!}}{n_3!\,(R-n_1-n_2-n_3)!}\right) \cdots$$

$$= \frac{R!}{n_1!\,n_2!\,n_3! \cdots n_M!}$$

$R = 9$



W_i	n_i
↑↑	3
↑↓	2
↓↑	2
↓↓	2
	$9 = R$ ✓

page 42

Entropy $S_{tot} = \log M_{tot} = \log(R!) - \sum_{i=1}^{M} \log(n_i!)$

Assume all $n_i \gg 1$ and approx. $\log(n!) \approx n \log n - n$

$$\boxed{\begin{aligned} S_{tot} &\approx R \log R - \cancel{R} - \sum_i (n_i \log n_i - \cancel{n_i}) \qquad n_i = p_i R \\ &= R \cancel{\log} R - R \sum_i p_i (\log p_i + \cancel{\log} R) \\ &= -R \sum_i p_i \log p_i \end{aligned}}$$

page 44

Must be maximal since in therm. equil. ...