Recap: $Z = \sum_i e^{-\beta \varepsilon_i}$, $\beta = \frac{1}{k_B T}$

Canonical Ensemble (const N, V, T)

$$A = -k_B T \ln Z(N,V,T) = \langle E \rangle - T\langle S \rangle$$

$$Z = \frac{1}{h^{3N} N!} \int d\underline{X}\, e^{-\beta H(\underline{X})}$$

potential + kinetic E

$$Q = h^{3N} N!$$

units

mixing entropy (indisting.)

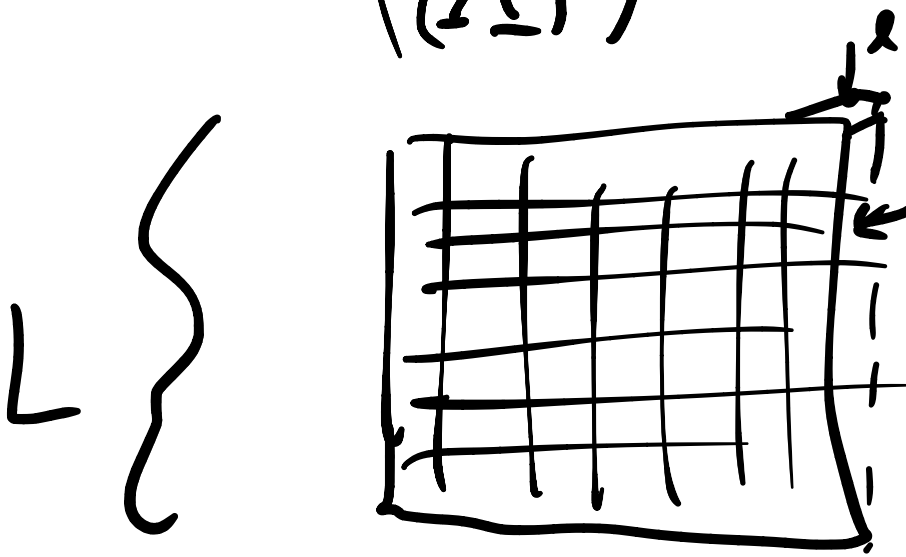
$$X = (q_1^x, q_1^y, q_1^z, \ldots, q_N^x, q_N^y, q_N^z, p_1^x, p_1^y, \ldots\ldots p_N^z)$$

$$\int dq_1 dq \ldots q_N = V^N$$

$$\int dp_1\, dp_2 \ldots dp\; e^{-\sum p^2/2mk_BT} = (2\pi m k_B T)^{3/2}$$

$$Q \sim \left(\frac{V}{(\Lambda)^3}\right)^N$$

Λ – thermal wavelength



$v = l^3$

$$l = \frac{L}{\Lambda}$$

$$V = L^3, \quad L \sim V^{1/3}$$

$$\langle \varepsilon \rangle = \sum \varepsilon_i P_i = \sum \varepsilon_i \left(e^{-\beta \varepsilon_i} / Z \right)$$

$$= \frac{1}{Z} \sum \varepsilon_i e^{-\beta \varepsilon_i}$$

$$Z = \sum e^{-\beta \varepsilon_i}$$

$$\frac{de^{ax}}{dx} = ae^{ax}$$

$$\frac{\partial Z}{\partial \beta} = \sum -\varepsilon_i e^{-\beta \varepsilon_i}$$

$$\frac{de^{ax}}{da} = xe^{ax}$$

$$\frac{\partial \ln Z}{\partial \beta} = \frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{-1}{Z} \sum \varepsilon_i e^{-\beta \varepsilon_i} = -\langle \varepsilon \rangle$$

$$\boxed{\langle \varepsilon \rangle = -\partial \ln Z / \partial \beta}$$

$$C_V = \left(\frac{\partial \langle \varepsilon \rangle}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\left[-\frac{\partial \ln Z}{\partial \beta}\right]\right)_V$$

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

$$\beta = \frac{1}{k_B T}, \quad \frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2}$$

$$= -k_B \beta^2 \left(\frac{\partial \varepsilon}{\partial \beta}\right)_V$$

$$C_V = -k_B \beta^2 \left(\frac{\partial}{\partial \beta}\left[-\frac{\partial \ln Z}{\partial \beta}\right]_V\right)_V$$

$$= k_B \beta^2 \frac{\partial^2}{\partial \beta^2}(\ln Z)$$

practice

$$C_V = k_B \beta^2 \cdot \left[\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 \right]$$

$$= \frac{1}{k_B T^2} \mathrm{Var}(\varepsilon) \quad \checkmark$$

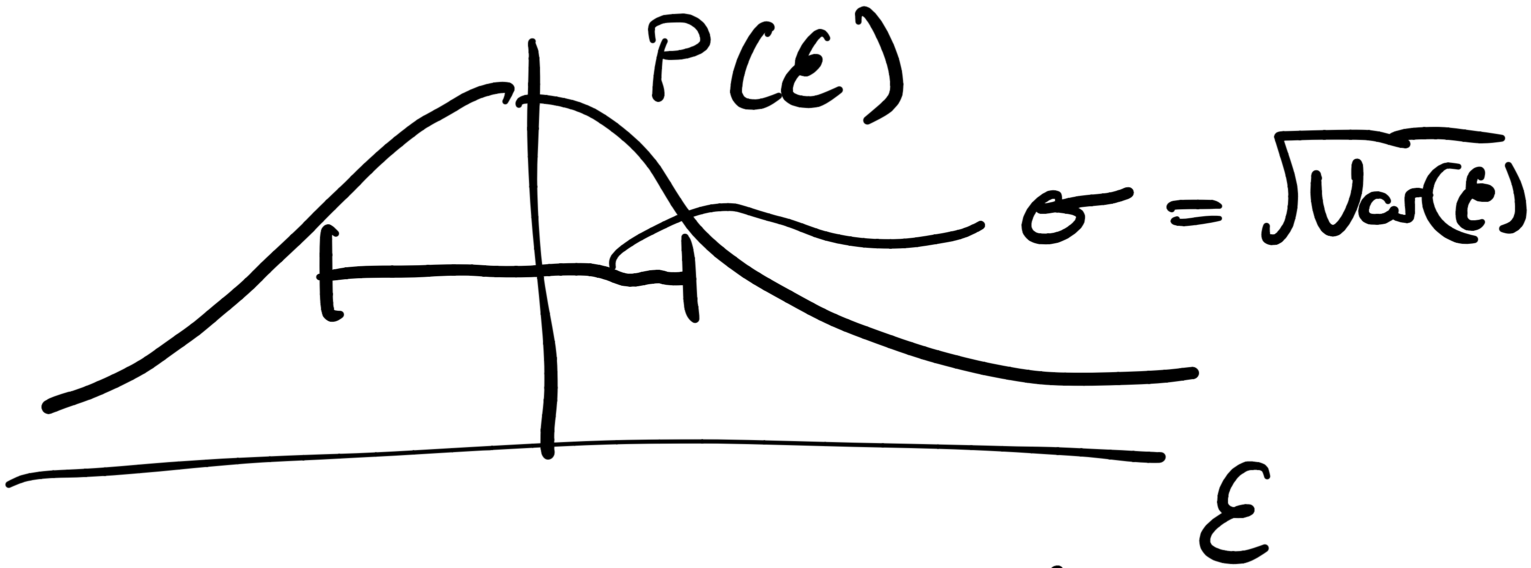
Spread of energies $\propto C_V$

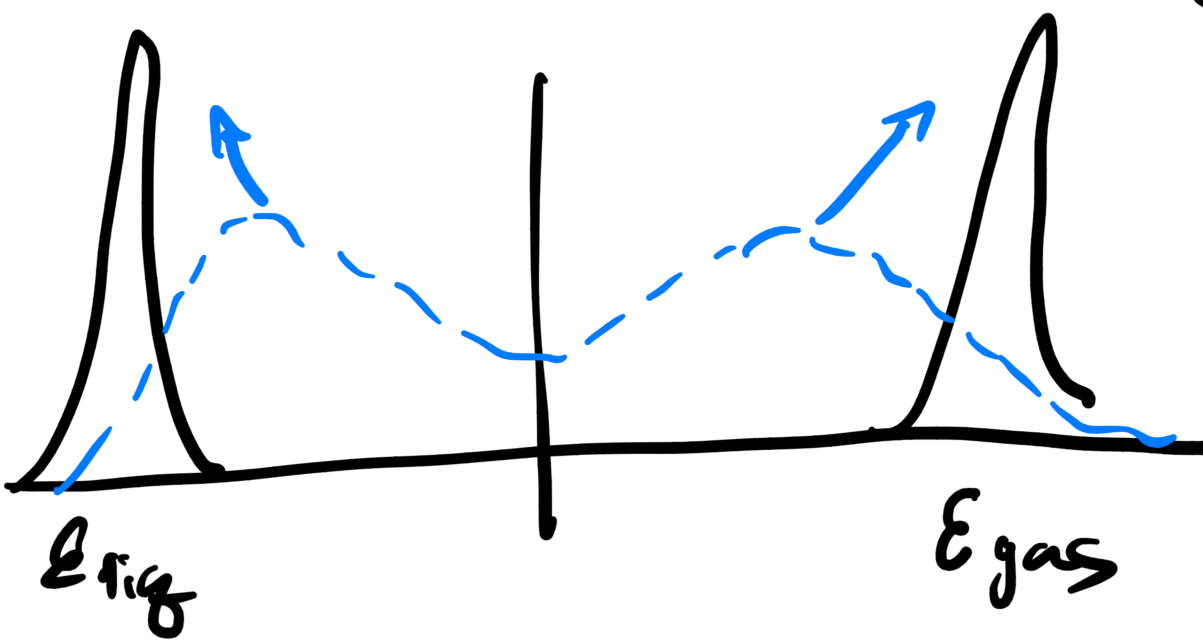
① $\frac{\partial \varepsilon}{\partial T} \propto \mathrm{Var}(\varepsilon)$, example

- fluctuation – dissipation theorem
- linear response

(2) heat capacity $\propto$ variance energy

variance in $\mathcal{E}$ can be big in 2 ways



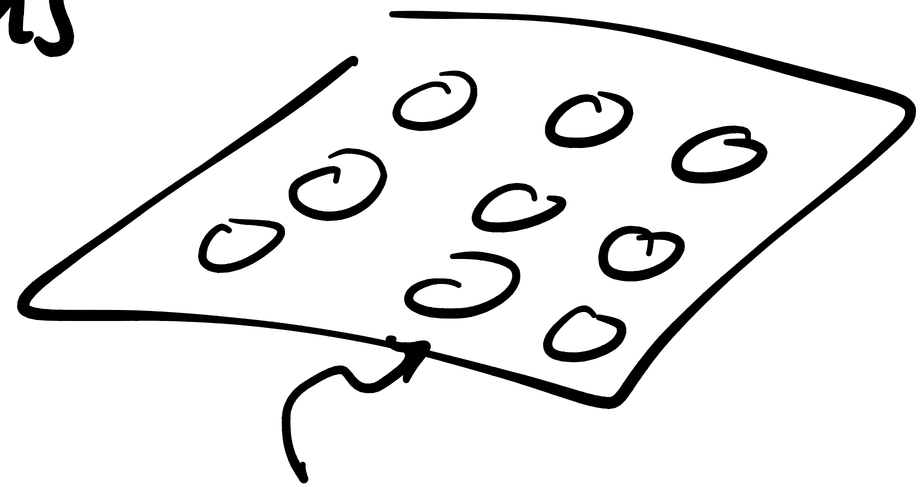


Magnetism

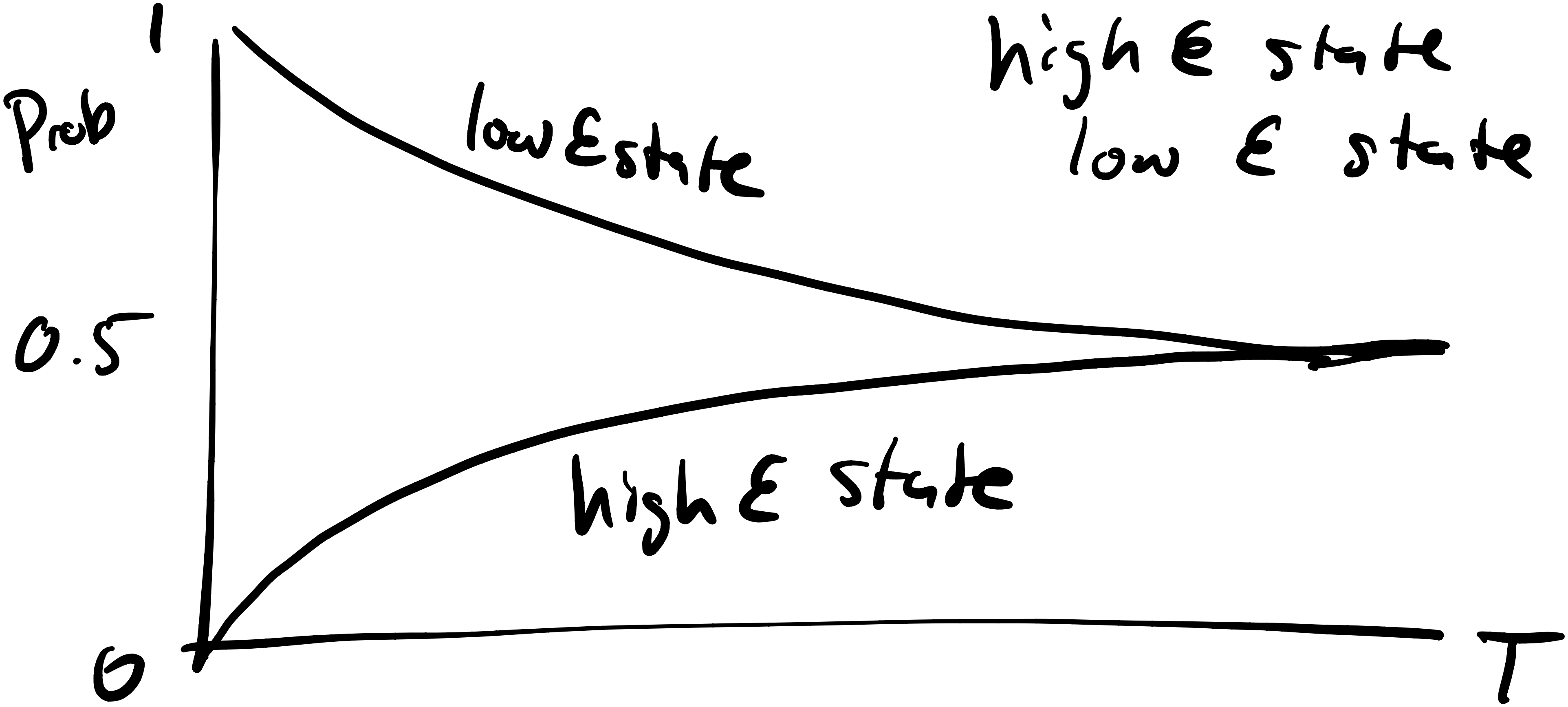
2-level systems

ε_2 —

ε_1 ↿

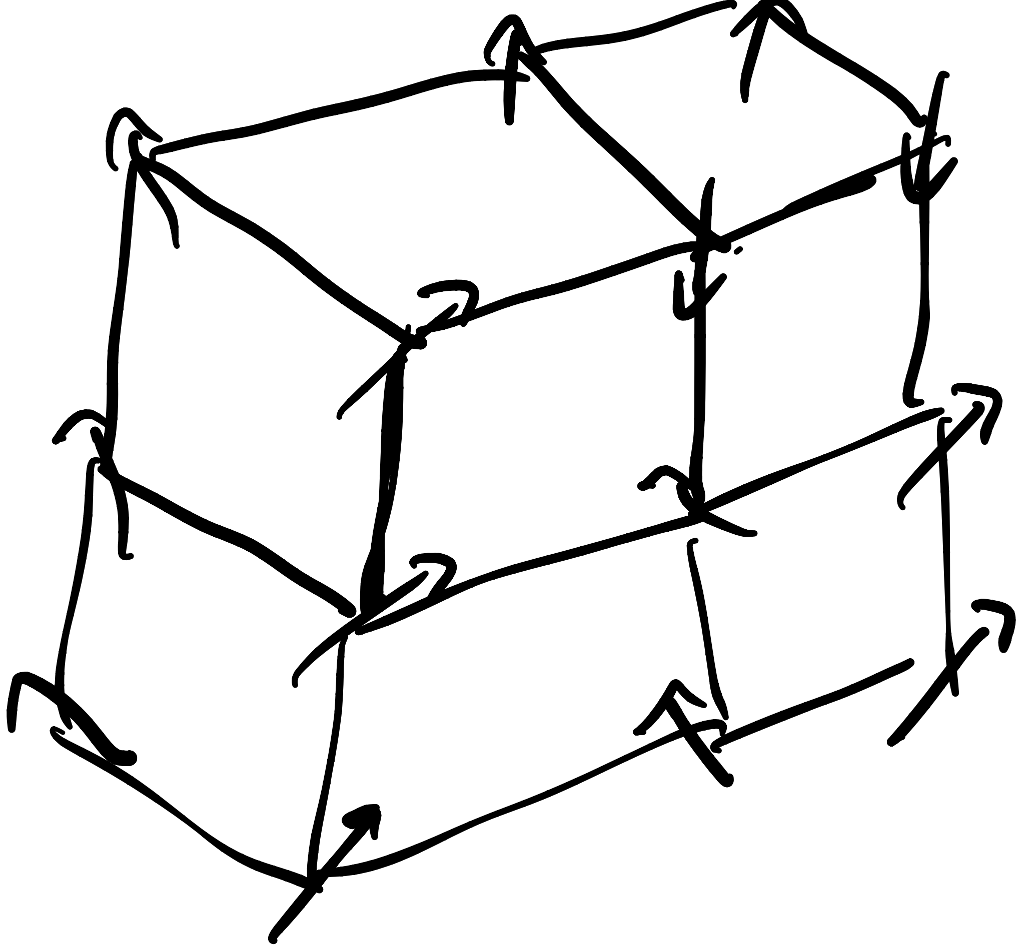


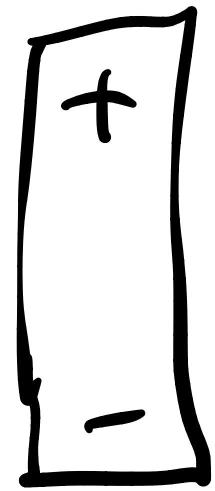
$$Z_{TLS} = \sum_{i=0}^{1} e^{-\beta \varepsilon_i}$$



$$P_i \propto e^{-\beta \varepsilon_i} = e^{-\varepsilon_i / k_B T}$$

$$\langle \varepsilon \rangle = \sum \varepsilon_i P_i \begin{cases} \xrightarrow{\text{high } T} (\varepsilon_0 + \varepsilon_1)/2 \\ \xrightarrow{\text{low } T} \varepsilon_0 \end{cases}$$





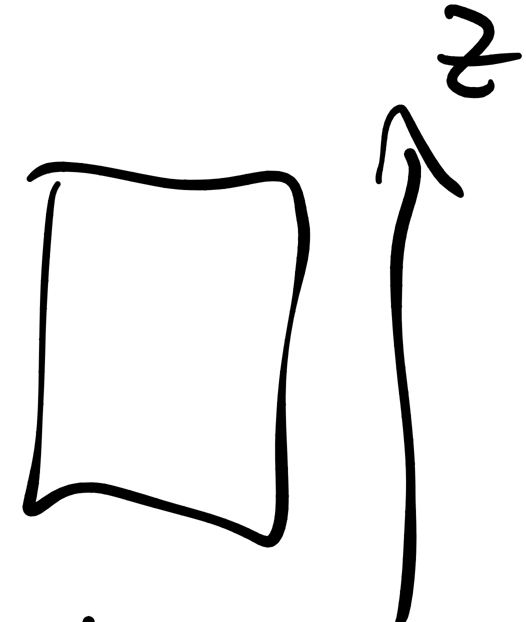
$(\uparrow\downarrow) \leftarrow$ cancel out

spins like to align (ferromagnetic)

if in a field, then they'll tend to align with the field

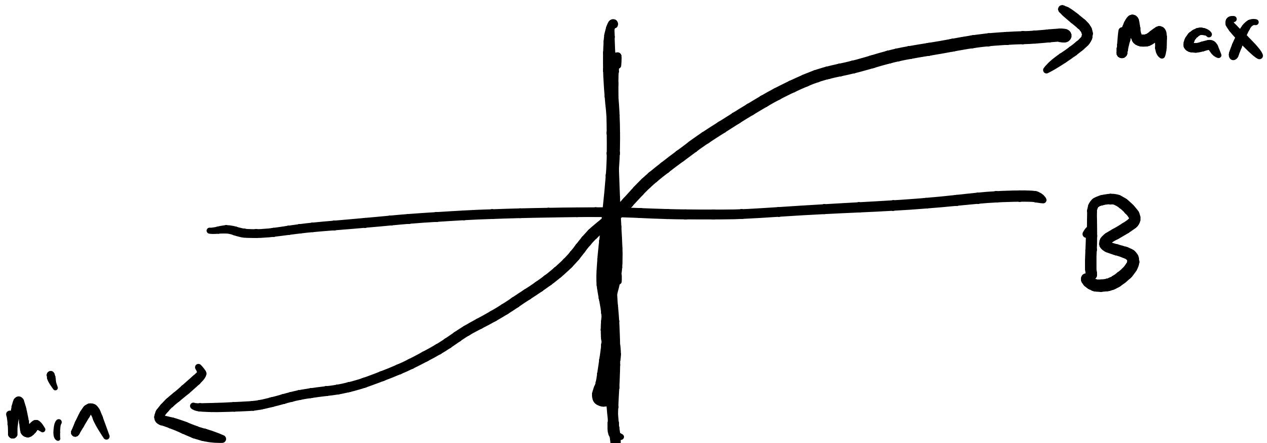
$$M = \sum_i \vec{\mu}_i \cdot \hat{z}$$

magnetic moment



maximum for N spins is $N\mu$

minimum is $-N\mu$



$m = \frac{M}{N\mu}$ $\Big\{$ from $\begin{matrix} +1 \\ -1 \end{matrix}$

$+B$ @ high T, lower T

so spins stuck

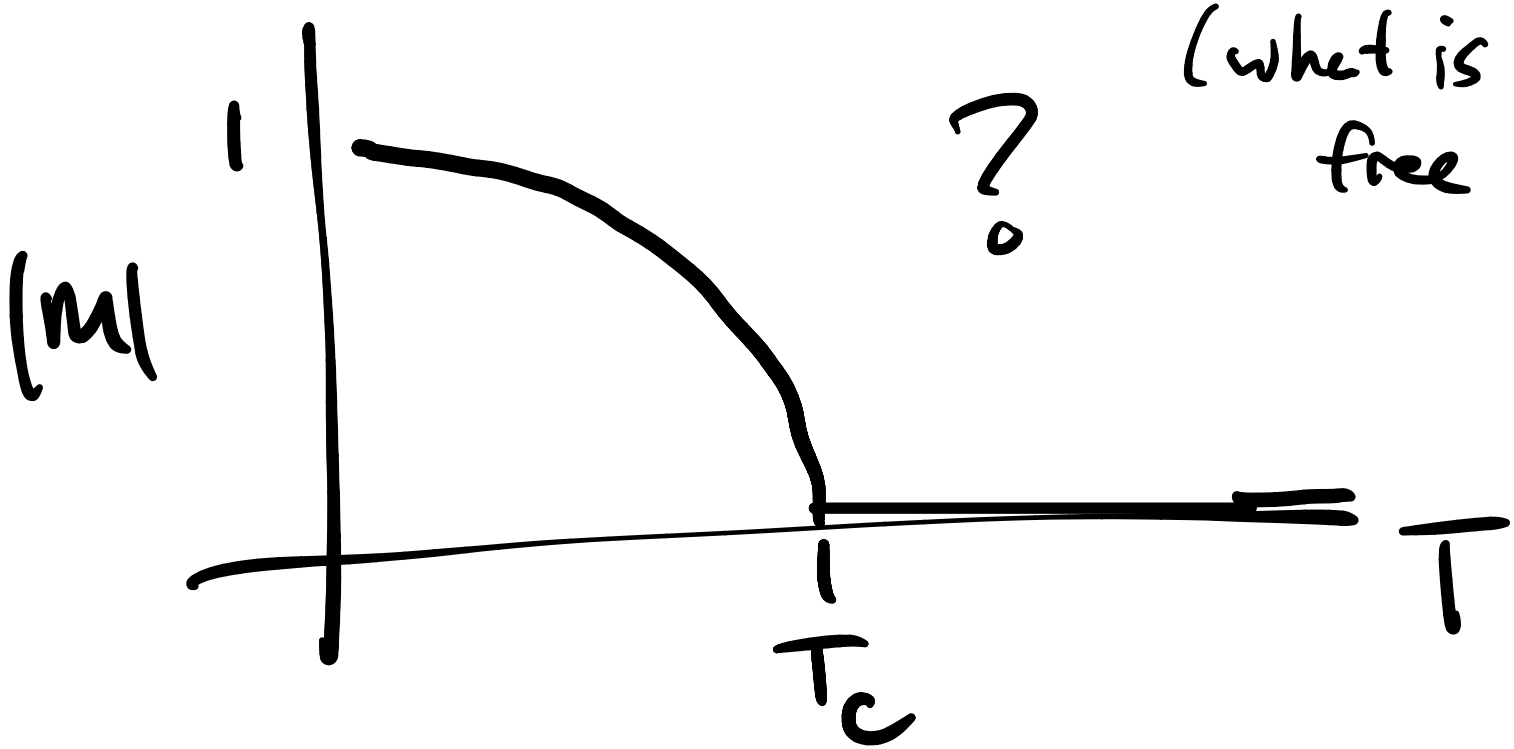
remove field → magnet

What if you don't have a field?

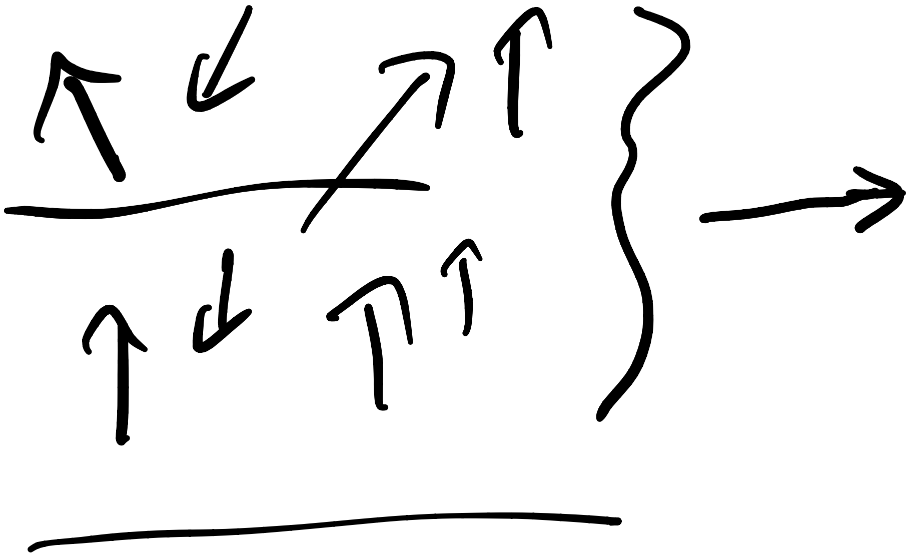
@ high T $\langle m \rangle = 0$

$\langle \vec{\mu} \rangle = 0$

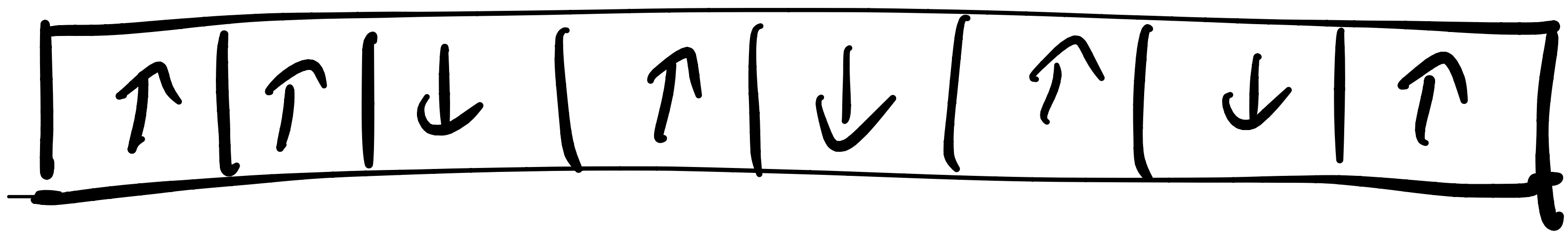
@ low T do all spins align, $|\langle m \rangle| > 0$



(what is lowest free energy)



Ernst <u>Ising</u>



S.A. 1d – no phase transitions

2d – yes!, Onsager exact solution

3d+ – yes p.t., no solution, analytical Z

S_i ← site $= \pm 1/2$ (± 1 or $0, 1$)

$\mathcal{E}_{field} = -h s_i$ pointing up

(low energy is good)

$\mathcal{E}_{neighbors}$

$= -J s_i s_{i-1} - J s_i s_{i+1}$

$= -\frac{J}{2} s_i (s_{i-1} + s_{i+1})$

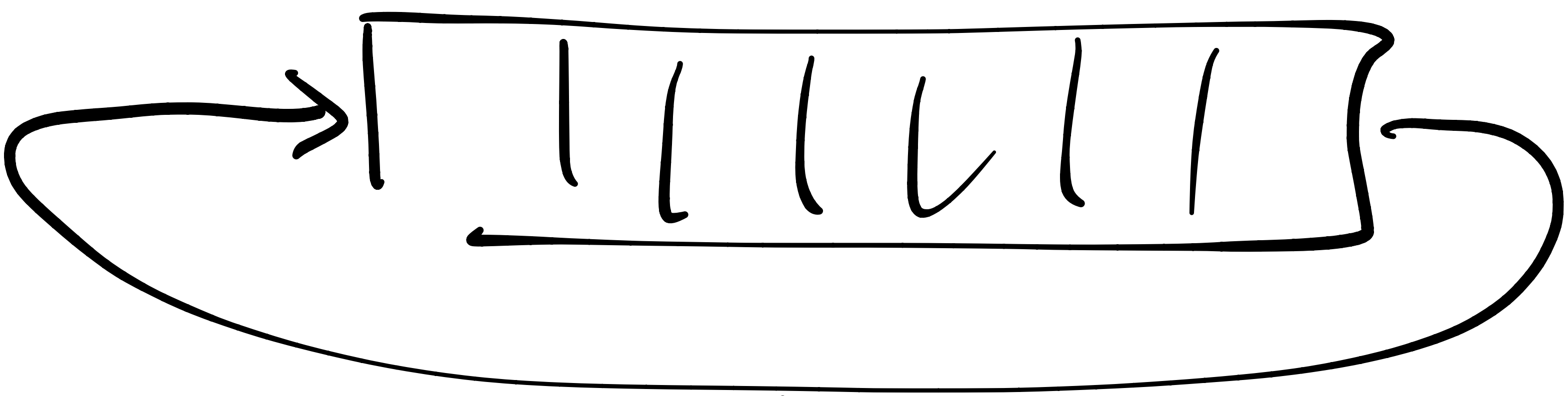
← don't double count

~~and~~ ferromagnit (like align)

$$E_{total} = \sum_{i=2}^{N-1} -\frac{J}{2} s_i (s_{i-1} + s_{i+1}) - h s_i$$

(+ ends)

$\sum_{i=1}^{N}$ if $s_{N+1} = s_1$



periodic boundaries
pseudo infinite

$$Z = \sum_{\text{states}} e^{-\beta E(s_1 \ldots s_N)}$$

$$= \sum_{s_1=-1/2}^{+1/2} \sum_{s_2} \sum_{s_3} \cdots \sum_{s_N} e^{-\beta E(s_1 \ldots s_N)}$$