Partition function

$$Z = \sum_{\text{states } i} BF(i)$$

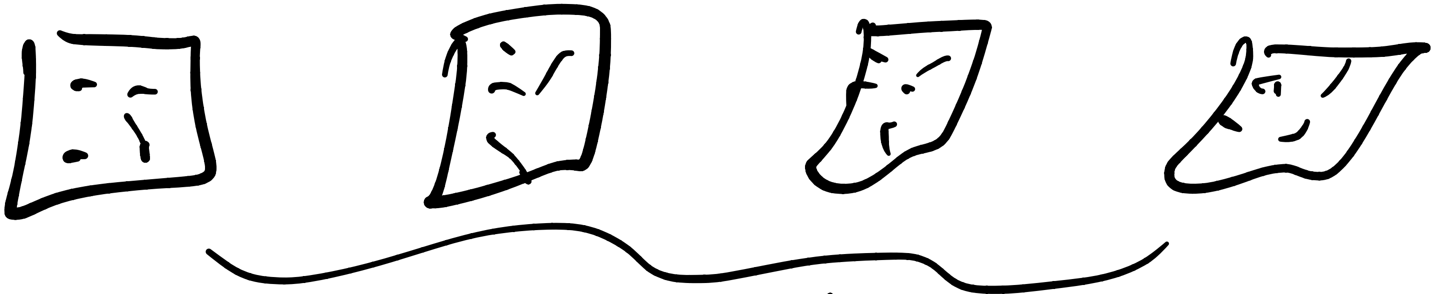
← Boltzmann factor (weigh of state i)

$$P(i) = BF(i)/Z$$

what is $P(i)$ for constant N, V, T

states are the different arrangements of atoms

Assert: maximize entropy for an ensemble of configurations, with constraints



ensemble

constraint that $\langle \mathcal{E} \rangle$ is fixed

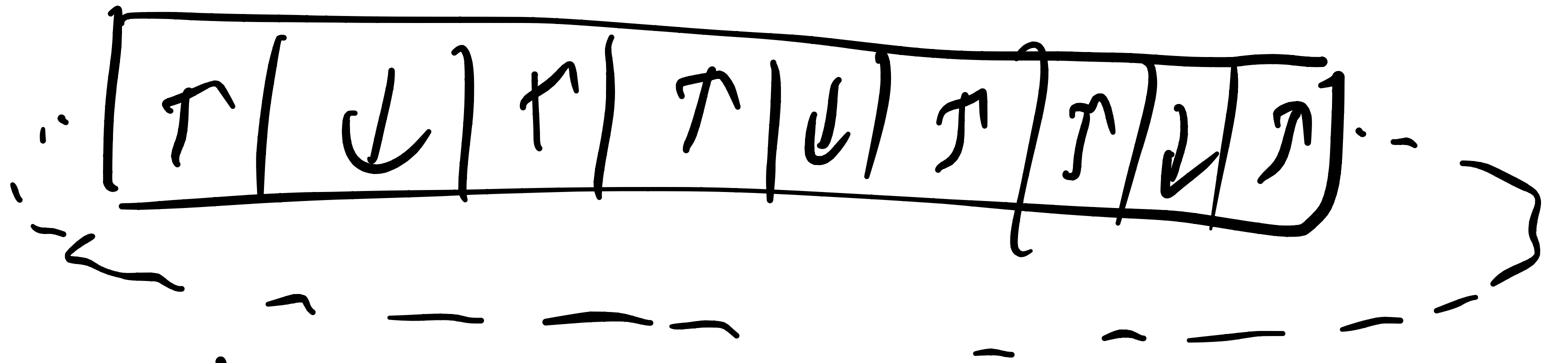
total energy for all of them is fixed

$\ln \Omega$, with $\sum_i m_i = M$ $\quad \sum_i m_i \epsilon_i = \mathcal{E}$

$P_i = \frac{m_i}{M}$ proportional to $e^{-\alpha} e^{-\beta \epsilon_i}$

$\sum P_i = 1 \Rightarrow \quad P_i = e^{-\beta \epsilon_i} / \sum_i e^{-\beta \epsilon_i}$

Ising model



$$E = \sum_{i=1}^{N} \underbrace{-J s_i s_{i+1}}_{\text{neighbors}} - h s_i$$

field

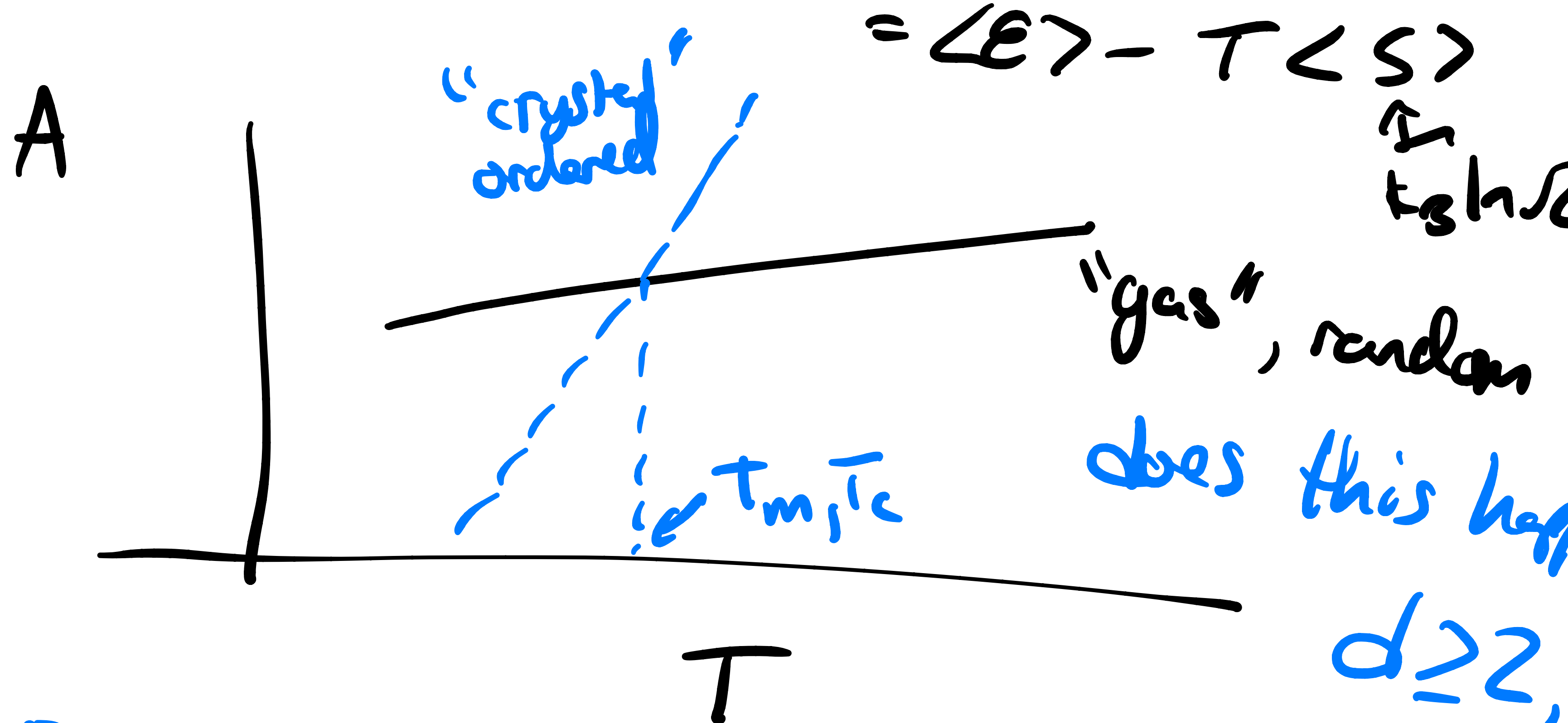
$J > 0$, lowers energy to point in the same direction

Do they point all in the same direction?

What decides if there is a phase transition

$$A = -k_B T \ln Z$$
$$= \langle E \rangle - T \langle S \rangle$$

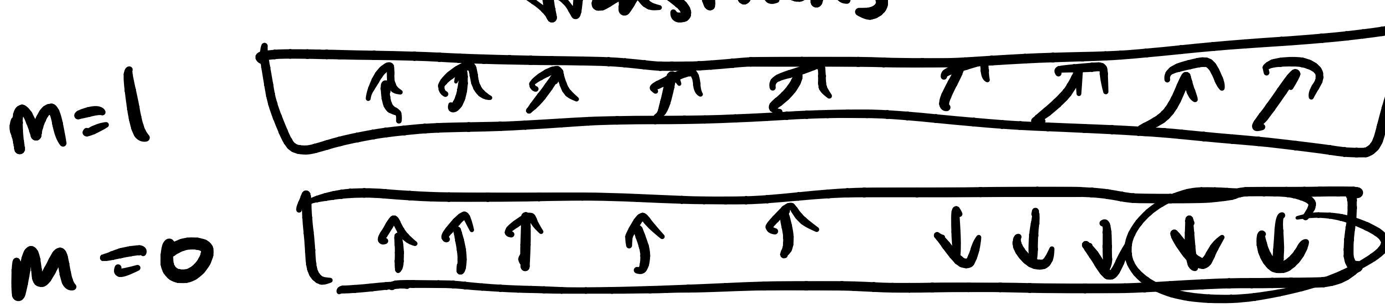
$k_B \ln \Omega$



does this happen?

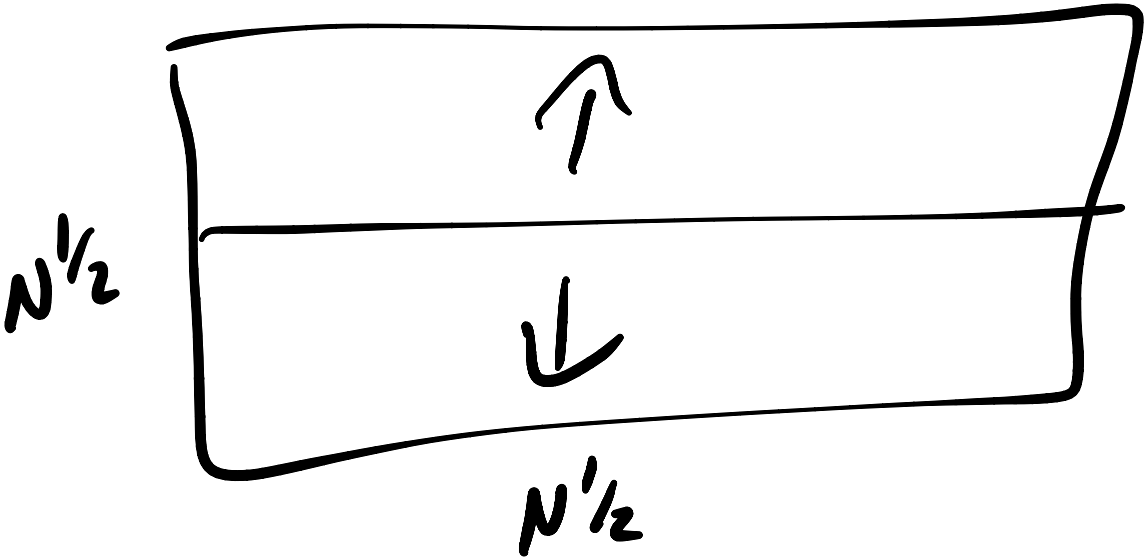
$d \geq 2$, yes

$h=0$
$d=1$, no phase transitions



$E_{min} \sim -N\left(\frac{J}{4} + \cancel{\frac{h}{2}}\right)$

$E = E_{min} + J/4$



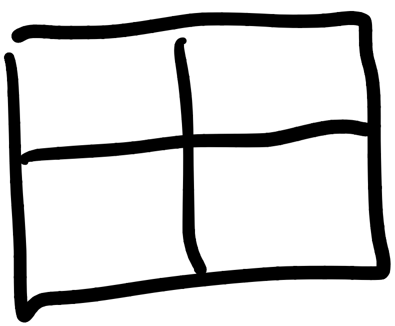
$h = 0$

$\mathcal{E} = \mathcal{E}_{min} + cJ$

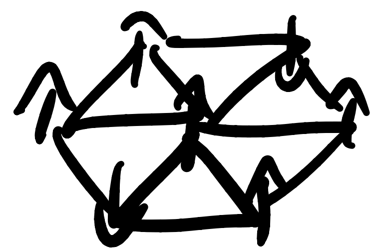
$c \sim N^{1/2}$

interface scales like $N^{1/2}$, $\mathcal{E} \propto N$

~ surface tension



$$\sum_{\langle ij \rangle} -J s_i s_j$$



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

\# states is

$2 \times 2 \times 2 \ldots = 2^N$

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

$$\sum_{s_1 = \pm 1/2} \sum_{s_2 = \pm 1/2} e^{-\beta E(s_1, s_2)} = e^{-\beta E(+,+)} + e^{-\beta E(+,-)} + e^{-\beta E(-,+)} + e^{-\beta E(-,-)}$$

what is $\langle s_i \rangle$?

$$E = \sum_{i=1}^{N} -J \underbrace{s_i s_{i+1}}_{\text{neighbors}} - h s_i$$

field

$$\sum_{\text{states}_i} \sum_{j=1}^{N} s_j \; e^{-\beta E(\text{state}_i)} \Big/ Z$$

$$e^{+\beta h \sum_{j=1}^{N} s_j}$$

$$\langle s \rangle = \frac{1}{N} \sum_{j=1}^{N} s_j$$

$$\frac{\partial \ln Z}{\partial h} = \frac{1}{Z} \cdot \frac{\partial Z}{\partial h} = \frac{\beta}{Z} \sum_{\text{states}_i} \left(\sum_j s_j\right) e^{-\beta E(i)}$$

$$\langle s \rangle = \frac{1}{N} \langle \sum s_j \rangle = \frac{k_B T}{N} \partial \ln Z / \partial h = -\frac{1}{N} \frac{\partial \ln A}{\partial h}$$

What cases can we solve:

$$\langle s \rangle = \frac{k_B T}{N} \frac{\partial \ln Z}{\partial h}$$

① $T \to \infty$, BF $e^{-E/k_B T} \to 1$

$$Z = \sum_{\text{states}} (1) = 2^N$$

$$\partial \ln Z / \partial h = 0 \implies \langle s \rangle = 0$$

② $J = 0$, independent

$$Z = \sum_{\text{states}} e^{+\beta h \sum_{j=1}^{N} s_j}$$

$$Z = \sum_{\text{states}} e^{\beta h s_1} e^{\beta h s_2} e^{\beta h s_3} \cdots e^{\beta h s_N}$$

$$= \underbrace{\sum_{s_1 = +/- 1/2} e^{\beta h s_1}}_{z \text{ 1 spin partition function}} \sum_{s_2 = \pm 1/2} e^{\beta h s_2} \cdots \sum_{s_N = \pm 1/2} e^{\beta h s_N}$$

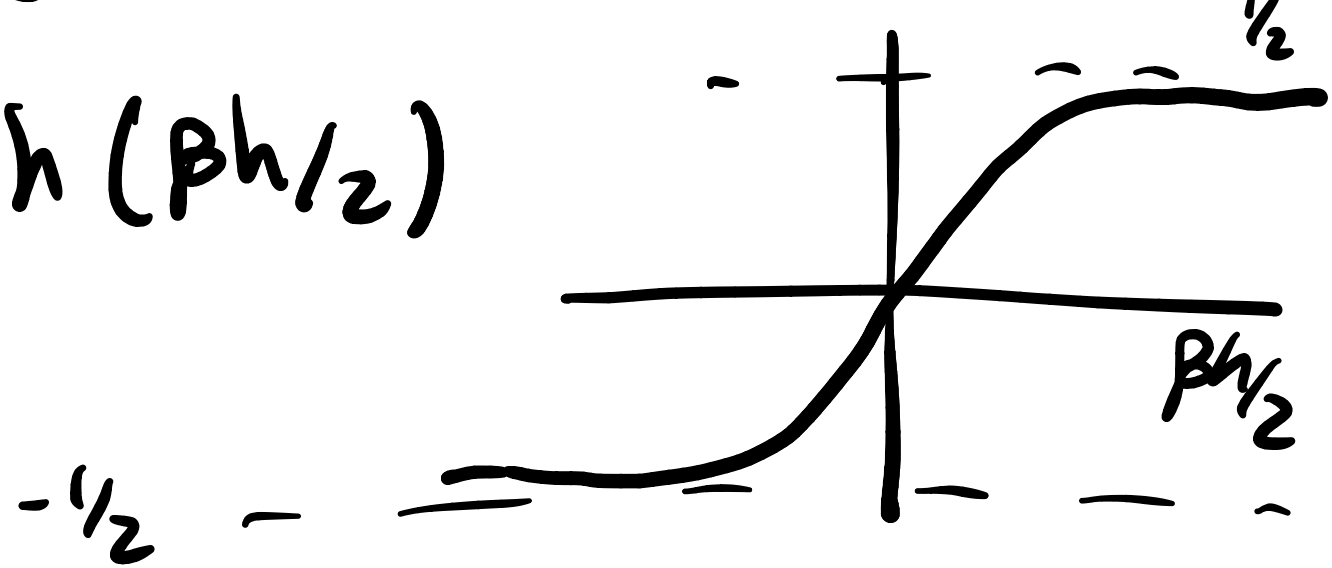
$$z = e^{\beta h/2} + e^{-\beta h/2}$$

$$Z = z^N = (e^{\beta h/2} + e^{-\beta h/2})^N$$

$$\langle s \rangle = \frac{k_B T}{N} \frac{\partial \ln \left[e^{\beta h/2} + e^{-\beta h/2} \right]^N}{\partial h}$$

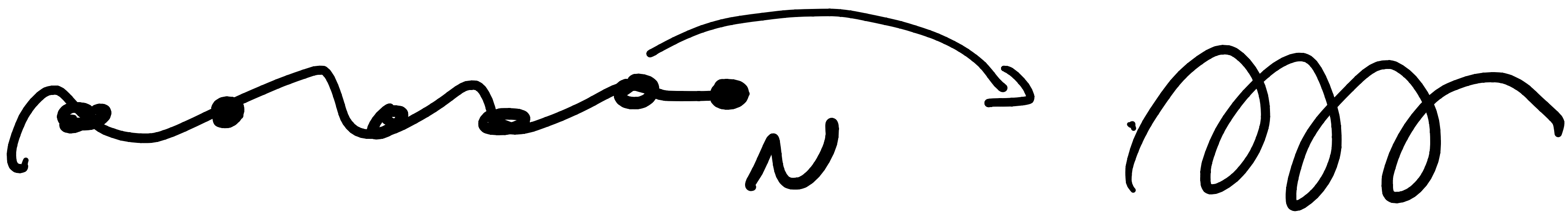
$$= k_B T \; \frac{\beta/2 \, e^{\beta h/2} - \beta/2 \, e^{-\beta h/2}}{e^{\beta h/2} + e^{-\beta h/2}}$$

$$= \frac{1}{2} \tanh(\beta h/2)$$



If $J > 0$, solvable in 1d, no phase transition except at $T = 0$

Helix-Coil model (Zimm-Bragg)



(secondary structure) α-helix

C	C	C	C	C	C

$N=6$

C	C	C	H	H	H

$N=6$

2^N states

$\varepsilon_c = 0 \qquad -h/2$

$\varepsilon_H = -\epsilon \sim h/2$

for independent case

$$Z = \sum_{\text{states}}^{2^N} e^{-\beta E(\text{state})}$$

$$e^{\beta \epsilon} = k$$

one residue: $Z = 1 + e^{\beta\epsilon} = 1 + k$

$$Z = e^{-\beta h/2} + e^{\beta h/2} = e^{-\beta h/2}\left(1 + e^{+\beta h}\right)$$

$$Z = (1+k)^N$$

$$\binom{N}{n_H}$$

CCCC
HCCC
CHCC etc
CCHC
CCCH

$$Z_4 = (1+k)^4 = 1 + 4k + 6k^2 + 4k^3 + k^4$$

$$Z = \sum_{n_H} \binom{N}{n_H} \underbrace{K^{n_H}}_{\text{"Boltzmann factor"}}$$

$$f_H = \frac{\langle n_H \rangle}{N}$$

$$f_H = \frac{1}{N} \sum_{n_H} n_H P(n_H)$$

$$\frac{\partial \ln Z}{\partial K} = \frac{1}{Z} \sum n_H \binom{N}{n_H} K^{n_H - 1} \frac{K}{K}$$

$$= \frac{1}{K} \langle n_H \rangle$$

$$f_H = \langle n_H \rangle / N = \frac{K}{N} \partial \ln Z / \partial K$$

ϵ

0

$$Z = e^{0} + e^{-\beta\epsilon}$$

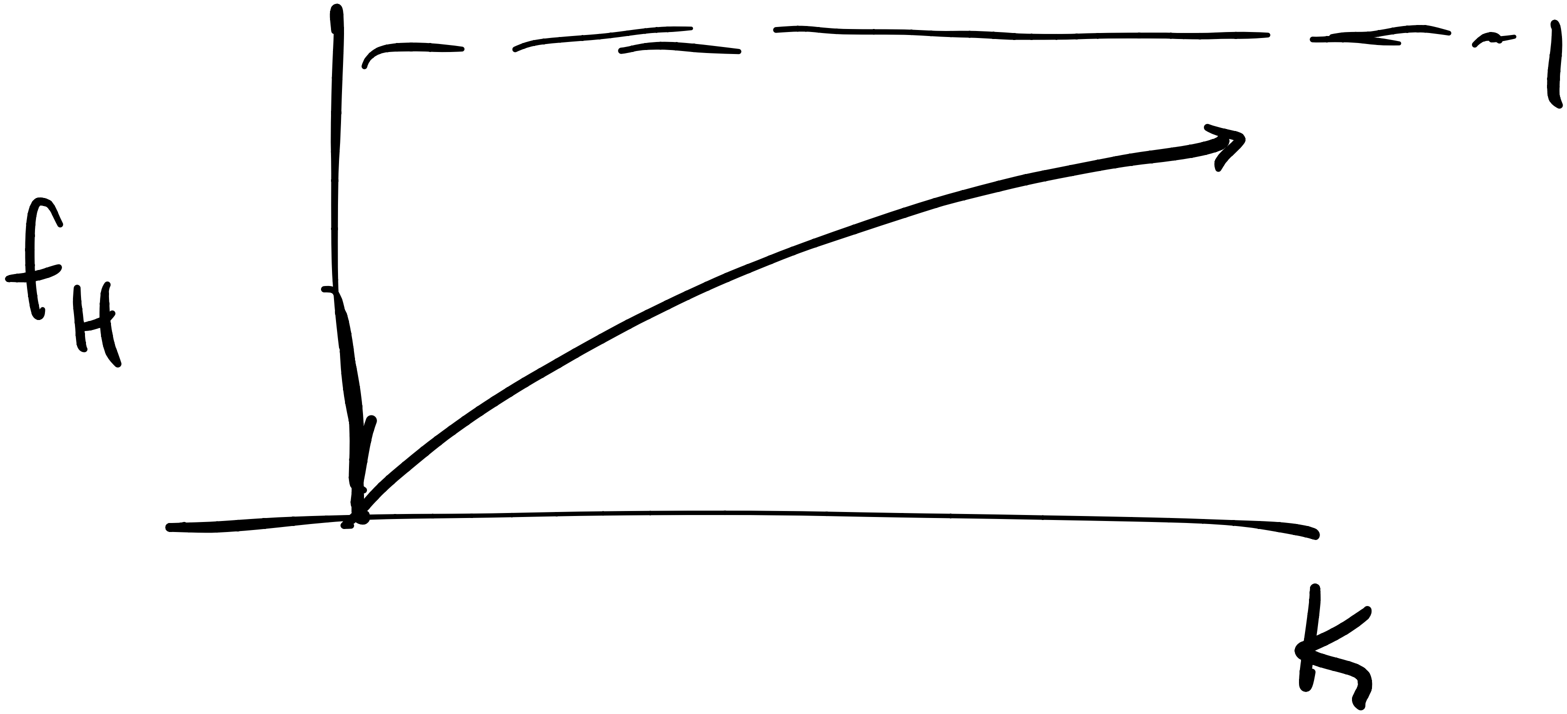
$$= 1 + e^{-\beta\epsilon}$$

$+\epsilon$

$-\epsilon$

$$Z = e^{-\beta\epsilon} + e^{+\beta\epsilon}$$

$$= e^{\beta\epsilon}(1 + e^{-2\beta\epsilon})$$



$$Z = (1+K)^N$$

$$f_H = \frac{K}{N}\frac{\partial \ln Z}{\partial K} = K \cdot \frac{}{1+K} = \frac{K}{1+K} = \frac{1}{1+1/K}$$

extra fact, different residues

$$Z = (1+K_\alpha)^{N_\alpha}(1+K_\beta)^{N_\beta}(1+K_\gamma)^{N_\gamma}$$

3 types

next time, what if there is coupling

$$\begin{array}{ccccccc} & & & & \tau\ \ \tau\ \ \tau & & \\ C & C & C & H & H & H & H \\ 1 & 1 & 1 & & K^4 \ \tau^3 & & \end{array}$$