MATH327: StatMech and Thermo

Thursday, 19 February 2026

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Something to consider

Should we expect a system's internal energy expectation value $\langle E \rangle$ to depend on whether or not we can label its particles?

Recap

Canonical ensemble (T, N) $\qquad p_i = \frac{1}{Z} e^{-\beta E_i} = e^{(F - E_i)/T}$

Partition function $\qquad Z = \sum_i e^{-\beta E_i} = e^{-F/T}$

Helmholtz free energy $\qquad F = -T \log Z$

Today

Start application — observable effects from information

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

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

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

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

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

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

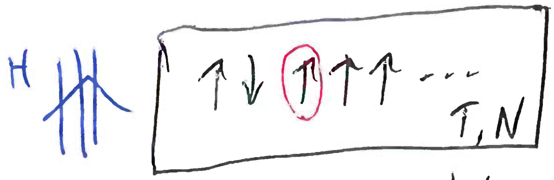
Application: Information

Info content $\rightarrow$ physically observable effects

knowable in principle

Compare distinguishable vs. indistinguishable spin

(i) Dist'able spins at fixed positions in solid



$M = 2^N$ micro-states w_i with energies E_i

and $p_i = \frac{1}{Z} e^{-E_i/T}$

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

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

Start with partition function

$$Z_D = \sum_i e^{-\beta E_i} = \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} \cdots \sum_{s_N=\pm 1} \exp\left[\beta H \sum_n s_n\right]$$

$\left(x = \beta H = \frac{H}{T}\right)$

$$= \left(\sum_{s_1=\pm 1} e^{x s_1}\right)\left(\sum_{s_2} e^{x s_2}\right) \cdots \left(\sum_{s_N} e^{x s_N}\right)$$

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

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

Now predict

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

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

Strategy: Expand around simpler limits

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

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

"Absolute zero" $\to$ single "ground" (micro-) state $\quad E_0 = -NH$

$\to$ zero entropy

Expansion ~~a~~ involves contributes from "excited" state with $E_i > E_0$

$\to$ suppressed $p_i \propto e^{-E_i/T}$

For this spin system energy levels are separated by constant gap

$$\Delta E = E_{n_-+1} - E_{n_-} = 2H$$

Gap controls approach to $T \to 0$ limit

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

$$= -(1-e^{-2\beta H})(1-e^{-2\beta H} + \mathcal{O}(e^{-4\beta H}))$$

$$= -1 + 2e^{-2\beta H} + \mathcal{O}(e^{-4\beta H})$$

$$= -1 + 2e^{-\Delta E/T} + \mathcal{O}(e^{-2\Delta E/T})$$

$x = -e^{-2\beta H}$

$|x| \ll 1$

$$\frac{1}{1-x} = \sum_{k=0}^{\infty} x^k$$

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

$-\beta H + 2\beta H e^{-\beta \Delta E} + \ldots$

$$= \cancel{-\beta H} + \beta \Delta E e^{-\beta \Delta E} + \cancel{\beta H} + e^{-\beta\Delta E} + \ldots$$

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

$\log(e^x + e^{-x}) = \log(e^x(1+e^{-2x}))$

$= x + e^{-2x} + \ldots$

$\beta \Delta E \gg 1$

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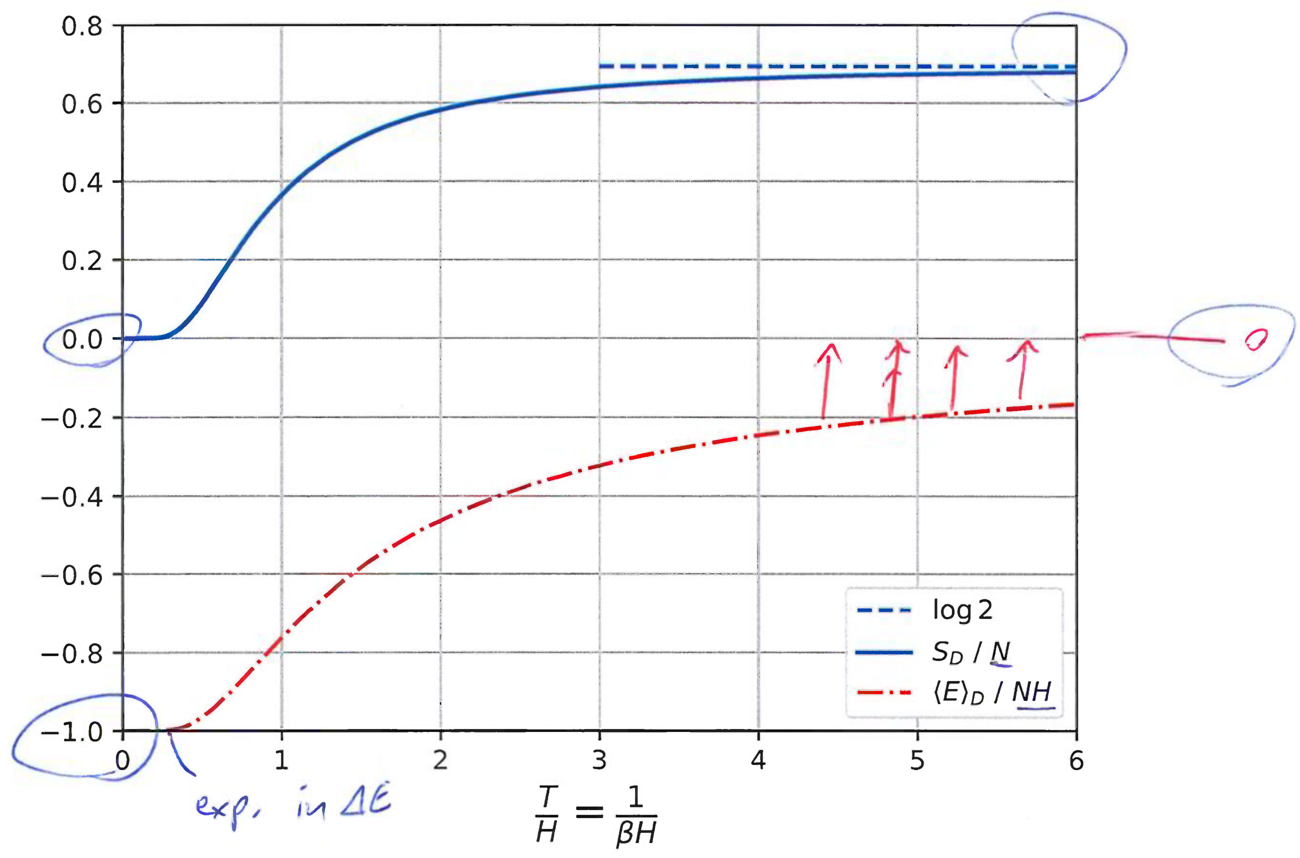
0.8
0.6
0.4
0.2
0.0
−0.2
−0.4
−0.6
−0.8
−1.0
0
1
2
3
4
5
6
log 2
S_D / N
$\langle E \rangle_D$ / NH
$\frac{T}{H} = \frac{1}{\beta H}$
exp. in ΔE
0

High-temp. $\beta \to 0$

$$\frac{\langle E\rangle_D}{NH} = -\tanh(\beta H) = -\beta H + \frac{(\beta H)^3}{3} + O(\beta^5 H^5) \to 0 \text{ linearly}$$

$$\frac{S_D}{N} = -(\beta H)^2 + O(\beta^4 H^4) + \log 2 + \log(\cosh(\beta H))$$

$$\log\left(1 + \frac{1}{2}(\beta H)^2 + O(\beta^4 H^4)\right)$$

$$\frac{1}{2}(\beta H)^2 + O(\beta^4 H^4)$$

$$\frac{S_D}{N} = \log 2 - \frac{1}{2}(\beta H)^2 + O(\beta^4 H^4)$$

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As $T \to \infty$, $S_D \to N \log 2 = \log 2^N = \log M$ ~ micro-canonical

All $p_i = \frac{1}{Z} \underbrace{e^{-\beta E_i}}_{\to 1} \approx \frac{1}{\sum_i \underbrace{e^{-\beta E_i}}_{\to 1}} = \frac{1}{M}$

$\beta E_i = \frac{E_i}{T}$

Indist'able spins move (slowly) in gas (one-dim'l)

H ↑↓↑↑↑ . . .

$N=2$ spins → ↑↑ ↓↓ {↑↓ + ↓↑}

3 micro-states not 2^N

Only knowable info is total $\{n_+, n_-\} \leftrightarrow E_{n_-}$

One micro-state for each energy level!

Example: Micro-states for $N=4$ have $E = -4H, -2H, 0, 2H, 4H$
(all up) (all down)

In general only $M_I = N+1$

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Label w_k for $E_k = -NH + 2Hk = -H(N-2k)$ $k = 0, \dots, N$

$\Delta E = 2H$

Start with partition function

$$Z_I = \sum_{k=0}^{N} e^{-\beta E_k} = \sum_k e^{\beta H(N-2k)} = e^{N\beta H} \sum_{k=0}^{N} \left(e^{-2\beta H}\right)^k \qquad x = e^{-2\beta H} < 1$$

$$\sum_{k=0}^{N} x^k = \sum_{k=0}^{\infty} x^k - \sum_{k=N+1}^{\infty} x^k$$

$$= \frac{1}{1-x} - x^{N+1} \sum_{l=0}^{\infty} x^l = \frac{1-x^{N+1}}{1-x}$$

$$Z_I = e^{N\beta H}\left(\frac{1-e^{-2(N+1)\beta H}}{1-e^{-2\beta H}}\right)$$

$$F_I = -\frac{\log Z_I}{\beta} = -NH - \frac{1}{\beta}\log\left(1-e^{-2(N+1)\beta H}\right) + \frac{1}{\beta}\log\left(1-e^{-2\beta H}\right)$$

$F_I \neq F_D \rightarrow \langle E \rangle_I \neq \langle E \rangle_D$ and $S_I = S_D$ as well (HW)

Preview: Classical, non-relativistic ideal gases

↘ Not quantum

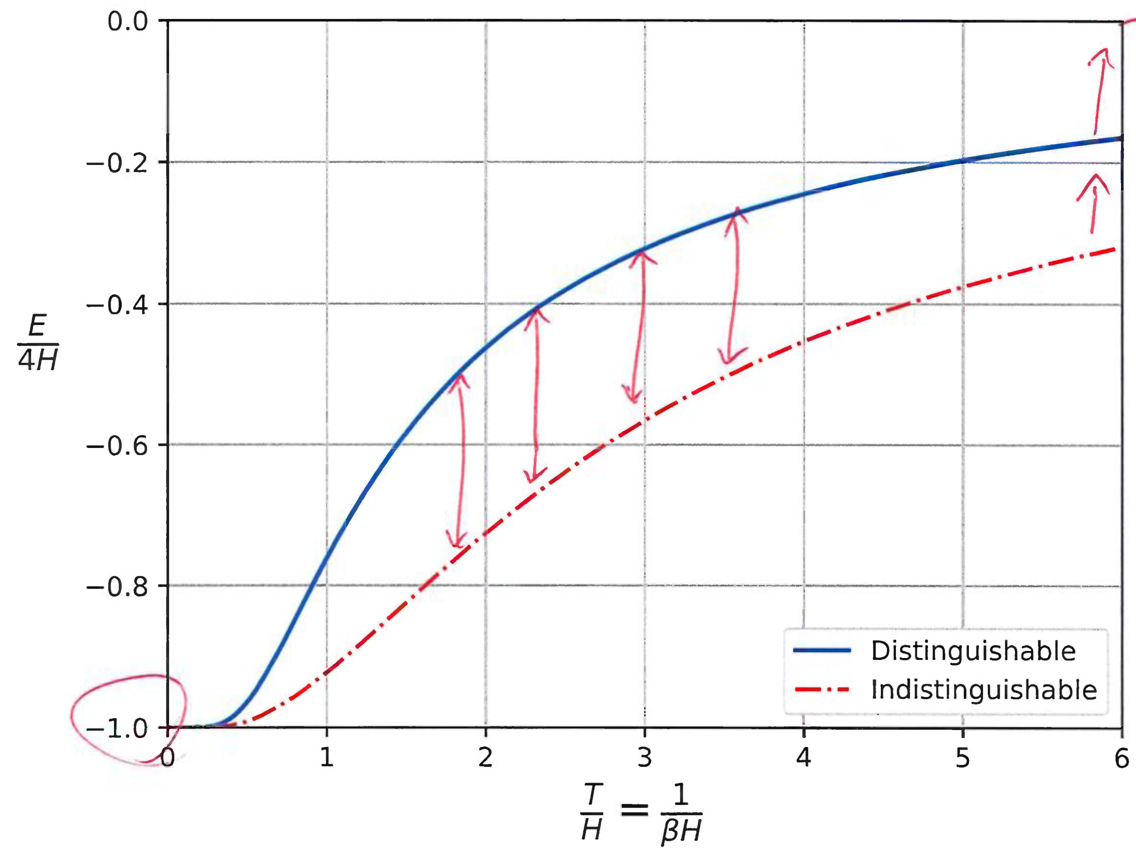
Non-rel. means slow vs. speed of light

$$E_n = \frac{1}{2m} p_n^2 \qquad \text{for mass } m > 0$$

inner product $p^2 = \vec{p}\cdot\vec{p} = p_x^2 + p_y^2 + p_z^2$

Ideal means no interactions between particles

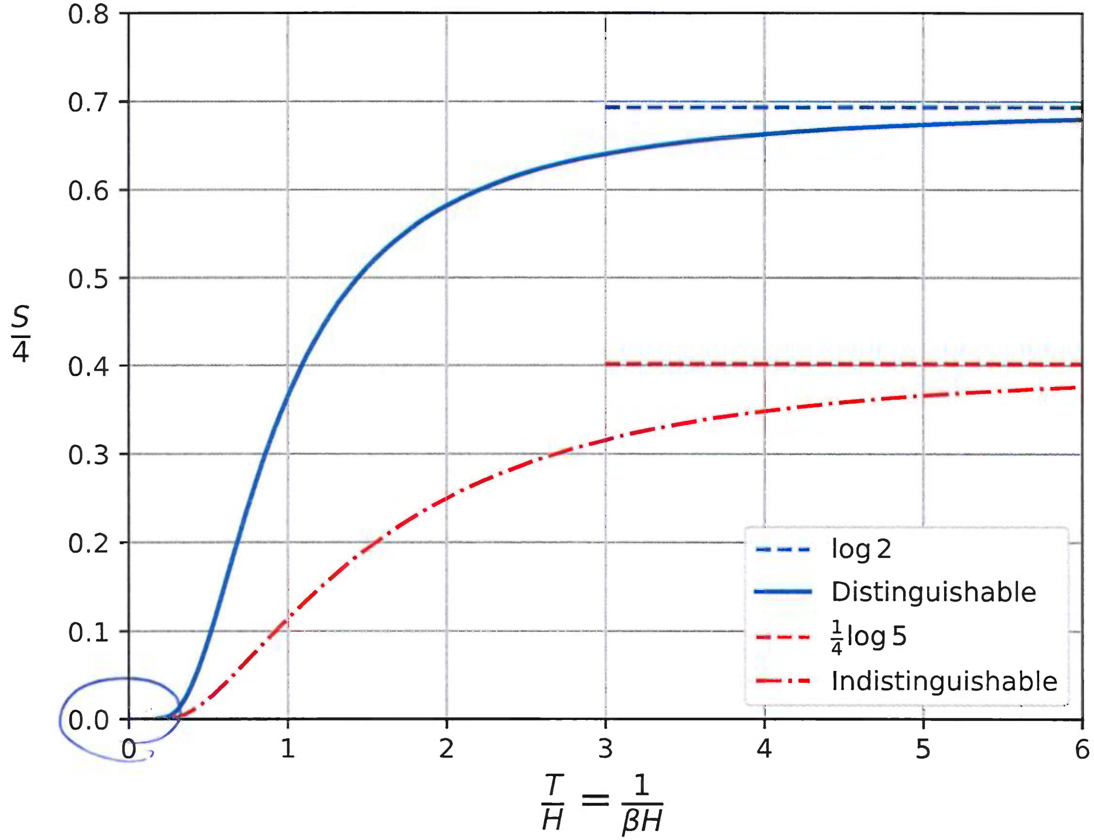
$N=4$



Same $\langle E \rangle_I \to 0$
as $T \to \infty$
$\langle E \rangle_I$ approaches slower

Same $T \to 0$ limits (single ground state)
$\langle E \rangle_I$ approaches faster
Differ for finite non-zero T
Physically measurable effects from intrinsic info content

$N=4$



$S \to \log M$

$M_D = 2^N \implies \frac{S}{N} \to \log 2$ ✓

$M_I = N+1 \implies \frac{S}{N} \to \frac{\log(N+1)}{N}$