A brief review of basic Statistical Mechanics

We mostly understand the chemical world in terms of Quantum Mechanical _energy_ eigenstates:

$$\hat{H} |n\rangle = E_n |n\rangle$$

eigenstate or eigenfunction

↗ Hamiltonian Operator

↖ eigenenergy

At _thermal_ _equilibrium_, the probability of finding the system in any given energy eigenstate is:

$$P_n \propto \underbrace{e^{-\beta E_n}}_{\text{Boltzmann factor}}$$

$$\beta = \frac{1}{k_B T}$$

P_n is formally the probability of a given _copy_ of the system being found in state $|n\rangle$

Probabilities have _rules_:

$$0 \le P_n \le 1 \quad \leftarrow \text{Bounded}$$

$$\sum_n P_n = 1 \quad \leftarrow \text{Normalized}$$

$$P_n = \frac{e^{-\beta E_n}}{\sum_n e^{-\beta E_n}}$$

If we consider energy _levels_ which have degeneracy:

$$\left. \begin{array}{l} |n\rangle \\ |m\rangle \\ |o\rangle \end{array} \right\} \quad \text{If } E_n = E_m = E_0$$

these are _degenerate_ states

g_ℓ = degeneracy of level ℓ.

$$P_\ell = \frac{g_\ell \, e^{-\beta E_\ell}}{\sum_\ell g_\ell e^{-\beta E_\ell}}$$

Consider what happens to P_n at temperature extremes:

$$P_n = \frac{e^{-\beta E_n}}{\sum_n e^{-\beta E_n}}$$

as $T \to 0$ $(\beta \to \infty)$ $\longrightarrow$ $\begin{cases} P_0 \to 1 \\ P_{n \neq 0} \to 0 \end{cases}$ ground state becomes only populated state as $T \to 0$

as $T \to \infty$ $(\beta \to 0)$ $\longrightarrow$ $P_n = \frac{1}{N}$ where N = total number of states (all states equally likely)

$\boxed{\text{At what temperature can } P_1 > P_0 ?}$

- Never at equilibrium, they can only be equal

- The system can be found or set up with $P_1 > P_0$ in a non-equilibrium process.

The classical equivalent of a QM state is a point in phase space : $(\vec{q}, \vec{P})$

3N vector of particle positions   3N vector of particle momenta

$\begin{cases} \vec{q} = \{ q_{1x}, q_{1y}, q_{1z}, q_{2x}, q_{2y}, q_{2z} \} \\ \vec{P} = \{ P_{1x}, P_{1y}, P_{1z}, P_{2x}, P_{2y}, P_{2z} \} \end{cases}$

for 2 particles each is a vector in 6-space

$(\vec{q}, \vec{P})$ gives all positions & momenta of all particles at one time

Consider a simple Harmonic oscillator:

$$V(x) = \frac{1}{2} m\omega^2 x^2$$
$$T(p) = \frac{p^2}{2m}$$

$$H(x,p) = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$$

Classical

$$H = \frac{p^2}{2m} + \frac{1}{2} m\omega^2 x^2$$

The Hamiltonian describes the future motion & behavior of both QM & CM system

Quantum

$$\hat{H} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2} m\omega^2 \hat{x}^2$$
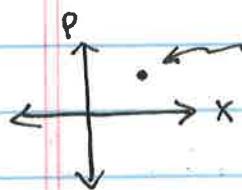
a point $(x(t), p(t))$ describes the instantaneous configuration of the system completely

$\psi_n(x), \ \psi_n(p)$
or $\ |n\rangle$

ⸯ no QM equivalent other than the wavefunction
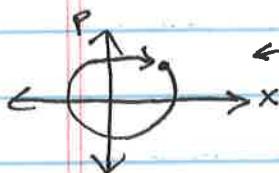
a trajectory or path in phase space traces out a time history of the system as it evolves

$$\psi_n(t) = e^{-i\hat{H}t/\hbar} \ \psi_n(0)$$

QM propagator moves wavefunct in time.
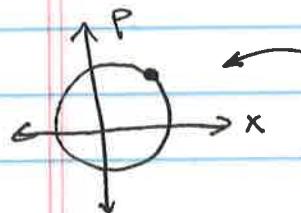
a closed path or orbit is a stable state that returns to a previous configuration exactly at a later time. Orbits are stable in time for conservative systems

$$\hat{H}\psi_n(x) = E_n \psi_n(x)$$

energy eigenstates are stable states

$$\psi_n(t) = e^{-i\hat{H}t/\hbar} \ \psi_n(0)$$
$$= e^{-iE_n t/\hbar} \ \psi_n(0)$$

rotating phase factor but not an operator
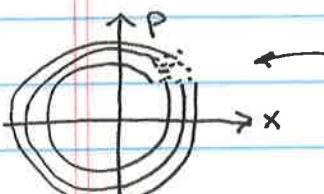
If we start off a cloud of trajectories this is an ensemble of different initial configurations each with a distinct energy.

$$\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3$$
$$\cdots$$
ⸯ a mixed state

QM   Classical

State $\psi(x)$ $\longleftrightarrow$ phase space point $(\vec{q}, \vec{p})$

P_n $\longleftrightarrow$ density of ensemble around
a state: $\rho(\vec{q}, \vec{p}) \, d\vec{q} \, d\vec{p}$

$e^{-\beta E_n}$ $\longleftrightarrow$ $e^{-\beta \mathcal{H}(\vec{q}, \vec{p})}$

$Q = \sum_n e^{-\beta E_n}$ $\longleftrightarrow$ $Q = \iint e^{-\beta \mathcal{H}(\vec{q}, \vec{p})} \, d\vec{q} \, d\vec{p}$

$\langle A \rangle = \dfrac{1}{Q} \sum_n A_n \, e^{-\beta E_n}$ $\longleftrightarrow$ $\langle A \rangle = \dfrac{1}{Q} \iint A(\vec{q}, \vec{p}) \, e^{-\beta \mathcal{H}(\vec{q}, \vec{p})} \, d\vec{q} \, d\vec{p}$

Let's parse this last one:

$$\langle A \rangle = \underbrace{\frac{1}{Q}}_{\substack{\text{Normalization} \\ \text{factor} \\ \text{(partition} \\ \text{function)}}} \underbrace{\iint}_{\substack{\text{Sum over} \\ \text{states}}} \underbrace{A(\vec{q}, \vec{p})}_{\substack{\text{property A in} \\ \text{that state}}} \underbrace{e^{-\beta \mathcal{H}(\vec{q}, \vec{p})}}_{\substack{\text{probability of} \\ \text{being in that} \\ \text{state}}}$$

Structural properties: $A(\vec{q}, \vec{p}) = A(\vec{q})$

Dynamical properties: $A(\vec{q}, \vec{p})$ does not simplify

Structural Averages: $\langle A \rangle = \dfrac{\iint A(q) \, e^{-\beta \mathcal{H}(q, p)} \, dq \, dp}{\iint e^{-\beta \mathcal{H}(q, p)} \, dq \, dp}$

$= \dfrac{\int A(q) \, e^{-\beta V(q)} \, dq}{\int e^{-\beta V(q)} \, dq} = \dfrac{1}{Z} \int A(q) e^{-\beta V(q)} \, dq$

Z = configurational partition function or configurational integral. We can use it when the properties we are interested in are structural.

<u>Statistical Ensemble</u>   <u>Thermodynamic Free Energy</u>

$Q(N,V,T)$ = canonical partition function $A = -k_B T \ln Q$

$\Xi(\mu,V,T)$ = grand canonical P.F $pV = +k_B T \ln \Xi$

$\Delta(N,P,T)$ = isobaric isothermal $G = -k_B T \ln \Delta$

$\Omega(N,V,E)$ = microcanonical $S = -k \ln \Omega$

<u>Partition Functions</u> are important because derivatives of these functions provide properties we <u>care</u> about.

$$\langle E \rangle = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

$$\mu = -k_B T \left(\frac{\partial \ln \Delta}{\partial N} \right)_{T,P} = -k_B T \left(\frac{\partial \ln Q}{\partial N} \right)_{V,T}$$

Phase Transitions

In this phase diagram, the relevant thermodynamic state variables are P & T telling us that the Gibbs free energy controls spontaneous change:
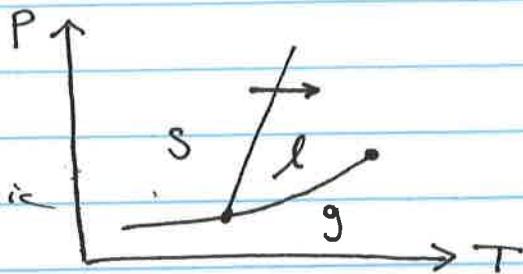
P ↑   S ℓ g → T

$$G(P, T, N_A, N_B, \dots)$$

← G can depend on P, T and all of the numbers of particles in each phase

In differential form:

$$dG = \left(\frac{\partial G}{\partial P}\right) dP + \left(\frac{\partial G}{\partial T}\right) dT + \left(\frac{\partial G}{\partial N_A}\right) dN_A + \left(\frac{\partial G}{\partial N_B}\right) dN_B$$

$$= V\, dP - S\, dT + \underbrace{\mu_A\, dN_A + \mu_B\, dN_B}$$

$$+ \sum_i \nu_i \mu_i\, d\lambda \quad \text{← extent of reaction}$$

↳ stoichiometric coefficients

A phase transition happens when 2 phases are in equilibrium:

$$A_{(s)} \rightleftharpoons A_{(\ell)}$$

At equilibrium, dT & dP are both 0, (and so is dG) so the condition for phase equilibrium is:

$$\sum_i \nu_i \mu_i = 0$$

or:

$$\mu_i^{(\alpha)}(T, P) = \mu_i^{(\beta)}(T, P)$$

↳ chemical potential in phase α   ↳ chemical potential in phase β

We also know that $dG = 0$ at the phase boundary,
(e.g. G is <u>continuous</u>)

Suppose we cross from solid to liquid

$dG = 0$, but $\left(\frac{\partial G}{\partial T}\right) = -S$, has a different <u>slope</u> on either side of the phase boundary

$S = \frac{S}{N}$

The "derivative" quantities are <u>discontinuous</u>

$V = \frac{V}{N}$

$C_p = \left(\frac{\partial S}{\partial T}\right)_p$

← 2nd derivative properties diverge at a phase boundary
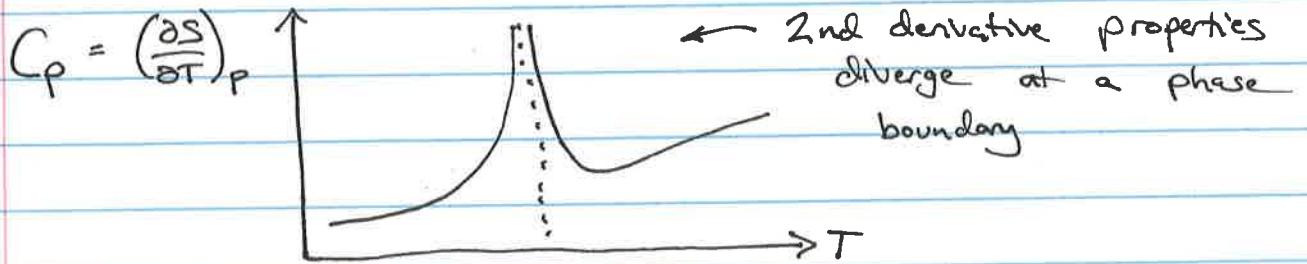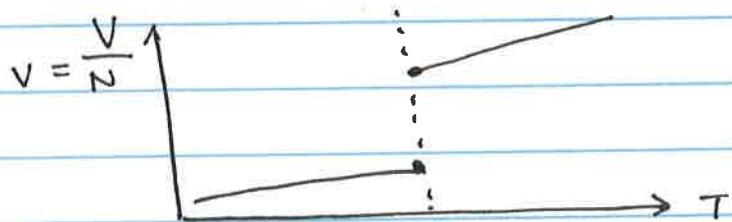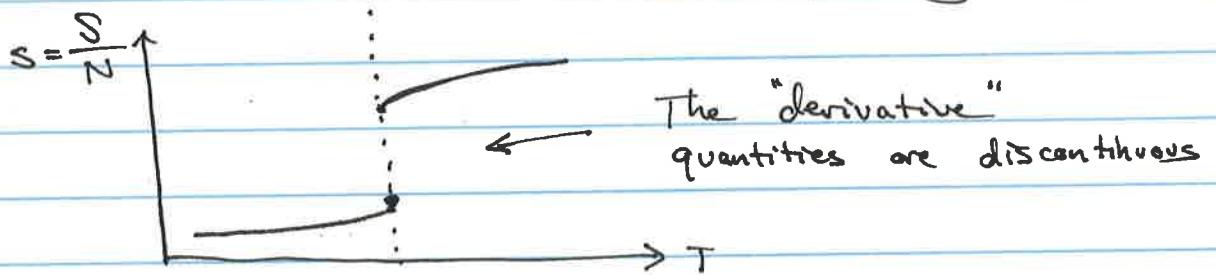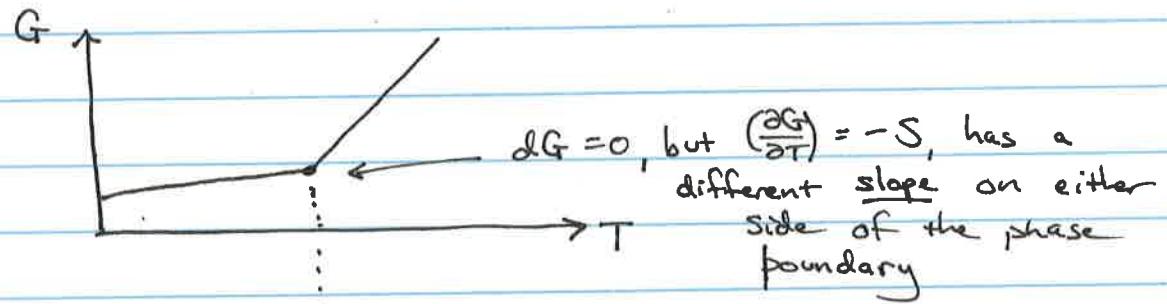
$C_p \approx |T - T_c|^{-\alpha} + \text{constant}$

$\alpha = $ <u>critical scaling exponent</u>

2nd order phase transitions

1st order derivatives (S,V) are continuous

2nd order derivatives are discontinuous
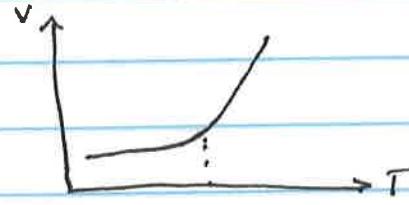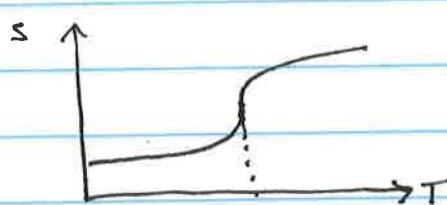
Field-space phase diagrams

| = 1st order, ┊ = 2nd order
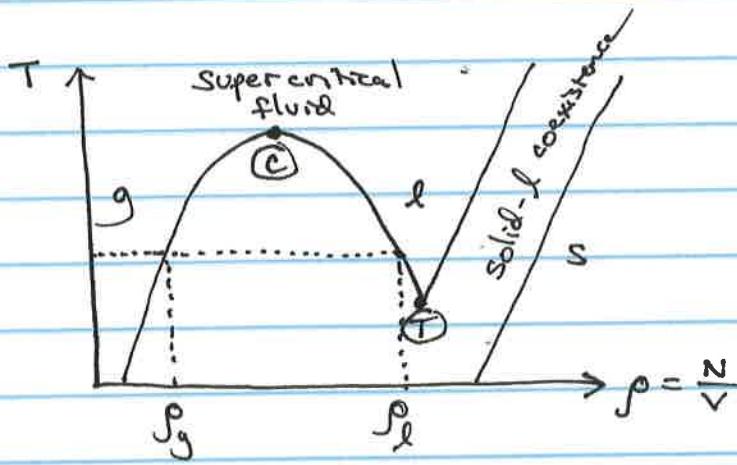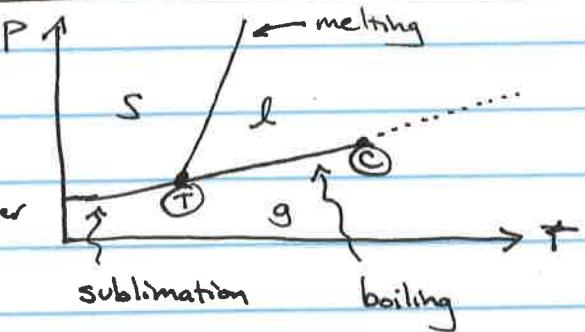
The field-space diagram is quite symmetric around the critical point:

$$\Delta\rho = \rho_\ell - \rho_g = \frac{(T-T_c)^\beta}{T_c}$$

In most fluids, $\beta \approx 0.326$. This is the <u>second</u> critical exponent.

Can we model this complex behavior?

Energy of intermolecular interactions:

too close is forbidden

not much interaction out here

most molecules are attractive at short range
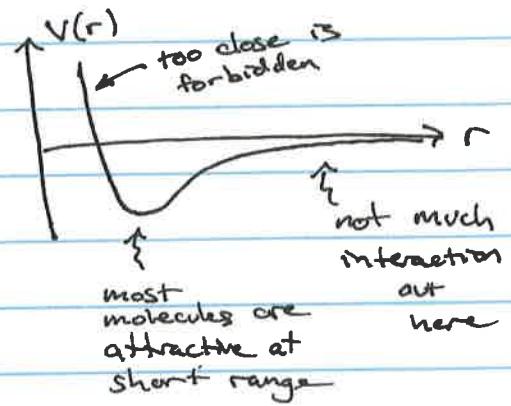
A simple square-well model:

$-\epsilon$
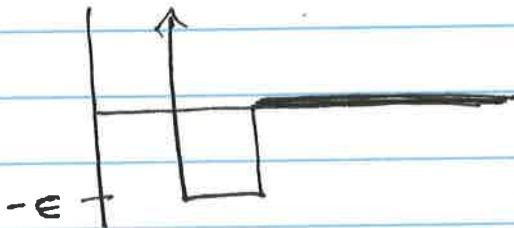
We can implement this model simply as a lattice gas:

$s_1 = 1$ $s_2 = 0$

$] -\epsilon$
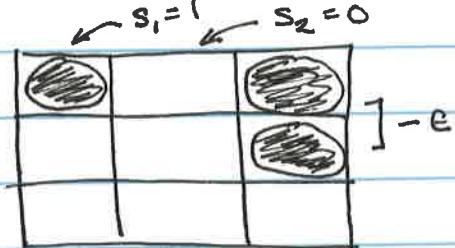
site variables s_i are 1 or 0.   1 = occupied   0 = unoccupied

Limiting site occupation to 1 prevents overlap and energy of lattice will depend on how many adjacent sites are occupied.

The lattice gas is an important model for l-g and l-s phase transitions and it maps exactly onto a spin model for magnetic phase transitions.

$\sigma_1 = +1$ $\sigma_2 = -1$
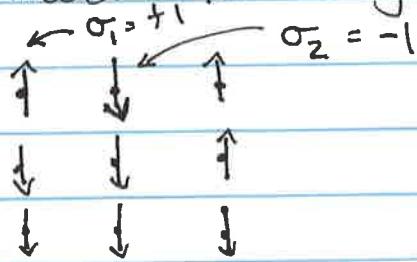
This is exactly the same model after a simple transformation

We can write down the energy for a configuration of the lattice:

$$\mathcal{H} = -\sum_n h_n \sigma_n - \frac{1}{2}\sum_n \sum_{n'} J_{nn'}\sigma_n \sigma_{n'} - \frac{1}{6}\sum_n \sum_{n'} \sum_{n''} L_{nn'n''}\sigma_n \sigma_{n'}\sigma_{n''} \cdots$$

Interaction of spins with external field

Interactions of spins with each other

3-body interactions

$$\sigma_n = \pm 1$$

The **Ising Model** is a simplification. We stop at pairwise interactions and only include contributions from **Nearest Neighbors** :

$$J_{nn'} = \begin{cases} 0 & \text{if } n=n' \\ J & \text{if } n \text{ \& } n' \text{ are nearest neighbors} \\ 0 & \text{if } n \text{ \& } n' \text{ are } \underline{not} \text{ nearest neighbors} \end{cases}$$

$$H_n = H \quad \longleftarrow \text{ } \underline{uniform} \text{ field}$$

$$\mathcal{H}_{ising} = -H\sum_n \sigma_n - \frac{J}{2}\sum_n \sum_{n'\in NN(n)} \sigma_n \sigma_{n'}$$

The **Ising** model is discrete ($\sigma_n = \pm 1$) and <u>short ranged</u>

<u>Basic Properties of the Ising Model</u>

What is the configuration when $T = 0$ (and $H=0$)?

With $J > 0$, $\mathcal{H} = -\frac{J}{2}\sum_{nn'}\sigma_n \sigma_{n'}$

Ferromagnetic States

↑↑↑↑↑↑
↑↑↑↑↑↑

or

↓↓↓↓↓↓
↓↓↓↓↓↓

all spins point in same direction

symmetric solutions

What happens if the coupling, $J < 0$:

With $J < 0$:

$$\begin{matrix} \uparrow & \downarrow & \uparrow & \downarrow & \uparrow & \downarrow \\ \downarrow & \uparrow & \downarrow & \uparrow & \downarrow & \uparrow \\ \uparrow & \downarrow & \uparrow & \downarrow & \uparrow & \downarrow \end{matrix} \Bigg\}$$ anti-ferromagnetic all spins surrounded by spins going in the opposite direction

(Is this state symmetric?)

What happens if the field is on ($H \neq 0$)?

We break the symmetry:

$$\begin{matrix} \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \end{matrix}$$ now has a different energy than $$\begin{matrix} \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \end{matrix}$$

Connecting to the Lattice Gas

$$\mathcal{H}_{LG} = -\frac{\epsilon}{2} \overset{NN}{\underset{n,n'}{\sum}} S_n S_{n'} \quad \leftarrow S_n = 0,1$$

$V(r)$
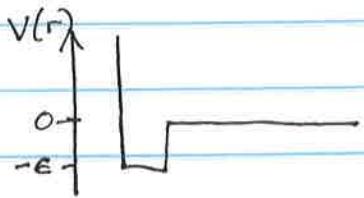
nearest neighbors
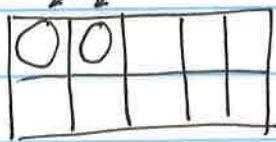
$$\mathcal{H}_{ising} = \frac{J}{2} \overset{NN}{\underset{n,n'}{\sum}} \sigma_n \sigma_{n'} - H \underset{n}{\sum} \sigma_n \qquad \sigma_n = \pm 1$$

$$Q_{ising} = \underset{\{\sigma_n = \pm 1\}}{\sum} e^{-\beta \mathcal{H}_{ising}} = \underset{\{\sigma_n = \pm 1\}}{\sum} e^{-\frac{\beta J}{2} \sum_{n,n'} \sigma_n \sigma_{n'} + \beta H \sum_n \sigma_n}$$

$\updownarrow$ energy of that lattice state

$\updownarrow$ sum over all possible states of the lattice

Consider the Grand canonical Partition Function for the Lattice Gas

$$\Xi_{LG} = \underset{\{S_n = 0,1\}}{\sum} e^{-\beta \mathcal{H}_{LG}} e^{\beta \mu N} = \underset{\{S_n = 0,1\}}{\sum} e^{\frac{\beta \epsilon}{2} \sum_{n,n'} S_n S_{n'} + \beta \mu \sum_n S_n}$$

$\therefore \quad Q_{ising} \equiv \Xi_{LG} \quad$ with

$$\left.\begin{array}{l} J = 2\epsilon - 1 \\ H = 2\mu - 1 \\ \sigma_n = 2S_n - 1 \end{array}\right\} \begin{array}{l} \text{mapping from ising model} \\ \text{canonical P.F. to } \underline{\text{Grand}} \\ \text{canonical P.F. for Lattice Gas!} \end{array}$$

Solve one of these problems and you've solved the other also!

What do we want to know?

$$C_v \sim |T - T_c|^{-\alpha} + c$$

To get C_v, we need $A(T)$

To get $A(T)$, we need to solve Q_{ising}

$$\Delta \rho = \rho_l - \rho_g \sim \frac{(T - T_c)^{\beta}}{T_c}$$

$$\langle \rho \rangle = \frac{\langle N \rangle}{V} = \frac{1}{V} \frac{\partial \ln \Xi_{LG}}{\partial (\beta \mu)}$$

$$= \frac{1}{V} \frac{1}{\Xi} \sum_{\{S_n = 0, 1\}} \left(\sum_n S_n \right) e^{\cdots}$$

what's the equivalent to ρ for the ising model?

$$\langle m \rangle = \frac{1}{Q_N} \sum_{states} \left(\sum_n \sigma_n \right) e^{-\beta \cdots}$$

$$= \frac{1}{N} \frac{\partial \ln Q_{ising}}{\partial (\beta H)} \quad \longleftarrow \quad \text{net or bulk magnetization of the ising lattice}$$

$\langle m \rangle = $ magnetization

for ferromagnetic phases
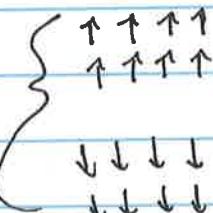
↑ ↑ ↑ ↑
↑ ↑ ↑ ↑ $\langle m \rangle = +1$

↓ ↓ ↓ ↓
↓ ↓ ↓ ↓ $\langle m \rangle = -1$

anti ferromagnetic
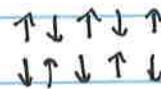
↑ ↓ ↑ ↓ ↑
↓ ↑ ↓ ↑ ↓ $\langle m \rangle = 0$

random $\langle m \rangle = 0$

A quick note about Frustration.   Let's assume $J < 0$
                                   (favors anti-aligned)

↑
            ⟵ a triangular lattice is
↑   ↓   frustrated when $J < 0$

Types of Frustration

Complete: situations like the triangular lattice where it is <u>impossible</u> to satisfy microscopic preferences

<u>Partial</u> :   involves higher order couplings:

$$\mathcal{H} = -\frac{J_1}{2} \sum_{n,n'}^{NN} \sigma_n \sigma_{n'} - \frac{J_2}{2} \sum_{n',n}^{NNN} \sigma_n \sigma_{n'}$$

$NNN \leftarrow$ <u>next nearest</u> neighbors

If $\underbrace{J_1 > 0}_{\text{prefers NN aligned}}$ and $\underbrace{J_2 < 0}_{\substack{\text{prefers NNN} \\ \text{anti-aligned}}}$

<u>Depending</u> on the strengths of J_1 & J_2, one term will "win"

<u>Irregular</u> frustration : $\mathcal{H} = -\frac{1}{2} \sum_{n,n'} J_{n,n'} \sigma_n \sigma_{n'}$

Pick values of $J_{n,n'}$ <u>randomly</u> on $[-1, 1]$

<u>Loca</u>lly frustrated structures depend on random variables

This shows up in spin glasses & neural networks