Wed 12 Feb   299 707

Recap

Entropy $S = -\sum_i p_i \log p_i$

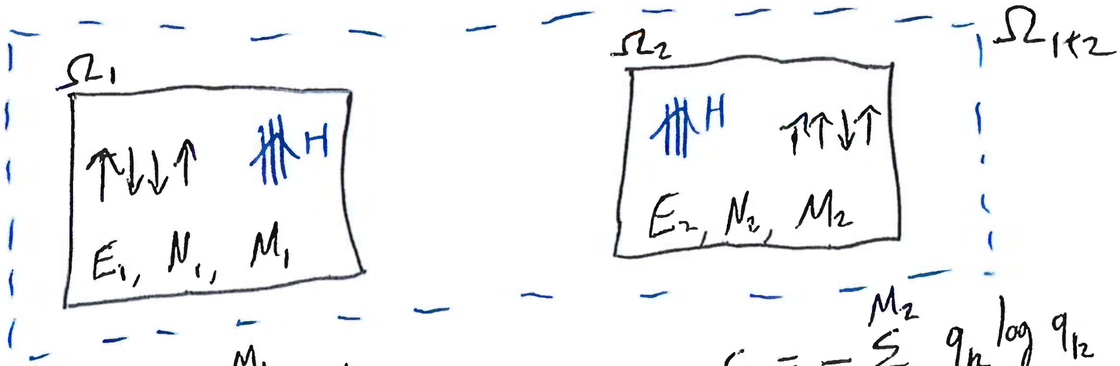
Extensivity

Today

Second law

↳ Generalized therm. equil.

Temperature

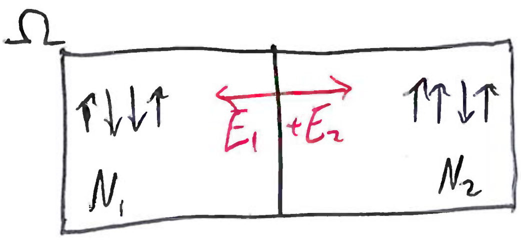


$S_1 = -\sum_{i=1}^{M_1} p_i \log p_i$ $S_2 = -\sum_{k=1}^{M_2} q_k \log q_k$

$S_{1+2} = S_1 + S_2$ $M_{1+2} = M_1 \cdot M_2$

Now put (equil.) subsystems in thermal contact

exchange energy
not particle



wait for equil.

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

subsystems are not

How many micro-states M for overall Ω?

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

Overall $M = \sum_{e_1} M^{(1)}_{e_1} M^{(2)}_{E-e_1}$ $\quad M^{(1)}_{E_1} \quad M^{(2)}_{E_2}$

Case $e_1 = E_1$ accounts for all $M_{1+2} = M_1 M_2$

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

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

Very special case

Result: $S = \log M \geq \log(M_1 M_2) = S_{1+2} = S_1 + S_2$

Second law of thermodynamics

When isolated subsystems in therm. equil. are brought into thermal contact entropy $S \geq S_1 + S_2$ can never decrease

Increases except in very special cases

More generally, entropy never decreases as time passes (usually increases)

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

Holds for any stat. ensemble

Let's derive micro-canonical $p_i = \frac{1}{M} \rightarrow S = \log M$

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

Use <u>Lagrange multiplier</u>

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

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

2) Impose $\sum_i p_i = 1 \rightarrow \dfrac{\partial \bar{S}}{\partial \lambda} = 0$ so max $\bar{S} \leftrightarrow$ max $S = \bar{S}(\lambda = 0)$

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

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

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

$$S = \log M$$

page 34

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

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Micro-canonical temperature like entropy

Derived quantity, stable in therm. equil., $T(E,N)$

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

If we add energy

<u>large</u> increase in entropy $\rightarrow$ <u>small</u> temperature

& vice versa

<u>Example</u>: Spin system $E = -H(2n_+ - N)$

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

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

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

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

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

page 35

In general $M(E_{n_-}) = \binom{N}{n_-} = \frac{N!}{n_-!\, n_+!} = \binom{N}{n_+}$

For T, need derivative of $S = \log M$

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

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

Spin system is random walk in energy space

Each spin is step of $\pm H$ in energy $(H>0)$

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

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

All 2^N walks (spin configs) equally likely

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

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

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

$\mu = 2p - 1 = 0$

$\sigma^2 = 4pq = 1$

Integrate distribution using constant approx.

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

$$\text{So } M(E) \approx \frac{2^N}{\sqrt{2\pi N}} \exp\left[\frac{-E^2}{2NH^2}\right]$$

page 36

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

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

Unexpected Features:

T diverges if $E \to 0$ $\quad (n_+ \approx n_-)$

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

$\to$ Adding energy reduces # of micro-state

Definition: <u>Natural</u> systems have $T > 0$

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

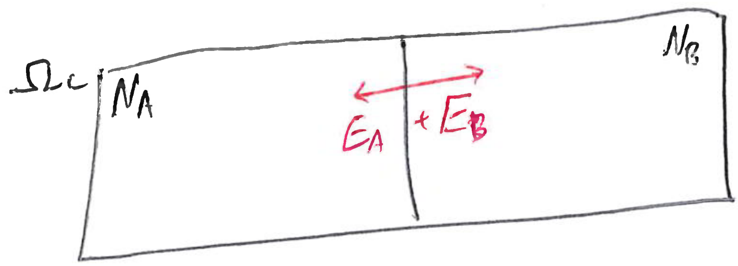
Minimum natural $T_{min} = H > 0$ for minimum $E_0 = -NH$

<u>Adding energy increases</u> ~~from~~ temperature until $n_- \approx n_+$

More generally check for sensible behaviour from formal def. by considering <u>heat exchange</u>

1) Two isolated micro-canonical subsystems

2) Put in thermal contact, equilibrate to T_C



3) Re-isolate the two subsystems

Check expectation that energy flows from hotter to colder system

Let $E_S' = E_S + \Delta E_S$ $\qquad \Delta E_A = -\Delta E_B$

Taylor expand

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

page 38

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

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

page 38

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

Energy flowed from hotter Ω_A (reduce T_A') to colder Ω_B (increase T_B')

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

" $\qquad \Omega_B \qquad$ " $\qquad \Omega_A$

Special case $T_A = T_B \rightarrow \Delta E_A = 0 \qquad T_S' = T_S$

Preview: Complete isolation required by micro-canonical ensemble is unrealistic

More practical: <u>Canonical enesemble</u>