Phase transitions

We're familiar with phase transitions

1) What is happening "microscopically"
2) what is happening "macroscopic"
3) What properties are "universal"

Ongoing work for ~100 years

Ongoing modern research

1) How to sample or predict phases from simulation

2) What happens in "unusual" environments - eg confinements

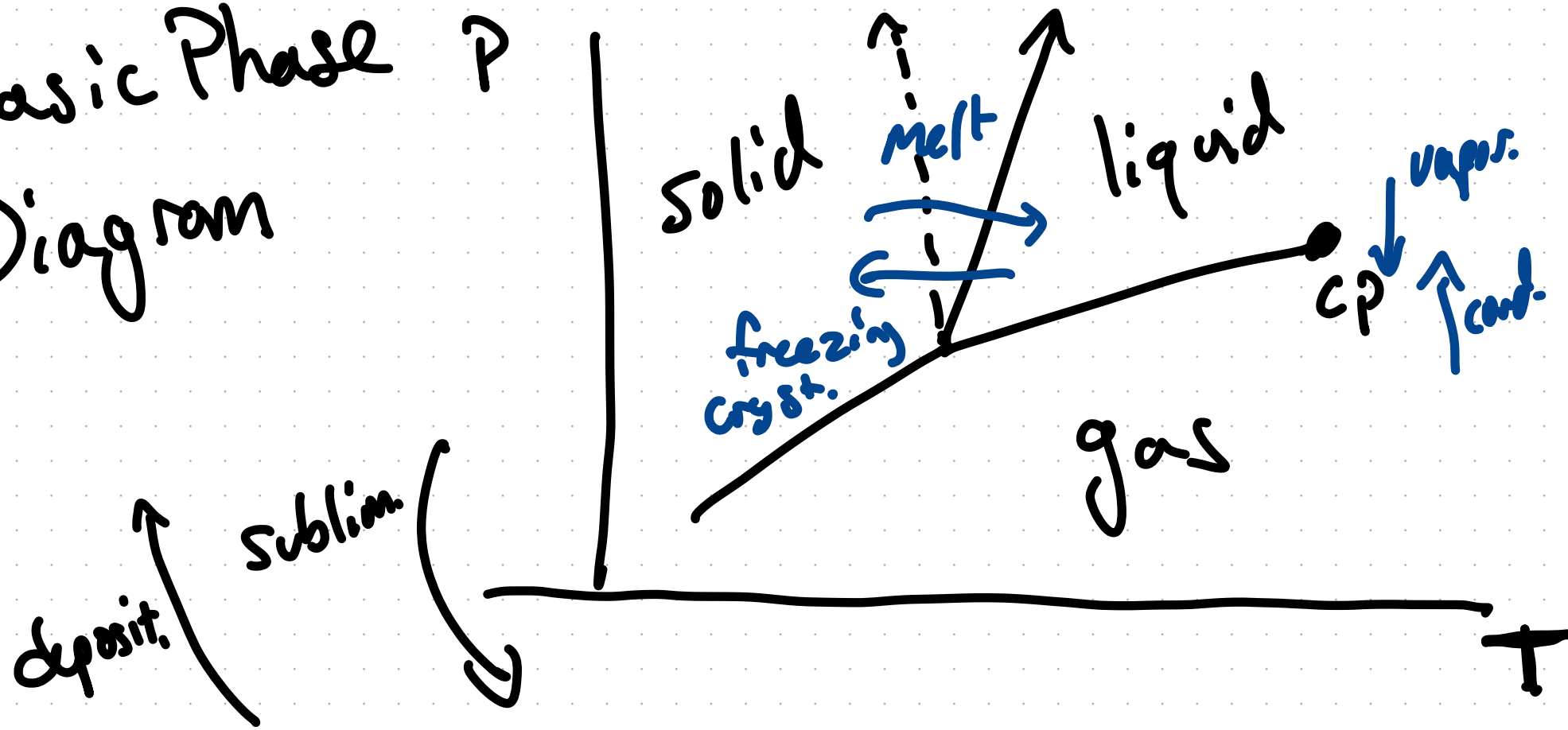
{ water in a nanotube
  inside of a protein
  at an interface

3) phase diagram of a many component system (lipids)

4) What happens out of equilibrium?
Active matter

Have to learn the basics first

Basic Phase Diagram

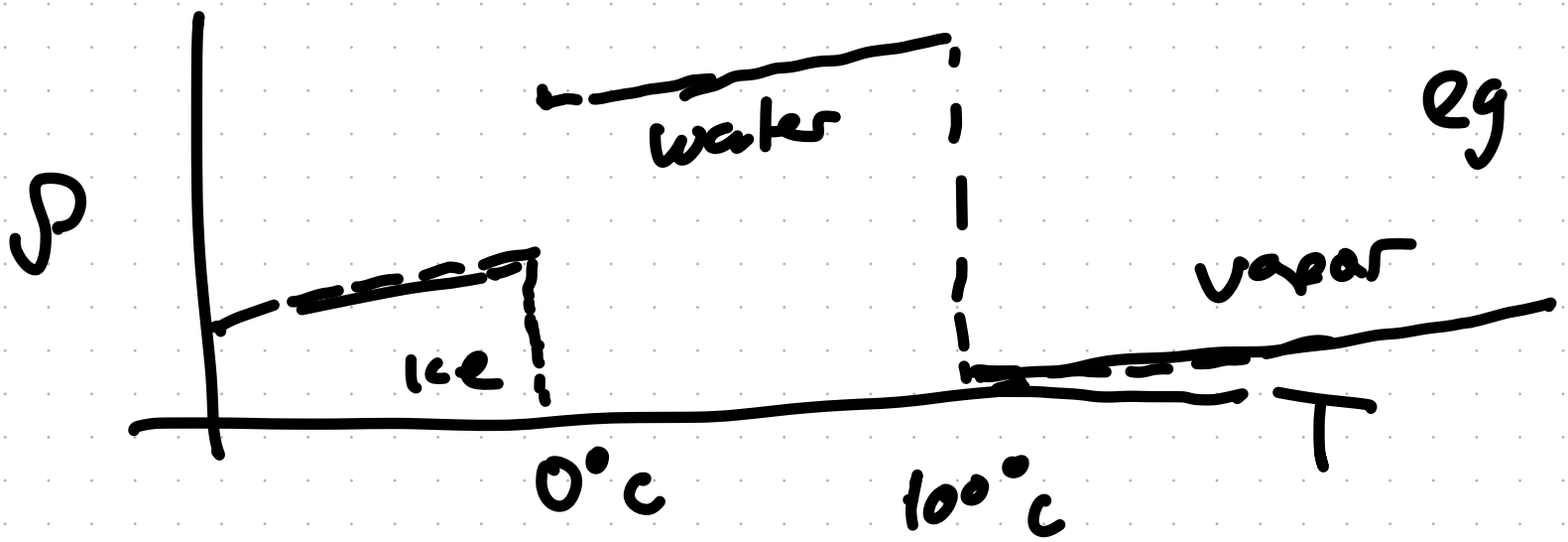


Cross a line → discontinuity in some quantity (eg density change)

1st order phase transition

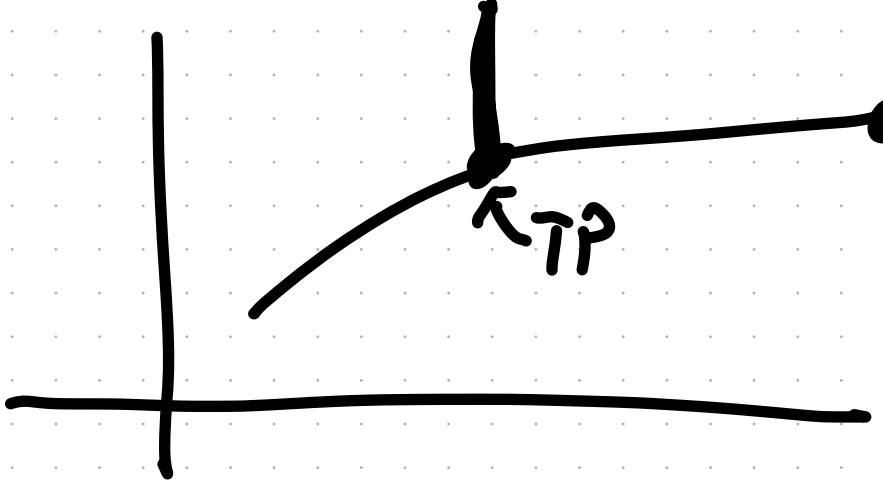
Ehrenfest: discontinuity in derivative of the free energy

[density ~ $1/(\partial A/\partial P)$]

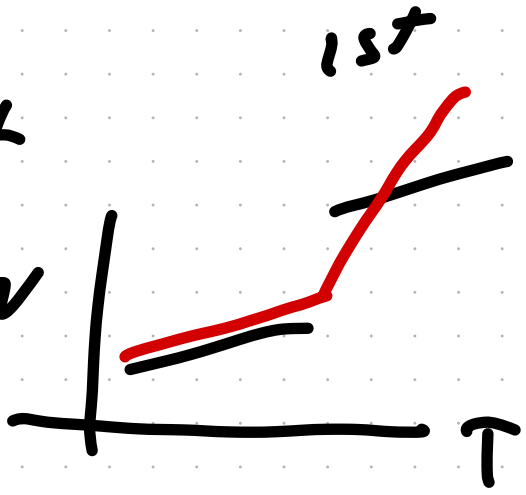


eg H_2O

Modern definition: "latent heat"



$\left(\frac{\partial A}{\partial T}\right| = \infty$



Approach critical point

2nd order phase transition

Ehrenfest! Continuous in first derivative
but discontinuous in 2nd derivatives

Modern "continuous" - diverging suscept &
power law divergence of correlation lengths

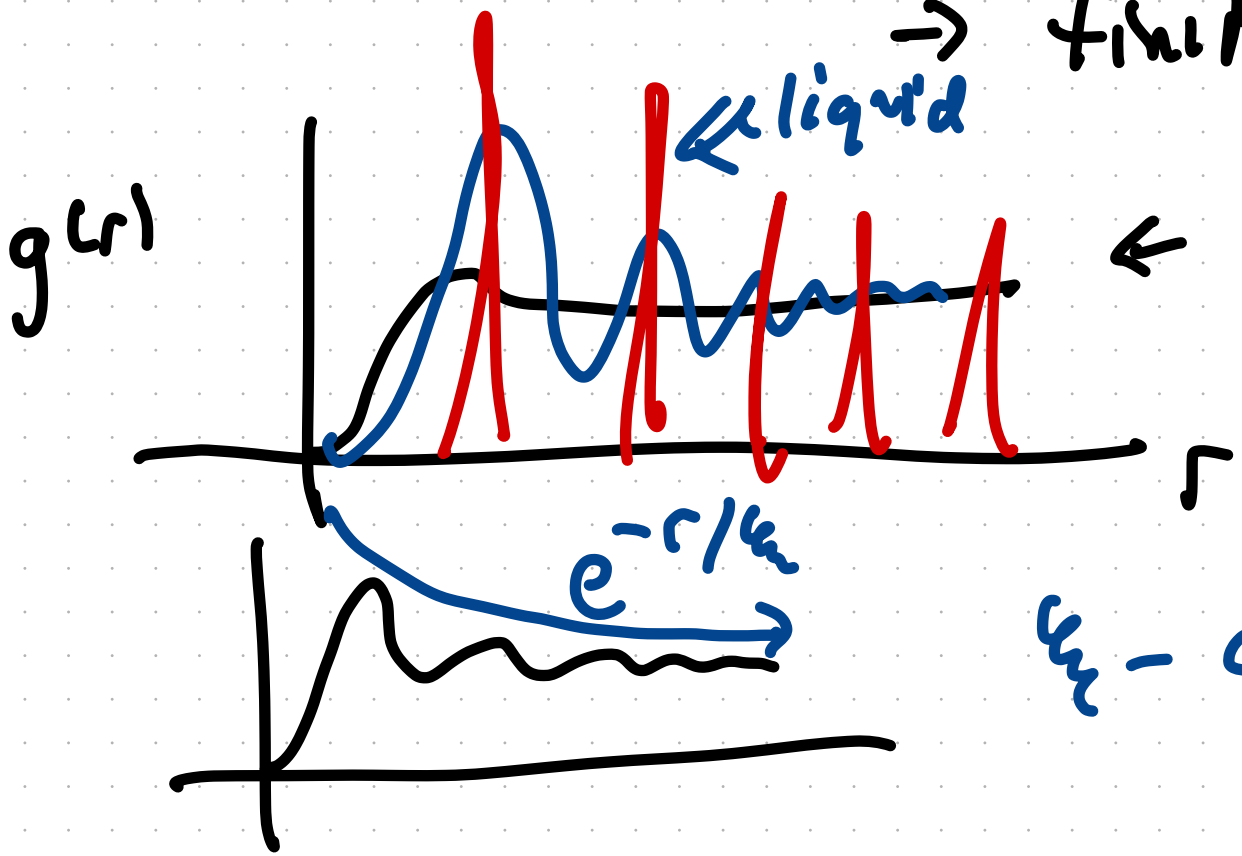
Typically: break some symmetry

liquid → solid

↑ rotationally invariant

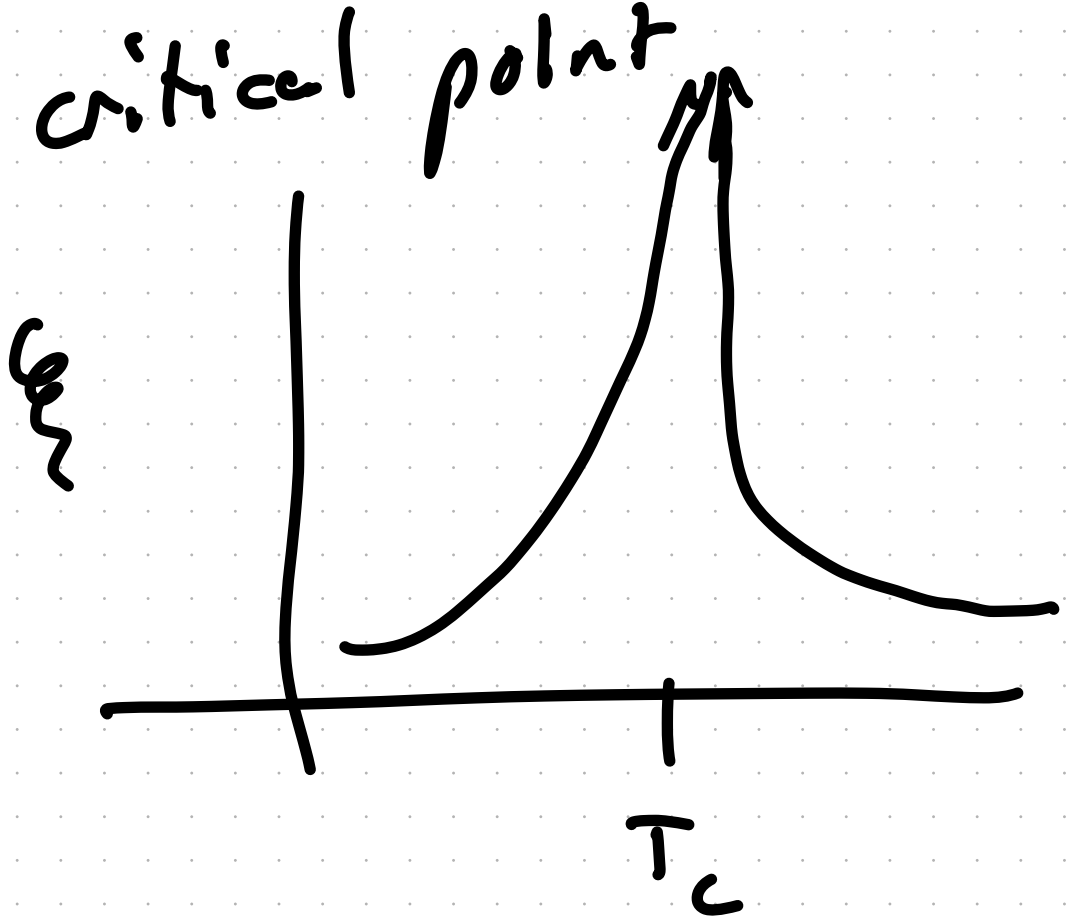
liquid ⇐ gas, ∞ correlation lengths

→ finite $g(r)$



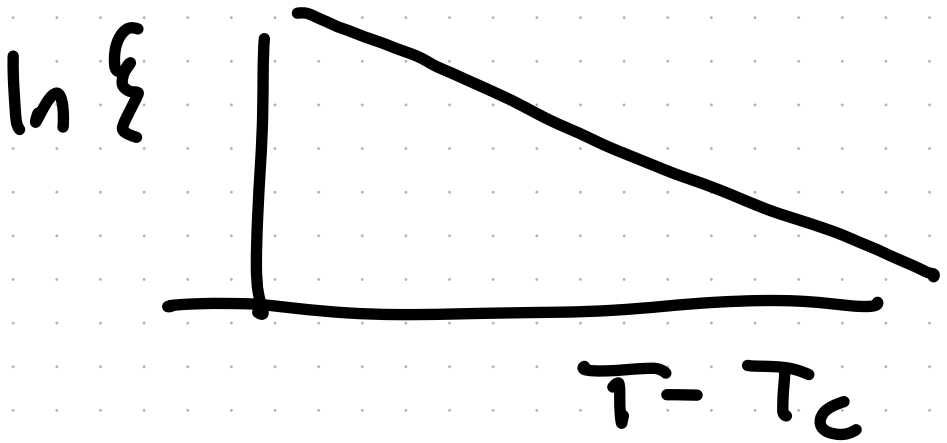
ξ – correlation length

@ critical point



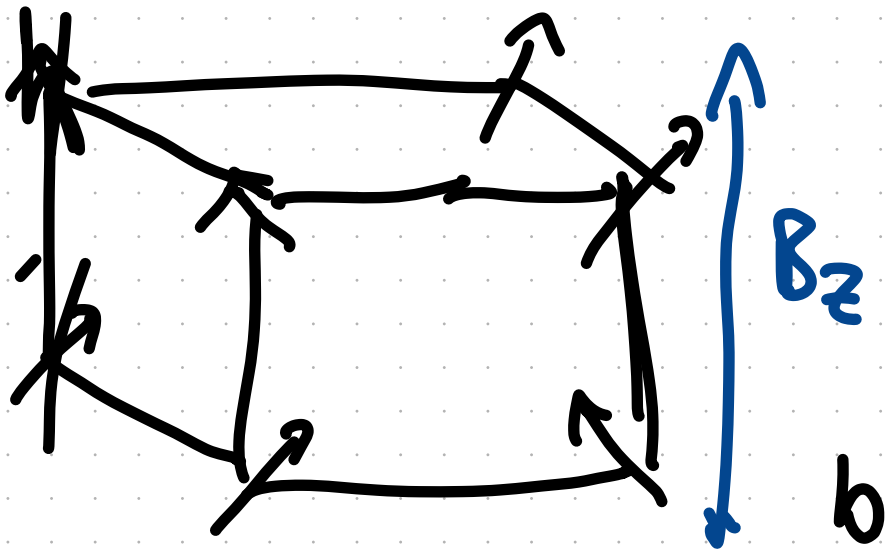
$\xi \sim (T - T_c)^{-a}$

power law



Model system

magnetization



spins like to point in the same direction

but entropy prevents it at large enough T

Lower temperature or add a B field, spins align

"order parameter" quantity that distinguishes the two phases

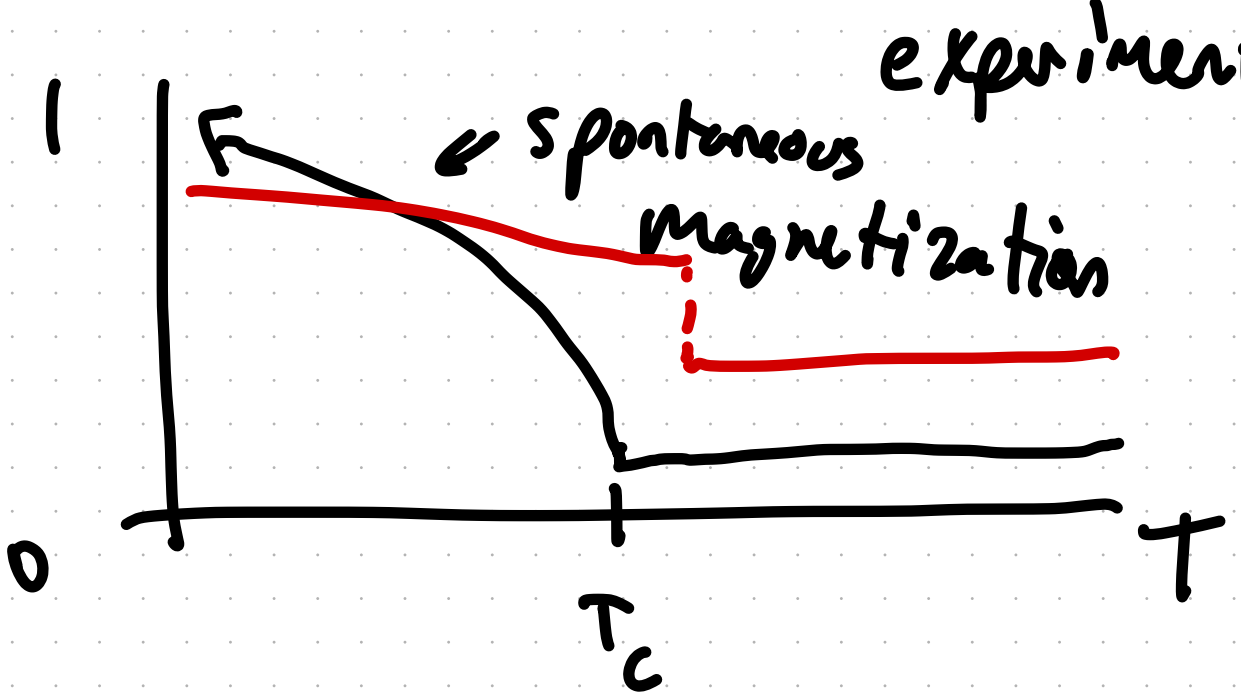
Eg L-G or L-S transition

$$\rho - \rho_L = \begin{cases} 0 & \text{in liquid} \\ \rho_s - \rho_L & \text{in solid} \\ \rho_g - \rho_L & \text{in gas} \end{cases}$$

for magnetization

$$M = \left| \left\langle \sum_{i=1}^{N} \sigma_i^z \right\rangle \right| \qquad m = \frac{M}{N}$$

experimentally



T_c - Curie temperature

Pierre Curie

Hamiltonian:

$$\mathcal{H} = -\frac{1}{2}\sum \hat{\sigma}_i \cdot J_{ij} \cdot \hat{\sigma}_j - \sum_i \gamma B \cdot \hat{S}_i$$

$$\hat{S}_i = \frac{\hbar}{2}\hat{\sigma}_i$$

$$-\sum_i \vec{h} \cdot \vec{\sigma}_i$$

$$h = \frac{\gamma \hbar B}{2}$$

Approximation

consider z direction

coupling

field

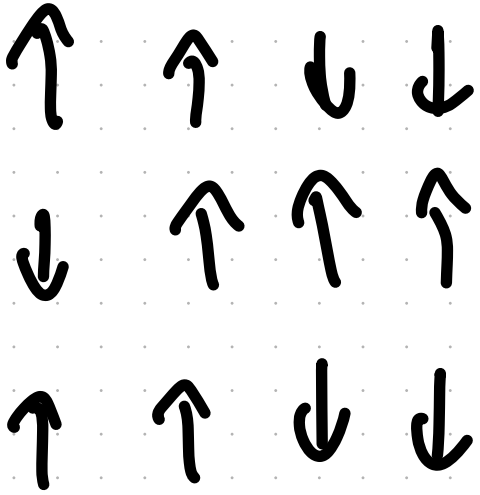
$$H = -\frac{1}{2}\sum_{i,j} J_{ij}\sigma_i\sigma_j - \sum_i h\sigma_i$$

$$\sigma_i = \left\{+\frac{1}{2}, -\frac{1}{2}\right\}$$

final approximation

$$J_{ij} = \begin{cases} J & \text{if } i \& j \text{ are neighbors} \\ 0 & \text{otherwise} \end{cases}$$

Nearest-neighbor



$s_i \in \pm 1$

$$H = -\frac{J}{2} \sum_{\langle ij \rangle} s_i s_j - h \sum_{i=1}^{N} s_i$$

$\sum_{\langle ij \rangle}$ only neighbors

"Ising model"

Ising Model (1924)

Can solve in 1d - no spontaneous mag.

Solved in 2d by Onsager in 1944

No solution in 3d yet ...

~~Very~~ easy to study on a computer

if $J>0$ and $h>0$, like to align up

$h<0$ like to align down

if $h=0$, $\mathcal{H}$ is minimized when

all up or all down

↑↑↑↑↑↑↑ ... ↑ $\quad -NJ = \varepsilon_{up}$

↓↓↓↓↓↓↓ ... ↓ $\quad -NJ = \varepsilon_{down}$

consider interface ← $m = 0$

...↑↑↑↑...↑↓↓↓↓...↓↓ $\quad \varepsilon = -NJ + J$

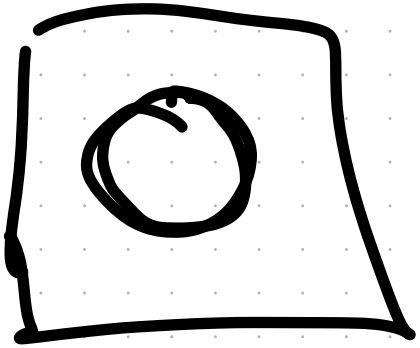
up down

$\varepsilon = \varepsilon_{min} + J$

@ $T=0$ all aligned @ equilibrium

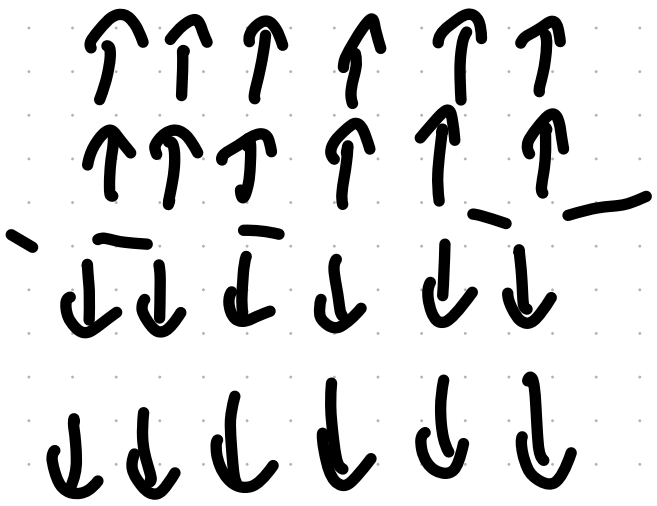
@ $T > 0$ minimize

$$A = E - TS$$



Interfaces are formed where not all spins are aligned and $\langle m \rangle = 0$

↙ "surface tension"



↳ interface

typical interface

$N^{1/2}$

$-NJ + N^{1/2} J$

$\approx M = 0$

can have S.M.

Even though 1d system has no S.M.,
map many problems onto it:
protein folding, adsorbtion of a gas

2d - has SM, even though not 3d
"isomorphic" liquid-gas