MATH327: Statistical Physics

Monday, 27 February 2023

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Something to consider

Last week we met the canonical partition function,

$$Z = \sum_i e^{-E_i/T},$$

which sums over all micro-states ω_i.

What can we do if there are uncountably many micro-states?

Recap

Micro-canonical temperature behaves sensibly

Canonical ensemble

Based on partition function $Z = \sum_i e^{-\beta E_i}$

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

derived energy $\langle E \rangle$, entropy S, heat capacity c_v

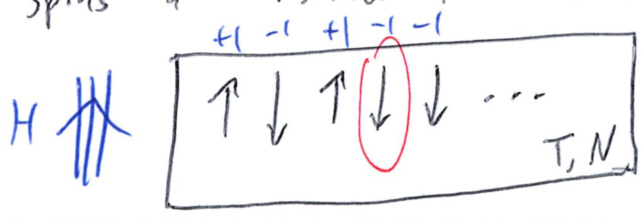
Application: Information

Pure info content → physically observable effects

(info content: knowable in principle)

Simple example: Spin systems with {distinguishable / indistinguishable} spins

Distinguishable spins at fixed locations in solid



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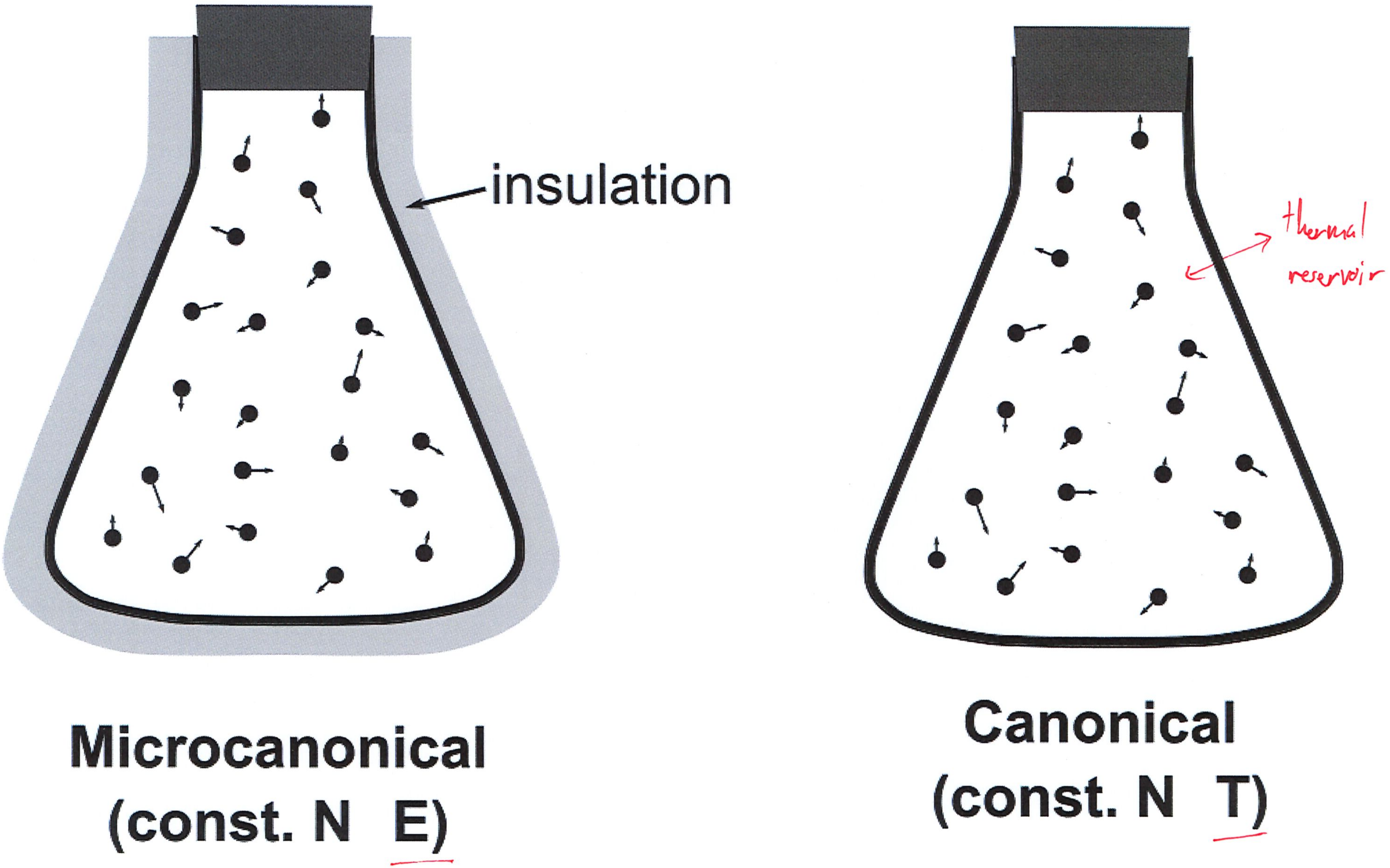


$M = 2^N$ micro-states w_i with energies E_i
and probabilities $p_i = \frac{1}{Z} e^{-E_i/T}$

Call parallel spins $s_n = 1$
anti-parallel spin $s_n = -1$

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

Start with the partition function

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

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

$$= \left(\sum_{s=\pm 1} e^{x s}\right)^N = \left(e^x + e^{-x}\right)^N = \left[2\cosh(\beta H)\right]^N$$

(Factorization)

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

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

$$= -N \frac{\partial}{\partial \beta} \log\left[2\cosh(\beta H)\right] = \frac{-N}{2\cosh(\beta H)} (2\sinh(\beta H)) \cdot H$$

page 50

$$= -NH \tanh(\beta H)$$

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

$\log(e^{\beta H})$

Low-temperature limit

$\beta \to \infty$ $\langle E \rangle_D = -NH \tanh(\beta H) \to -NH = E_0$ ✓

ground state

Absolute zero temperature $\to$ single ground state
zero entropy

$S_D \to -N\beta H + N\beta H = 0$

Low-temperature expansions

$T>0$ allows contributions from higher-energy micro-states $E_i > E_0$ "excited states"

suppressed $\sim p_i = e^{-E_i/T}$

Spin system → energy levels separated by constant energy gap

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

$$E = -H(2n_+ - N)$$

Gap controls approach to zero-temperature limits

$$\frac{\langle E \rangle_D}{NH} = -\tanh(\beta H) \qquad \text{expand } \beta H \gg 1 \qquad e^{-2\beta H} \ll 1$$

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

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

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

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

page 52

exponential suppression of excited-state effects

$$\frac{p_{n_-+1}}{p_{n_-}} = \frac{e^{-(E_{n_-+1})/T}}{e^{-E_{n_-}/T}} = e^{-\beta \Delta E}$$

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

$$\downarrow$$

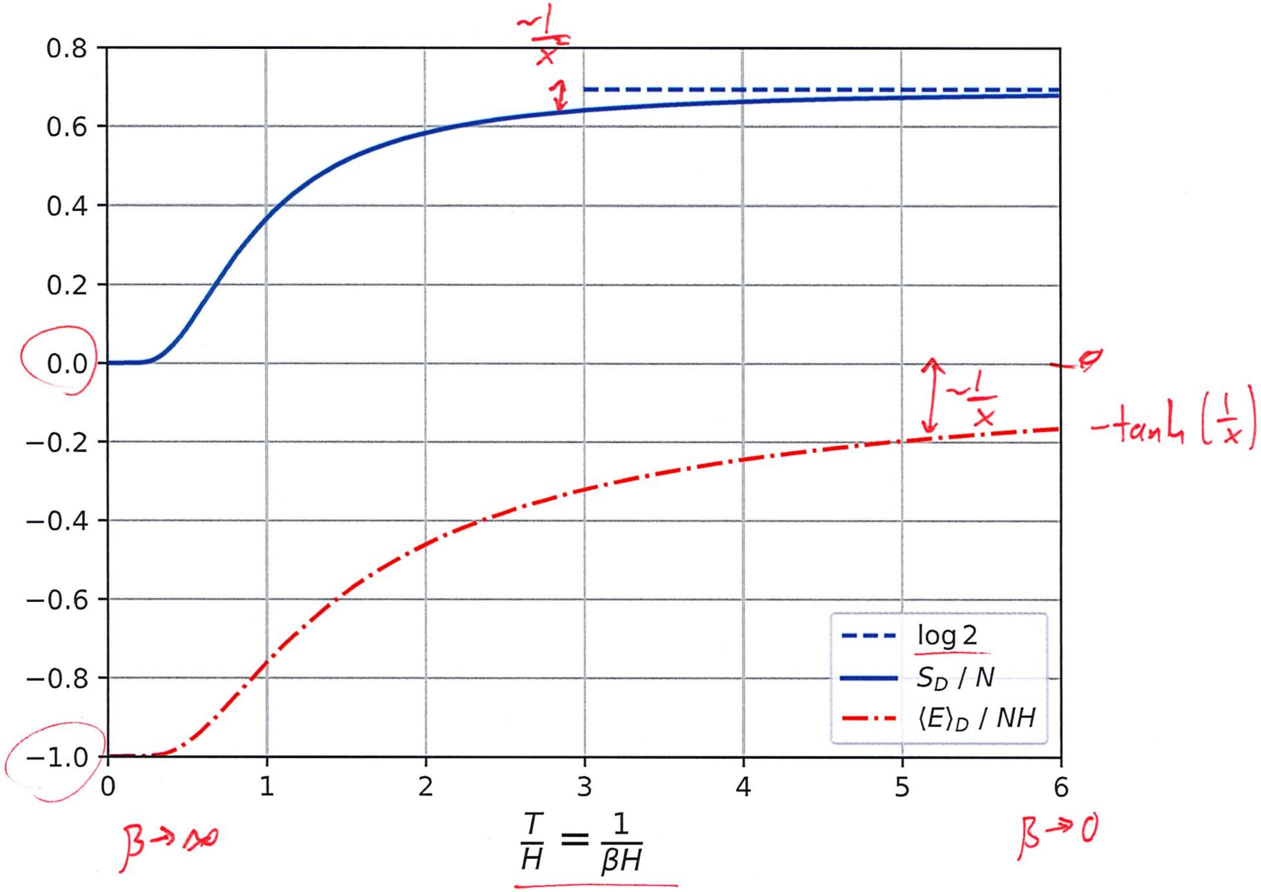
$$\cancel{1} + 2e^{-\beta\Delta E} + \mathcal{O}(e^{-2\beta\Delta E})$$

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

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

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

page 52


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
$\sim\frac{1}{x}$
$\sim\frac{1}{x}$
$-\tanh\left(\frac{1}{x}\right)$
$\beta \to \infty$
$\beta \to 0$

High-temperature expansions

$$\frac{\langle E\rangle_D}{NH} = -\tanh(\beta H) = -\beta H + \frac{(\beta H)^3}{3} + \mathcal{O}([\beta H]^5) \to 0 \quad \text{as } \beta \to 0 \; (T\to\infty)$$

$\beta H << 1$

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

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

$\downarrow$

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

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

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

Note $S_D \to N\log 2 = \log 2^N = \log M$ (micro-canonical)

as $T\to\infty$

all $P_i = \frac{1}{Z} e^{-E_i/T} \approx \frac{1}{Z} \approx \frac{1}{M}$ $\qquad Z = \sum_i e^{-E_i/T} \approx M$

Indistinguishable spins in freely moving gas (one-dim.)

H ⇈ $\uparrow \downarrow \uparrow \downarrow \downarrow \ldots$ T, N

$N=2$ spins $\to$ three micro-states, not 2^N

w_1 $\uparrow\uparrow$ $\quad \left\{\begin{matrix}\uparrow\downarrow \\ \downarrow\uparrow\end{matrix}\right\}$

w_2 $\downarrow\downarrow$ $\quad w_3$

In general, can only know total $\{n_+, n_-\}$ for each w_i ($\nearrow E_{n_-}$)

One micro-state for each energy level!

Example: For $N=4$, the micro-states are $E = -4H, -2H, 0, 2H, 4H$ (all up … all down)

$N+1$ micro-states in general

Label micro-state ω_k with $E_k = -NH + 2Hk = -H(N-2k)$

(ΔE) $k = 0, 1, \cdots N$

Start with partition function

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

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

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

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

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

~~Helm~~ Helmholtz free energy

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

Clearly different vs. $F_D = \frac{-N}{\beta} \log[2\cosh(\beta H)]$

↳ Lead to different $\langle E \rangle_I$ and S_I (homework)

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

Energy $\to 0$ as $T \to \infty$

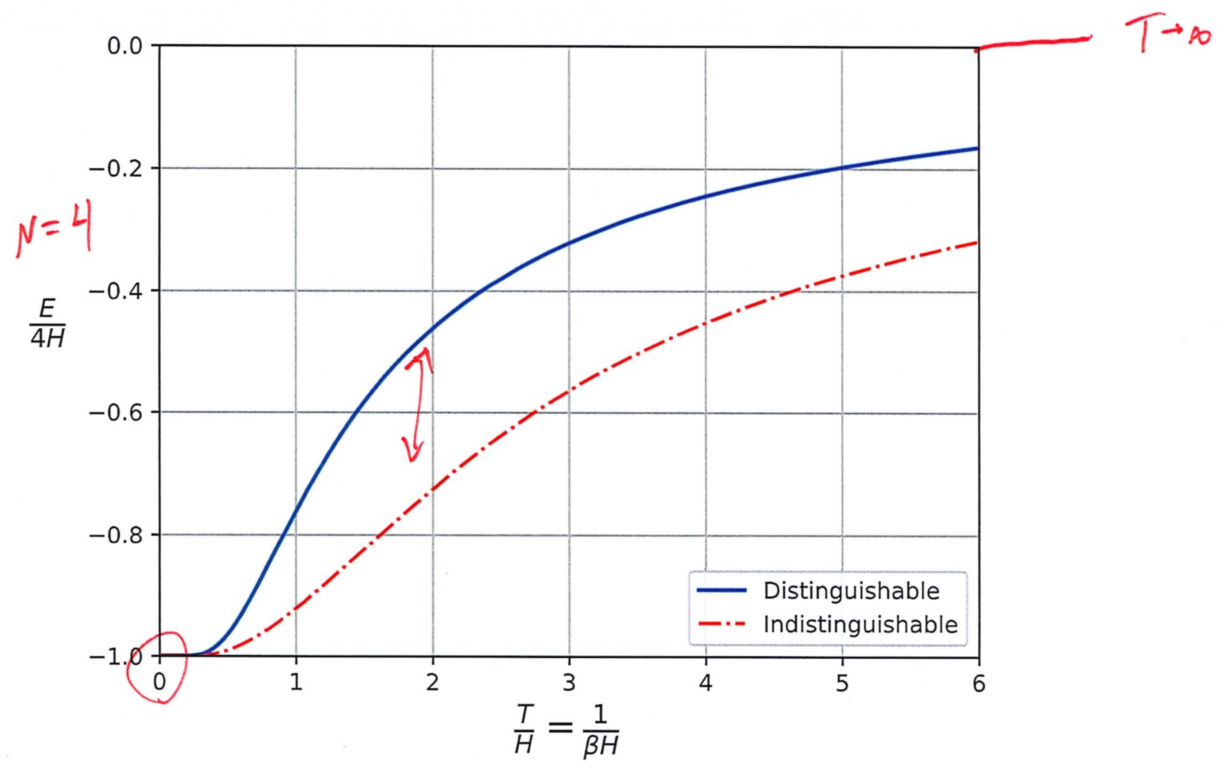
High-temperature $S_I \to \log(N+1) = \log M$

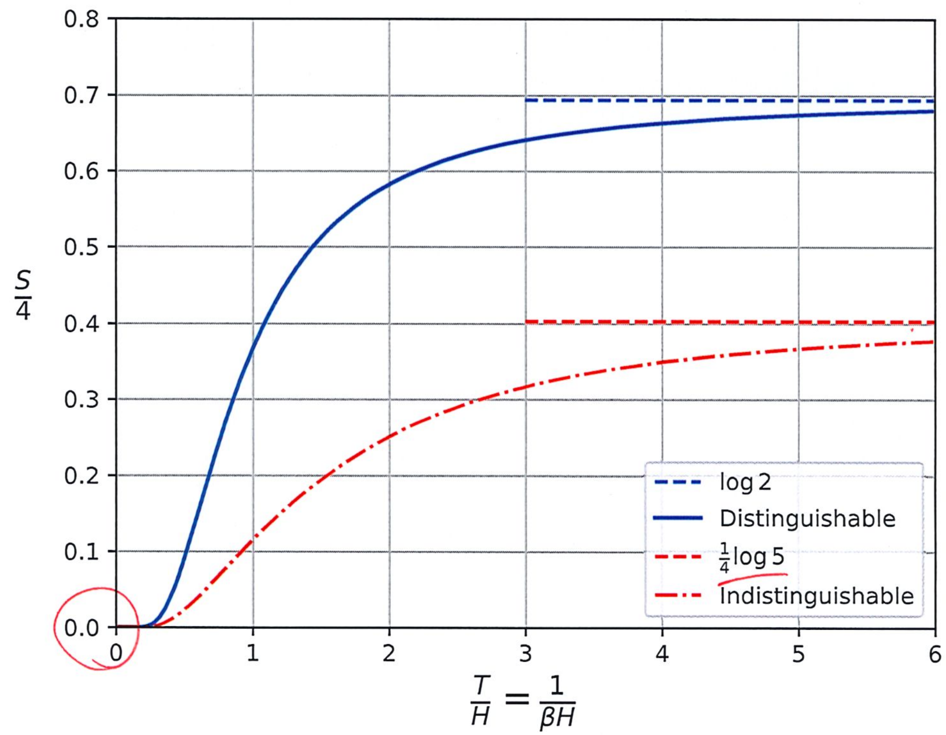
exponentially fewer micro-states

$N+1$ vs. $2^N = \exp(N \log 2)$

Physically measurable effects from intrinsic info content

"Information ~~is~~ is physical"


N=4
T→∞
0.0
−0.2
−0.4
−0.6
−0.8
−1.0
$\frac{E}{4H}$
0
1
2
3
4
5
6
$\frac{T}{H} = \frac{1}{\beta H}$
Distinguishable
Indistinguishable


0.8
0.7
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0.2
0.1
0.0
$\frac{S}{4}$
0
1
2
3
4
5
6
$\frac{T}{H} = \frac{1}{\beta H}$
log 2
Distinguishable
$\frac{1}{4}\log 5$
Indistinguishable

Application: Ideal gases

Classical, non-relativistic, ideal gases

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

Non-rel. means slow particles (compared speed of light)

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

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

Ideal means no interactions between particles

$$E = \frac{1}{2m} \sum_{n=1}^{N} p_n^2$$

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

Temperature T fixed by thermal reservoir

Start with partition function

$$Z = \sum_i e^{-E_i/T} \qquad E_i \text{ from continuous } \vec{p}_n$$

problem

Need to regulate system

↳ countable micro-states with well-defined partition func

Then limit of sum → integral

Declare that only possible momenta are

$$\vec{p} = (p_x, p_y, p_z) = \hbar \frac{\pi}{L} (k_x, k_y, k_z) \qquad k_{x,y,z} = 0, 1, 2, \ldots$$

countable

Planck constant

unit conversion from $\frac{1}{L}$ to p

Similar "quantized" momenta realized of nature

Here just ansatz

Energies are also countable

$$E_k = \frac{p^2}{2m} = \frac{\hbar^2\pi^2}{2mL^2}\left(k_x^2 + k_y^2 + k_z^2\right) = \varepsilon\left(k_x^2 + k_y^2 + k_z^2\right)$$

$$\varepsilon = \frac{\hbar^2\pi^2}{2mL^2}$$

Lowest energies

$$E = \varepsilon\{0, 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13, 14, 16, 17, \dots\}$$

No 7, 15, ~~16~~ ...

page 57