MATH327: StatMech and Thermo

Wednesday, 19 February 2025

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Something to consider

Systems governed by the canonical ensemble can have different internal energy E_i for each micro-state ω_i.

In the very special case that all micro-states have the same energy E, will we observe behaviour similar to the micro-canonical ensemble?

Recap

Canonical ensemble

Replica trick

Occupation #/prob. n_i / p_i for $\omega_i \in \Omega$

M_{tot} and $S_{tot} = -R \sum_i p_i \log p_i$ in therm. equil.

Today

Maximize entropy → partition function

Derive entropy, energy, etc.

Physics of information

Maximize entropy with constraints $\sum_i p_i = 1$

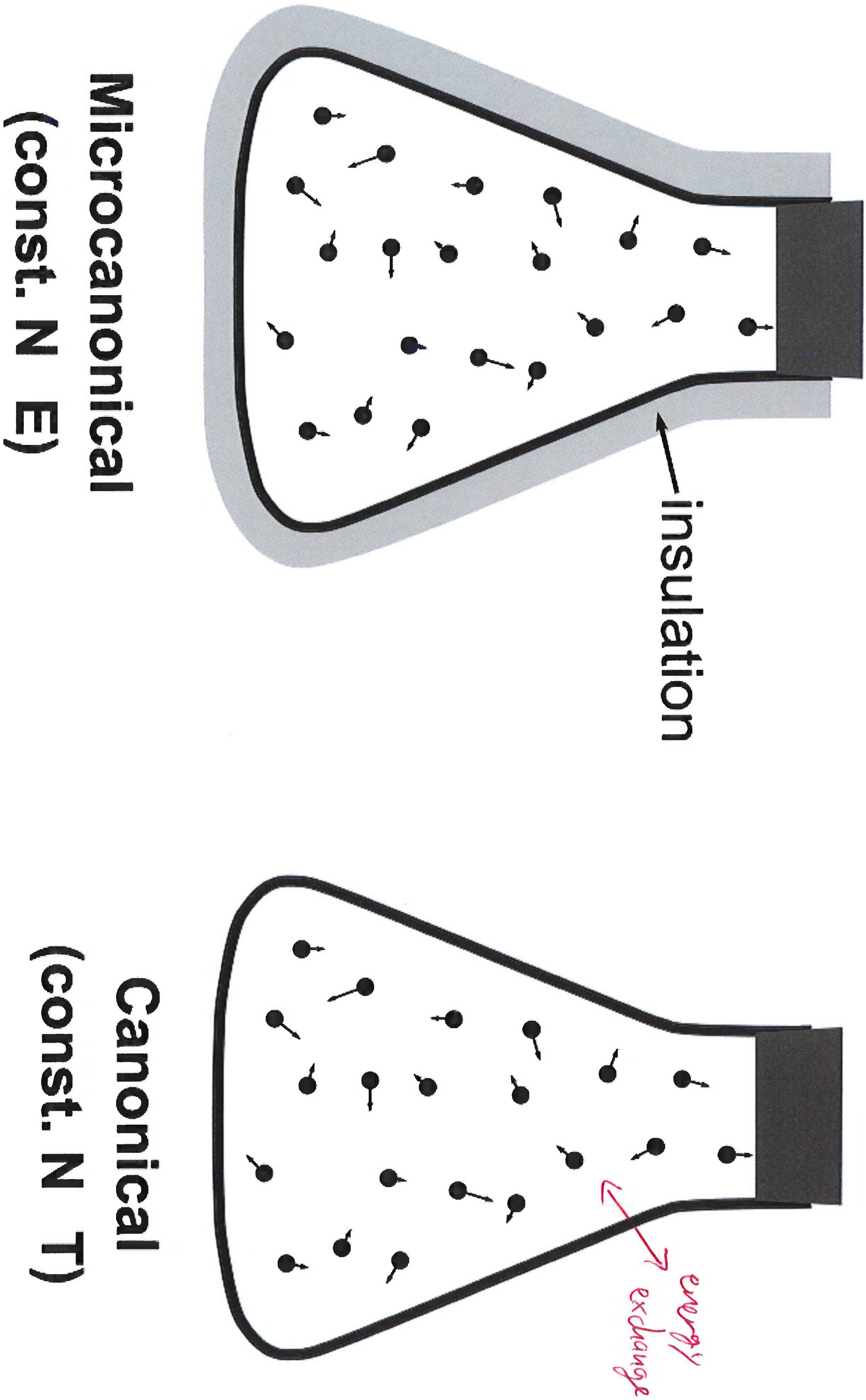
$R \sum_i p_i E_i = E_{tot}$

$$\overline{S} = -R \sum_i p_i \log p_i + \alpha\left(\sum_i p_i - 1\right) - \beta\left(R \sum_i p_i E_i - E_{tot}\right)$$

$$\frac{\partial \overline{S}}{\partial p_k} = 0 = -R(\log p_k + 1) + \alpha - \beta R E_k$$

$$\log p_k = -1 + \frac{\alpha}{R} - \beta E_k$$

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



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$$\boxed{P_k = \exp\left[-\left(1-\frac{\alpha}{R}\right) - \beta E_k\right] = \frac{\exp(-\beta E_k)}{\exp\left(1-\frac{\alpha}{R}\right)} = \frac{1}{Z} e^{-\beta E_k}}$$

Impose constraints:

$$\sum_i p_i = 1 = \frac{1}{Z}\sum_i e^{-\beta E_i} \rightarrow Z(\beta) = \sum_i e^{-\beta E_i}$$

<u>partition function</u>

$R \sum_i p_i E_i = E_{tot}$ relate to S_{tot}

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$$\boxed{\begin{aligned} S_{tot} &= -R\sum_i p_i \log p_i = -R\sum_i p_i \log\left(\frac{1}{Z}e^{-\beta E_i}\right) \\ &= R\log Z + R\beta\sum_i p_i E_i = R\log Z + \beta E_{tot} \end{aligned}}$$

So $\frac{1}{T} = \frac{\partial S}{\partial E} = \beta + E\frac{\partial \beta}{\partial E} + R\left(\frac{1}{Z}\frac{\partial \beta}{\partial E}\frac{\partial Z}{\partial \beta}\right)$

$$\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{1}{Z}\sum_i \frac{\partial}{\partial \beta} e^{-\beta E_i} = \frac{-1}{Z}\sum_i E_i e^{-\beta E_i}$$

$$= -\sum_i p_i E_i = \frac{-E_{tot}}{R}$$

$$\frac{1}{T} = \beta + \cancel{E\frac{\partial \beta}{\partial E}} + \cancel{R\left(\frac{-E}{R}\right)\left(\frac{\partial \beta}{\partial E}\right)} = \beta$$

We have derived the <u>Gibbs distribution</u>

$$p_i = \frac{1}{Z}e^{-E_i/T} \qquad Z = \sum_i e^{-E_i/T} \qquad \frac{1}{T} = \beta$$

Boltzmann factor

p_i are probability system Ω adopts micro-state w_i with energy E_i

<u>Reservoir unknowable</u> apart from fixing T ✓

Internal energy no longer conserved

Predict its expectation value

$$\boxed{\begin{aligned} \langle E\rangle(T) &= \sum_i p_i E_i = \frac{1}{Z}\sum_i E_i e^{-\beta E_i} \\ &= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{-\partial}{\partial \beta}\log Z \end{aligned}}$$

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How does $\langle E \rangle$ depend on T?

$$c_V = \frac{\partial}{\partial T}\langle E \rangle \geq 0$$

Heat capacity

Higher temperature $\rightarrow$ larger internal energy

Entropy $S = -\sum_i p_i \log p_i = -\sum_i p_i \log\left(\frac{1}{Z} e^{-\beta E_i}\right)$

$$= \log Z + \beta \sum_i p_i E_i = \log Z + \frac{\langle E \rangle}{T}$$

$$\langle E \rangle = T \cdot S - T \log Z$$

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Helmholtz free energy $\quad F(T) = -T \log Z$

$$Z = e^{-F/T}$$

$$p_i = \frac{1}{Z} e^{-E_i/T} = e^{(F - E_i)/T}$$

Derivatives of $F(T)$ give $\langle E \rangle (T)$ and $S(T)$

$$\langle E \rangle = \frac{-\partial}{\partial \beta} \log Z = \frac{\partial}{\partial \beta}\left(\frac{F}{T}\right) = \frac{\partial T}{\partial \beta} \frac{\partial}{\partial T}\left(\frac{F}{T}\right)$$

$$= \frac{-1}{\beta^2} \frac{\partial}{\partial T}\left(\frac{F}{T}\right) = -T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right)$$

$$\frac{\partial}{\partial T} F = \frac{\partial}{\partial T}(-T \log Z) = -\log Z - T \frac{\partial}{\partial T} \log Z$$

$$= -\log Z - \frac{\langle E \rangle}{T} = -S$$

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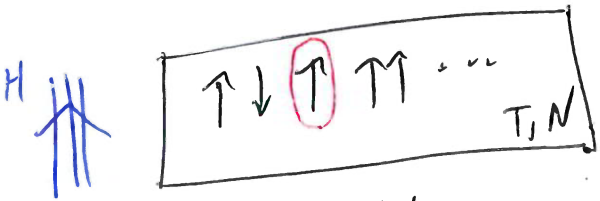
$$S = \frac{-\partial}{\partial T} F = \frac{\langle E \rangle - F}{T}$$

Application: Information

Pure $\underbrace{\text{info content}}_{\text{knowable in principle}}$ $\rightarrow$ physically observable effects

Consider systems of distinguishable vs. indistinguishable spin

Dist'able spins at fixed locations in solid



$M = 2^N$ micro-states ω_i with energies E_i
and probabilities $p_i = \frac{1}{Z} e^{-E_i/T}$

Notation: Call aligned $s_n = 1$, anti-aligned $s_n = -1$

Then $E_i = -H \sum_{n=1}^{N} s_n$ for ω_i specified by N $\{s\}$

Start with partition function $\qquad x = \beta H = H/T$

$$Z_D = \sum_i e^{-\beta E_i} = \sum_{s_1 = \pm 1} \cdots \sum_{s_N = \pm 1} \exp\left[\beta H \sum_n s_n\right]$$

$$= \left(\sum_{s_1 = \pm 1} e^{x s_1}\right) \cdots \left(\sum_{s_N = \pm 1} e^{x s_N}\right) = \left(\sum_{s = \pm 1} e^{x s}\right)^N$$

$$= \left(e^{x} + e^{-x}\right)^N = \left[2\cosh(\beta H)\right]^N$$

$$F_D = \frac{-\log Z_D}{\beta} = -\frac{N}{\beta} \log\left[2\cosh(\beta H)\right]$$

Now predict

$$\boxed{\langle E \rangle_D = \frac{\partial}{\partial \beta}(\beta F_D) = -N \frac{\partial}{\partial \beta} \log\left[2\cosh(\beta H)\right] = \frac{-N}{\cancel{2}\cosh(\beta H)} \left(\cancel{2}\sinh(\beta H)\right) H = -NH \tanh(\beta H)}$$

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$$S_D = \beta\left(\langle E \rangle_D - F_D\right) = -N\beta H \tanh(\beta H) + N \log\left[2\cosh(\beta H)\right]$$

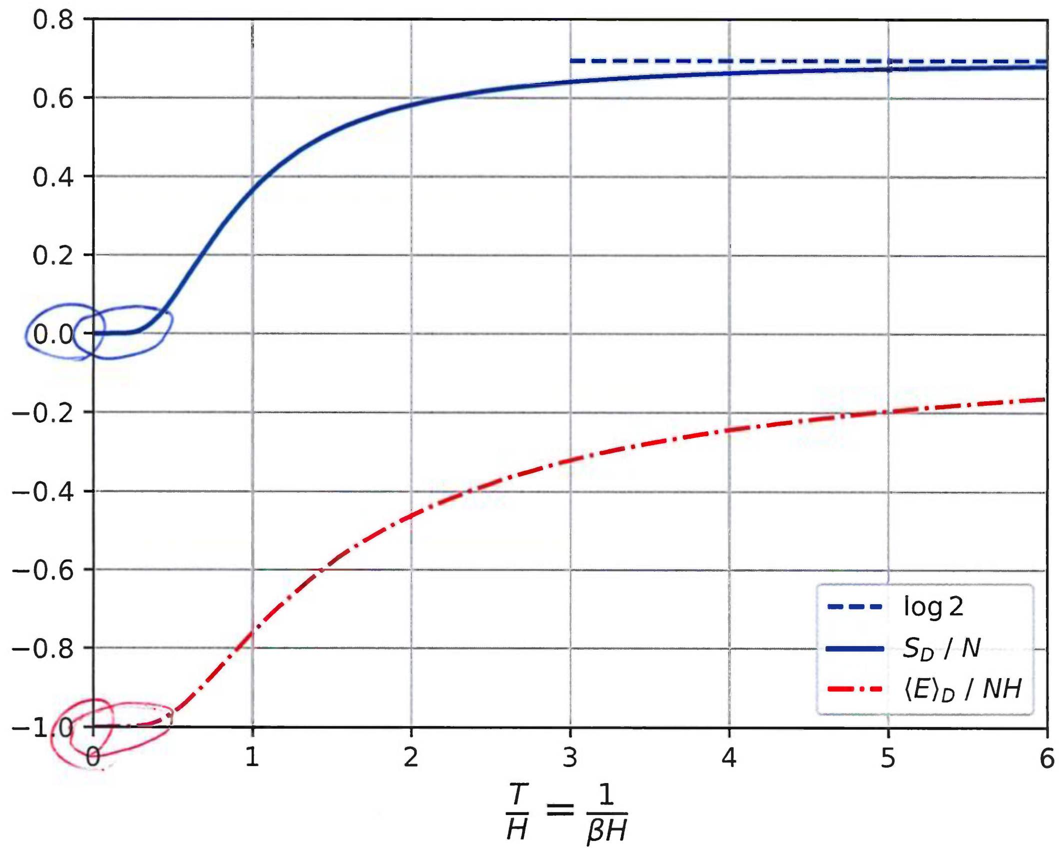
~~Start~~ Strategy: Expand around simpler limit

Low-temperature $\beta \to \infty$ $\qquad \frac{\langle E \rangle_D}{NH} = -\tanh(\beta H) = -1$

$2\cosh(\beta H) \to e^{\beta H}$ so $\frac{S_D}{N} \to -\beta H + \beta H = 0$

"Absolute zero" $\to$ single "ground" micro-state $\qquad E_0 = -NH$

$\to$ zero entropy (third law)


0.8
0.6
0.4
0.2
0.0
−0.2
−0.4
−0.6
−0.8
−1.0
0
1
2
3
4
5
6
$\frac{T}{H} = \frac{1}{\beta H}$
log 2
S_D / N
$\langle E \rangle_D$ / NH

Expand: Contributions from "excited" micro-states with $E_i > E_0$
suppressed $\sim p_i \propto e^{-E_i/T}$

Spin system $\rightarrow$ energy levels separated by constant gap
$\Delta E = \cancel{\Delta} E_{n_-+1} - E_{n_-} = 2H$

Gap controls approach to $T \to 0$ limit

$$\frac{\langle E \rangle_D}{NH} = -\tanh(\beta H) = \frac{-(1-e^{-2\beta H})}{1+e^{-2\beta H}} = -(1-e^{-2\beta H})(1-e^{-2\beta H} + \mathcal{O}(e^{-4\beta H}))$$

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$$\frac{1}{1-x} = \sum_{k=0}^{\infty} x^k \qquad |x| \ll 1 \qquad x = -e^{-2\beta H}$$

$$\frac{\langle E \rangle_D}{NH} = -1 + 2e^{-2\beta H} + \mathcal{O}(e^{-4\beta H}) = -1 + 2e^{-\Delta E/T} + \mathcal{O}(e^{-2\Delta E/T})$$

exponential suppression of excited-state effects

$$\frac{S_D}{N} = -\beta H \tanh(\beta H) + \log[2\cosh(\beta H)]$$

$$-\beta H + 2\beta H e^{-\beta \Delta E} + \mathcal{O}(\beta \Delta E\, e^{-2\beta \Delta E})$$

$$\log(e^{\beta H} + e^{-\beta H}) = \log[e^{\beta H}(1 + e^{-2\beta H})] = \beta H + \log(1 + e^{-2\beta H})$$

$$= \beta H + e^{-2\beta H} + \mathcal{O}(e^{-4\beta H})$$

$$\frac{S_D}{N} = -\cancel{\beta H} + 2\beta H e^{-\beta \Delta E} + \cancel{\beta H} + e^{-\beta \Delta E} + \mathcal{O}(\beta \Delta E\, e^{-2\beta \Delta E})$$

$$= \beta \Delta E\, e^{-\beta \Delta E} + e^{-\beta \Delta E} + \mathcal{O}(\beta \Delta E\, e^{-2\beta \Delta E})$$

$\beta \Delta E \gg 1$

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