MATH327: Statistical Physics

Friday, 1 March 2024

15 43 32

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

Start from partition function $\quad Z = \sum_i e^{-\beta E_i}$

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

Derive $\langle E \rangle$, S, heat capacity c_v

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

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

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

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

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

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

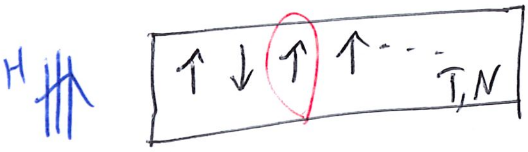
page 49

Application: Information

Pure info. content → physically observable effects
(info. content: knowable in principle)

Consider systems of distinguishable vs indistinguishable spins

Dist'able spins at fixed locations in solid



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

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

$$Z_D = \sum_i e^{-\beta E_i} = \sum_{s_1=\pm1} \cdots \sum_{s_N=\pm1} \exp\left[\beta H \sum_n s_n\right] \qquad x = \beta H = \frac{H}{T}$$

$$= \left(\sum_{s_1=\pm1} e^{xs_1}\right) \cdots \left(\sum_{s_N=\pm1} e^{xs_N}\right) = \left(\sum_{s=\pm1} e^{xs}\right)^N \qquad \text{(Factorization)}$$

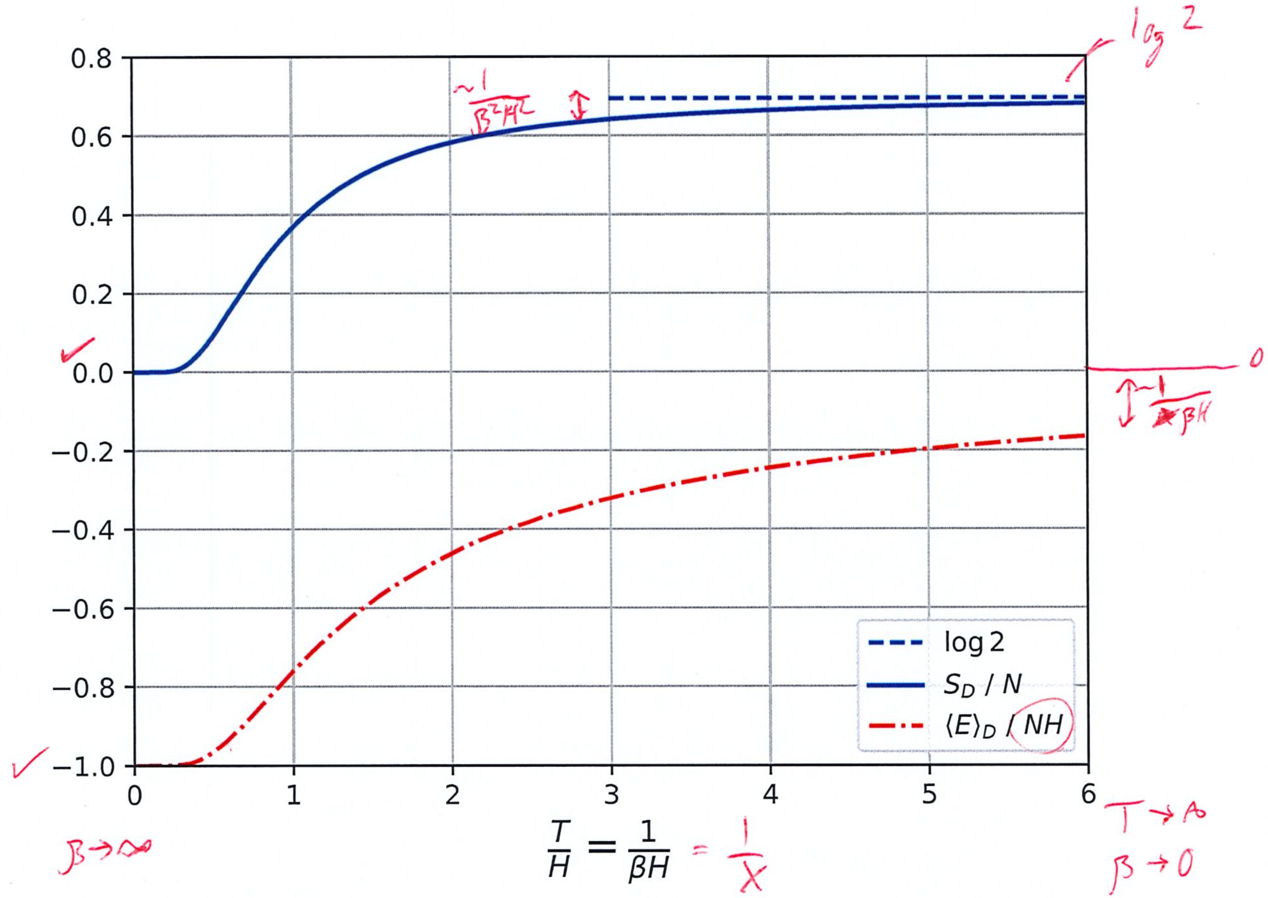
$$= \left(e^{x} + e^{-x}\right)^N = \left[2\cosh(\beta H)\right]^N$$

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

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

page 50

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



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
$\frac{T}{H} = \frac{1}{\beta H} = \frac{1}{X}$
log 2
S_D / N
$\langle E \rangle_D$ / NH
$\sim \frac{1}{\beta^2 H^2}$
log 2
0
$\sim \frac{1}{\beta H}$
$\beta \to \infty$
$T \to \infty$
$\beta \to 0$

Strategy: <u>Expand</u> around simpler limits

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

$$2\cosh(\beta H) \to e^{\beta H} \quad \text{so} \quad \frac{S}{N} \to -\beta H + \beta H \to 0$$

Absolute zero $\to$ single <u>ground</u> state $\qquad E_0 = -NH$

$\to$ zero entropy $\qquad$ (third law)

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

Spin system $\to$ <u>energy levels</u> separated by constant gap
$$\Delta E = E_{n_-+1} - E_{n_-} = 2H$$

Gap controls approach to $T \to 0$ limit

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

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

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

exponential suppression of excited-state effect

page 52

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

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

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

page 52

High-temperature $\beta \to 0$

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

(Recall micro-canonical $T \to \infty$ as conserved $E \to 0$)

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

$$\log 2 + \log\left[1 + \tfrac{1}{2}\beta^2 H^2 + \mathcal{O}(\beta^4 H^4)\right] = \log 2 + \tfrac{1}{2}\beta^2 H^2 + \mathcal{O}(\beta^4 H^4)$$

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

page 53

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

All $p_i = \frac{1}{Z} e^{-E_i/T} \approx \frac{1}{\sum_i e^{-E/T}} \to \frac{1}{M}$

Indist'able spins in freely ~~gas~~ moving gas (one-dim'l)

$H \uparrow\uparrow\uparrow \qquad \uparrow \downarrow \uparrow \uparrow \cdots$

$N=2$ spins $\to$ 3 micro-states $\qquad \uparrow\uparrow \quad \downarrow\downarrow \quad \{\uparrow\downarrow \text{ and } \downarrow\uparrow\}$

<u>not</u> 2^N

Only knowable information is total $\{n_+, n_-\} \to E_{n_-}$

One micro-state for each energy level!

$N=4$ micro-states are $E = -4H, -2H, 0, 2H, 4H$

all up $\qquad$ all down

In general only $N+1$ micro-states

page 54

Label w_k for $E_k = -NH + \underbrace{2Hk}_{\Delta E} = -H(N-2k) \qquad k = 0, 1, \cdots N$

Start with partition function

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

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

$x = e^{-2\beta H} < 1$

$$= \frac{1-x^{N+1}}{1-x}$$

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

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

Difference vs. $F_D \rightarrow$ different $\langle E\rangle_I$ and S_I (2nd homework)

Physically measurable effects from intrinsic info content

"Information is physical"

<u>Application:</u> Classical, non-relativistic ideal gases

$\hookrightarrow$ Not quantum, exactly know (x, y, z) and $\vec{p} = (p_x, p_y, p_z)$

Non-rel. means slow vs. speed of light

$$E_n = \frac{1}{2m} p_n^2 \quad \text{for mass } m$$

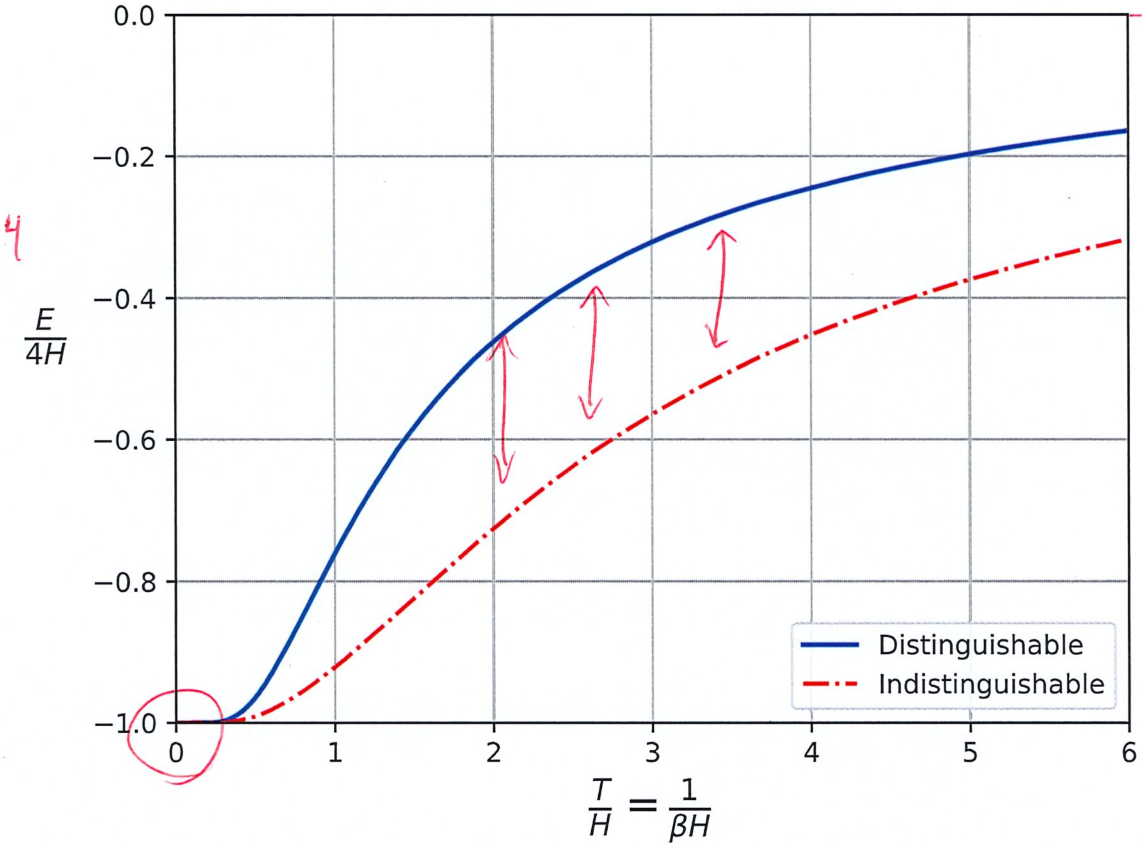
inner product $p^2 = \vec{p}\cdot\vec{p} = p_x^2 + p_y^2 + p_z^2$

Ideal means no interactions between particles

$$E_i = \frac{1}{2m}\sum_{n=1}^{N} p_n^2 \quad \text{for } \omega_i$$

Same $\langle E \rangle \to 0$ as $T \to \infty$

N=4



Differ for intermediate T

Same $T \to 0$ limits due to single ground state

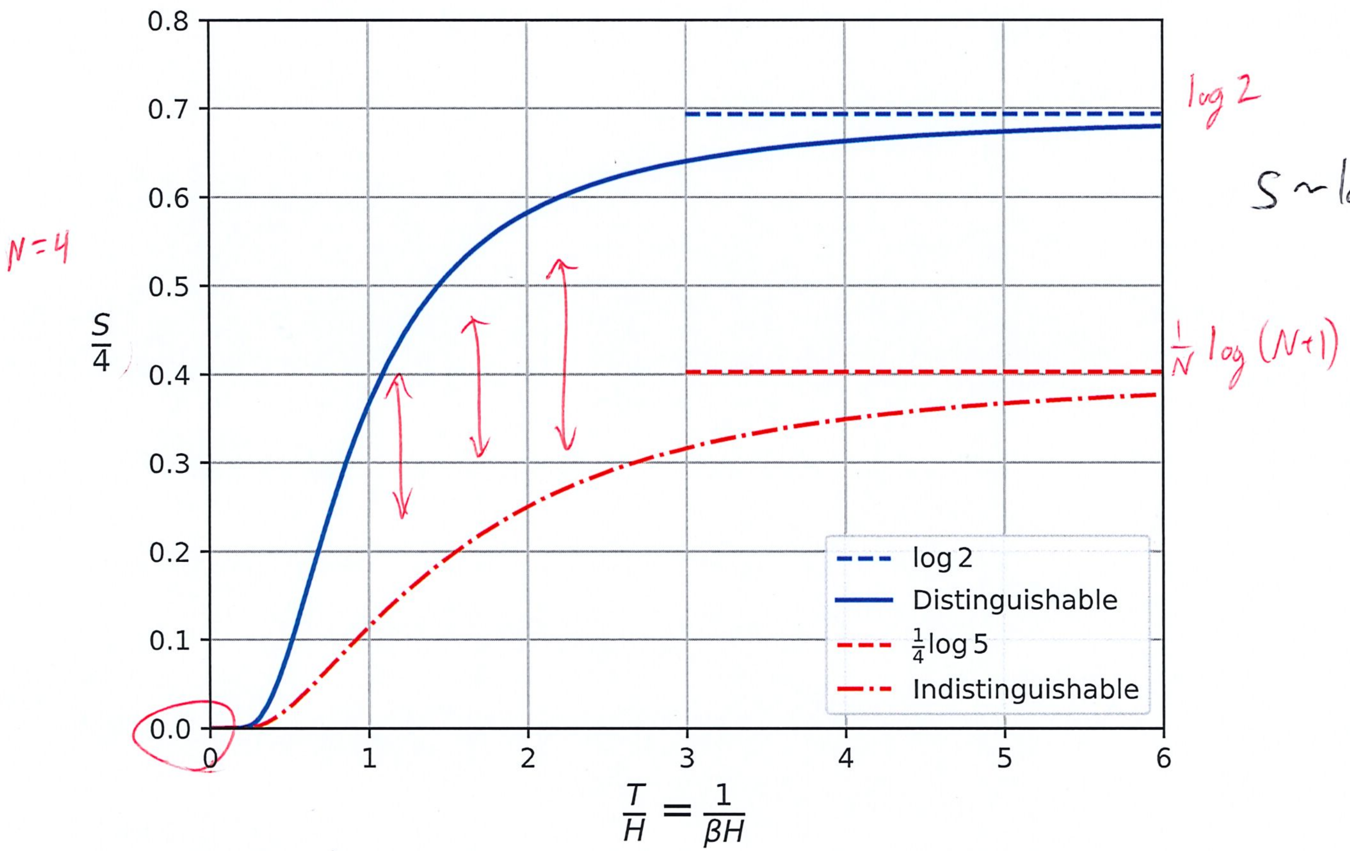
Indist'able approach faster since fewer excited micro-states

Exponentially fewer $M_I = N+1$

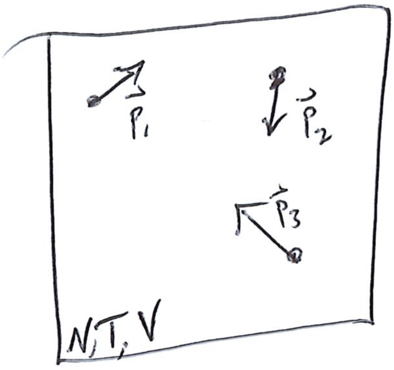
vs. $M_D = 2^N$

$\to$ Different $T \to \infty$ limits

$S \sim \log M$



Same $T \to 0$ limit



N particles in cubic box of volume $V = L^3$

T fixed by thermal reservoir

start with partition function $Z = \sum_i e^{-\beta E_i}$

problem

uncountable micro-states

depend on continuous $\{\vec{p}_n\}$

Need to <u>regularize</u> system

↳ countable micro-states with well-defined Z

Then take limit of sums → integrals