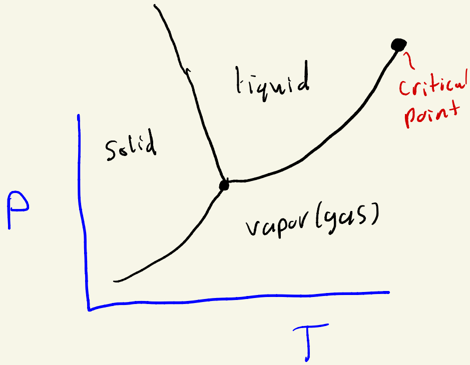
Phase transitions (overview)

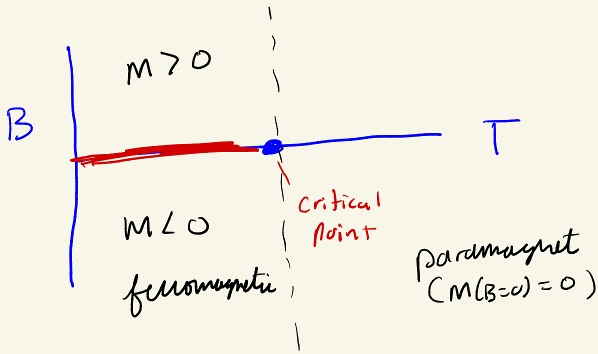
* we know there are different "phases" of matter

e.g. H_2O:



How does this rich behavior arise from a single $\hat{H}$ "just" by dialing a different T or P?
(or B+T for magnet)?

e.g. Ferromagnetic



Classification (old Ehrenfest scheme) of PT's

* n^{th} order P.T. = discontinuous behavior of n^{th} derivative of F

e.g. 1^{st} order $\quad \frac{S}{N} = -\frac{1}{N}\frac{\partial F}{\partial T}$ discontinuous (latent heat released)

"Modern" Classification

· define **order parameter** η of P.T. that is zero in one phase (high T) + non-zero in the "ordered" (low T) phase

e.g. $\vec{M} = \frac{1}{N} \langle \sum_i \vec{S}_i \rangle$ for ferromagnetic transition

$\rho_{liq} - \rho_{gas}$ in a liquid-gas transition

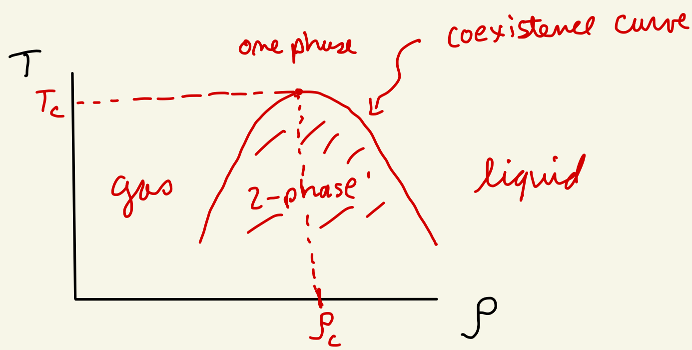
$\Rightarrow$ * Continuous phase transition ($\eta(T \to T_c^-)$ continuously vanishes as $T \to T_c^-$)

* Discontinuous PT (η abruptly goes from $\neq 0$ to 0 across some phase boundary)

> *Due to time constraints, our focus will be entirely on Continuous PTs since they're more interesting/challenging.

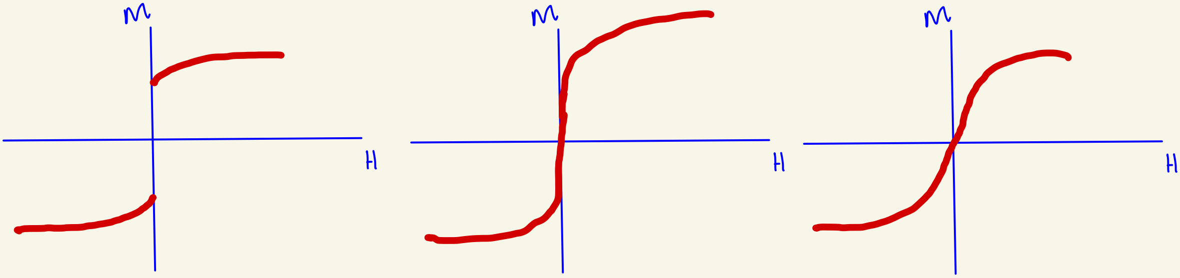
traditional methods don't explain these phenomena. This will lead us to one of the most powerful ideas in the past 50 years — the Renormalization Group (RG) of Ken Wilson.

e.g.

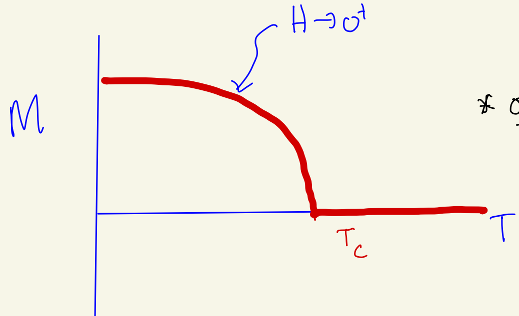


*order parameter $|\rho_L - \rho_G| \to 0$ on coexistence curve as approach T_c, ρ_c

e.g.: Uniaxial ferromagnet w/ external Mag. field H



$T < T_c$ $\qquad$ $T = T_c$ $\qquad$ $T > T_c$



* order parameter M rises continuously from zero at T_c

* Continuous phase transitions fall under the umbrella of what are called "critical phenomena" that are characterized by a diverging correlation length $\xi \to \infty$.

* Later on, we'll give a more mathematical definition of ξ in terms of 2-pt correlation functions of some observable (e.g., spins in a magnet). But for now, we can give a heuristic definition as follows, which also helps motivate why critical phenomena were an unsolved mystery until the Wilsonian RG came along in the late 1960's + early 70's.

* Heuristic def. of ξ: Take a macroscopic chunk of matter + measure some properties (e.g., energy + matter densities, magnetization, etc...). Now divide the chunk in half + measure the same quantities. You'll get the same values. If you keep repeating this process, eventually you'll resolve the microscopic constituents + your measurements will differ due to fluctuations.

** The length scale at which this happens is the correlation length ξ. **

Critical Exponents + universality

* Various TD quantities are found to exhibit Scaling (power law) behavior near the critical point

* Remarkably, these power laws seem only to depend on the underlying symmetries + spatial dimensionality of the system (i.e., no dependence on detailed microscopic dynamics "Universality".)

Uniaxial (Ising) Ferromagnet

$t \equiv \frac{T-T_c}{T_c}$

$C_v \sim |t|^{-\alpha}$

$M_{H=0} \sim |t|^{\beta} \quad t \to 0^-$

$\chi_{H=0} \sim |t|^{-\gamma}$

$\xi \sim |t|^{-\nu}$

$G(r) \sim \frac{1}{r^{d-2+\eta}}$ at $t=0$ in d-dim

connected 2pt $\langle M(r) M(0) \rangle_c$

exp. values (d=3)	
α	.110
β	.325
γ	1.2405
ν	.630
η	.032

"critical exponents"

These are the same (to exp. errors) for all uniaxial ferromagnets, even though the underlying $\hat{H}$'s can be very different for different materials

* But it gets weirder! You can define analogous exponents for the liquid-gas transition & those are the same for all materials AND they match the ferromagnetic values!

Power-laws for liquid-gas critical point

$C_V \sim |t|^{-\alpha}$ at $\rho = \rho_c$

$|\rho_L - \rho_G| \sim (-t)^{\beta}$

$\chi_T \sim |t|^{-\gamma}$

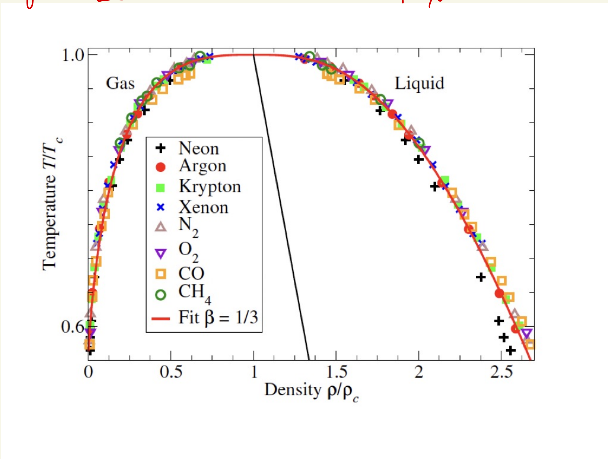
$\xi \sim |t|^{-\nu}$

$G(r) \sim \frac{1}{r^{d-2+\eta}}$ at $t = 0$

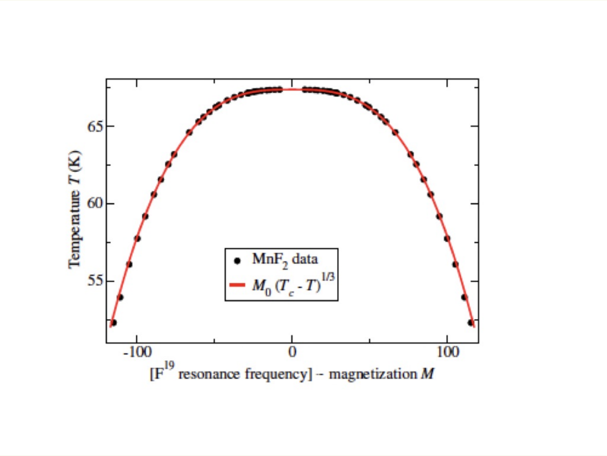
connected density-density correlator

$\langle \rho(r) \rho(0) \rangle_c$

from Sethna Stat. Mech text



* Remarkably, the values of critical exponents for all simple fluids are <u>the same</u> experimentally!!



* Even more surprising, they agree w/ the values measured for uniaxial Ferromagnets

* This insensitivity to the detailed microscopic dynamics is called "<u>Universality</u>".
In Nature, one finds that critical phenomena falls into different "<u>Universality Classes</u>", which are determined only by dimensionality, symmetries of the underlying Hamiltonian.

* Some "big picture" questions we will explore:

(1) Why do phase transitions exist at all?

The existence of non-analytic behavior in TD quantities should seem strange!

* Recall, all Thermodynamics is encoded in the partition function

$$\underbrace{Z}_{\text{Partition function}} = \mathrm{Tr}\, e^{-\beta \overbrace{H}^{\text{Hamiltonian}}} = e^{-\beta \overbrace{F}^{\text{Free Energy}}} \qquad \left(\beta = \frac{1}{k_B T} \right)$$

* Assuming H is a non-singular function of the DOF, Z is just a sum of terms that are analytic functions of the DOF & their couplings.

* How then, can any singular/non-analytic behavior arise in the calculated thermodynamics?

Answer: This is all true (i.e., no phase transitions) if the # of DOF is finite.

However, when we take the thermodynamic limit taking $N \to \infty$, we evade this apparent contradiction.

[i.e., an ∞-sum of analytic functions can develop non-analytic features!)

We'll briefly explore this for Ising Model

② How can we compute the phase diagram of a system as we change the external parameters (e.g. T, etc) that enter Z ?

a.) How can small changes in parameters (e.g., T or couplings in $\hat{H}$) have little effect on the atomic-scale physics but somehow get amplified + lead to wildly different large-scale behavior?

T_c versus $T_c + \epsilon$ in a ferromagnet

$\Rightarrow \xi = \infty$ versus $\xi =$ finite #

b) How can sizeable differences at the microscopic scale get de-amplified and lead to identical long distance behavior?

e.g.: Universality Classes

c.) How can we compute the critical exponents in the scaling relations?

* e.g., pre-RG approaches based on "mean field theory" can only give "simple" (i.e., integer or rational fractions like ½ etc.) values

* Even though, e.g., $\alpha_{MFT} = \frac{1}{2}$ versus

$\alpha_{\text{Liquid-gas}} = .327$

is not a "big" discrepancy, it's not possible, even in principle, to explain this discrepancy without new ideas (i.e. the RG)

The Ising Model (Uniaxial Magnet)

* We will eventually explain where universality comes from using Wilson's Renormalization Group (WRG) ideas.

* But for now, we can appeal to universality to limit our attention to the simplest model of a uniaxial ferromagnet – the Ising model – knowing in the long run that this will agree w/ more realistic/complicated models for its predictions of behavior near the critical point, & will also agree w/ any fluid models for physics near the liquid-gas transition!

* Consider a lattice of binary spins ($S_i = \pm 1$) w/ an external magnetic field H

$$\mathcal{H} = -J \sum_{\langle ij \rangle} S_i S_j - H \sum_i S_i$$

"nearest neighbors" only

$J > 0 \Rightarrow$ energetically preferable for neighboring spins to be aligned

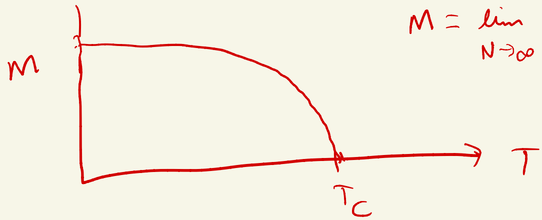
e.g. 1d lattice $J \sum_{\langle ij \rangle} S_i S_j = J (S_1 S_2 + S_2 S_3 + \cdots)$

$$= J \sum_{i=1}^{N} S_i S_{i+1}$$

* Is there a continuous pT from the ordered to non-ordered state?

$$M = \lim_{N\to\infty}\left(\lim_{H\to 0^+}\frac{\left\langle \sum_{i=1}^{N} S_i \right\rangle}{N}\right)$$

i.e.



* What are the critical exponents?

* Exact solutions exist for

1) $d=1$ (easy, see HW 8)

→ $M(H\to 0^+) \neq 0$ only for $T=0$

(no continuous PT)

2) $d=2$ (very hard, see advanced texts like Huang)

→ find $M \neq 0$ for $T < T_c$ where $T_c > 0$

→ critical exponents agree w/ Nature!

3) $d=3$ (Numerical solutions)

→ find $M \neq 0$ for $T < T_c$

→ critical exp. agree w/ Nature

* Weiss's Mean Field Theory

We do not bother going thru the exact solutions for the $d=1$ and $d=2$ Ising model, but instead we introduce a class of approximate methods, Mean Field Theories, that are a important step on our way to the ultimate solution to critical phenomena, the WRG.

* MFT can be motivated at varying levels of rigor. ~~In your HW's, you'll pursue the more microscopic approach to deriving MFTs using the Hubbard-Stratonovich transformation and performing a Steepest Descent evaluation of Z~~. In our class lectures, we'll follow the more phenomenological approach associated w/ Weiss (magnets), Van der Waals (fluids), and Landau/Ginzburg (general systems).

* Let's start w/ Weiss's MFT for the Ising model. We start with a simple observation: For $J=0$, the Ising model is trivial to solve:

$$Z(J=0,H,T) = \sum_{\{S_i\}} e^{\beta H \sum_i S_i} = \sum_{S_1} e^{\beta H S_1} \times \sum_{S_2} e^{\beta H S_2} \cdots \sum_{S_N} e^{\beta H S_N}$$

$$= \left(2\cosh\beta H\right)^N \quad \underline{\text{and}} \quad M = -\frac{1}{N}\frac{\partial F}{\partial H} = \tanh\frac{H}{k_B T}$$

* <u>Weiss's idea</u>: a given spin S_i feels an <u>effective</u> field due to the external H + an induced field coming from the average magnetization of the other spins, so that

$$Z(J\neq 0,H,T) \approx \sum_{\{S_i\}} e^{\beta \sum_i H_{eff}^{(i)} S_i}$$

$$= \prod_{i=1}^{N} 2\cosh\beta H_{eff}^{(i)}$$

* Since no one spin is "special," $H_{eff}^{(i)} = H_{eff}$ and

$$Z_{Weiss}(J,H,T) = \left[2\cosh\beta H_{eff}\right]^N$$

* Note of course that the J-dependence is hidden in H_{eff}.

* The question then is how to find H_{eff}?

* How to find H_{eff}?

$$H_N = -\sum_{\substack{ij \\ i\neq j}} J_{ij} S_i S_j - H \sum_i S_i$$

$$= -\sum_i S_i \left(\sum_{j\neq i} J_{ij} S_j + H \right) \qquad \text{let } S_j = \langle S_j \rangle + \underbrace{\left(S_j - \langle S_j \rangle\right)}_{\delta S_j}$$

δS_j treat as small and ignore

$$\therefore H_N \approx -\sum_i H_{eff}^{(i)} S_i \qquad H_{eff}^{(i)} = \sum_{j\neq i} J_{ij} \langle S_j \rangle + H$$

* but no spin is "special" so $\langle S_i \rangle = \langle S_j \rangle = M$

$$\therefore H_{eff} = M \sum_{j\neq i} J_{ij} + H \qquad J_{ij} = \begin{cases} J & i,j \text{ nearest neighbors} \\ 0 & \text{else} \end{cases}$$

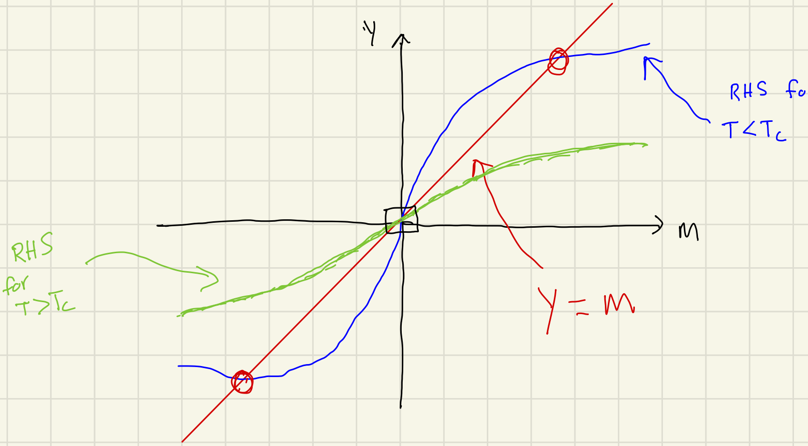
$$H_{eff} = 2dJM + H$$

Therefore, $Z_{MFT} = \left[2\cosh \beta H_{eff}\right]^N$ and $M = \tanh\left(\frac{H_{eff}}{k_B T}\right) = \tanh\left(\frac{2dJM + H}{k_B T}\right)$

* Setting $H=0$ we can see if there is some T_c below which $M \neq 0$:

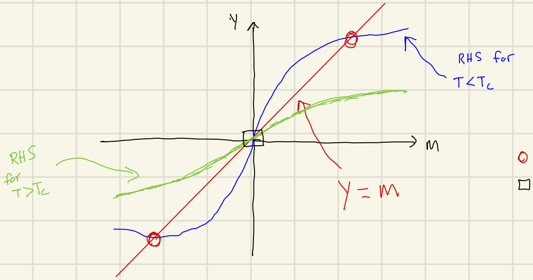
$$M = \tanh\left[\frac{2dJM}{k_B T}\right] \qquad \text{* let } T_c = \frac{2dJ}{k_B}$$

$$\boxed{M = \tanh\left[\frac{T_c}{T} M\right] \quad \text{solve graphically in the usual way...}}$$



○ = Stable Sol'n

□ = Unstable Sol'n

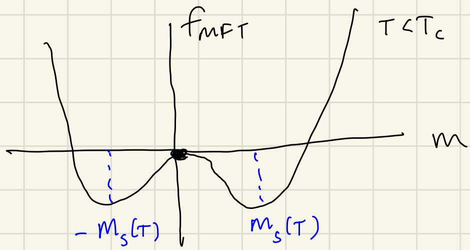


$$m = \operatorname{Tanh}\left[\frac{T_c}{T} m\right]$$

○ = Stable Sol'n
□ = Unstable Sol'n

what does this mean?

From Z_{MFT}, calculate f_{MFT} near $T \lesssim T_c$ (expand in powers of m)



$\Rightarrow$ Sol'n at $m=0$ for $T<T_c$ is not a minimum

* Critical Exponents

Reminder: 1) $C_{H=0} = -T \left.\frac{\partial^2 f}{\partial T^2}\right|_{H=0} \sim |t|^{-\alpha}$

2) $M_{H=0} = -\left.\frac{\partial f}{\partial H}\right|_{H=0} \sim |t|^{\beta}$

3) $\chi_T = \left.\frac{\partial M}{\partial H}\right|_T^{H=0} \sim |t|^{-\gamma}$

4) $M(t=0, H) \sim H^{1/\delta}$

5) $G(\vec{r}) = \langle s_i s_j \rangle_c \sim \frac{1}{r^{d-2+\eta}}$ at $t=0$
$|\vec{r}_i - \vec{r}_j| = r$

6) $\xi \sim |t|^{-\nu}$

Spatial correlations (needs a more sophisticated treatment than this type of MFT)

∴ Let's focus on the 4 exponents that don't have to do with spatial correlations.
Start from the MFT equation of state (EOS) relating M and H

$$M = \tanh\left[h + M\tau\right] \qquad \tau \equiv \frac{T_c}{T}, \quad T_c \equiv \frac{2dJ}{k_B}, \quad h \equiv \frac{H}{k_B T}$$

* For $h=0$ and $T \to T_c^-$, we can Taylor expand in m ($\ll 1$):

$$m \approx m\tau - \frac{1}{3}m^3\tau^3$$

$$\Rightarrow \frac{1}{3}m^3\tau^3 = m(\tau - 1)$$

$$\therefore m^2 \approx 3\left(\frac{\tau - 1}{\tau^3}\right) \approx 3t + \cdots$$

$$\Rightarrow m\Big|_{h=0} \sim t^{1/2} \Rightarrow \boxed{\beta = \frac{1}{2}}$$

* For $h \neq 0$ (but small) and $T = T_c^-$, again treat h + m as small and expand the EOS (after some tedious algebra):

$$\Rightarrow h \simeq m(1-\tau) + m^3\left(\tau - \tau^2 + \frac{\tau^3}{3}\right) + \cdots \qquad (XX)$$

Setting $\tau = 1$,

$$\Rightarrow h \sim \frac{m^3}{3} \quad \text{at } t = 0$$

$$\boxed{\therefore m \sim h^{1/3} \Rightarrow \delta = 3}$$

* Taking $\frac{\partial}{\partial h}$ of (XX) and setting $h=0$

$$\Rightarrow 1 \simeq \frac{\partial m}{\partial h}\Big|_{h=0}(1-\tau) + 3m^2\frac{\partial m}{\partial h}\Big|_{h=0}\left(\tau - \tau^2 + \frac{\tau^3}{3}\right) \cdots$$

$$1 \simeq \underbrace{\frac{\partial m}{\partial h}\bigg|_{h=0}}_{\chi_T}(1-\tau) + 3m^2 \underbrace{\frac{\partial m}{\partial h}\bigg|_{h=0}}_{\chi_T}\left(\tau-\tau^2+\frac{\tau^3}{3}\right) \cdots$$

$$1 \simeq \chi_T\left(1-\tau + 3m^2\left(\tau-\tau^2+\frac{\tau^3}{3}\right)+\cdots\right) \quad (\star)$$

* taking $T \to T_c^+$ where $m=0$,

$$\Rightarrow \chi_T \sim \frac{1}{1-\tau} = \frac{1}{1-\frac{T_c}{T}} = \frac{T}{T-T_c} = \frac{T}{T_c}\left(\frac{T_c}{T-T_c}\right) = t^{-1}$$

$$\boxed{\therefore \chi_T \sim t^{-1} \Rightarrow \gamma = 1}$$

* **Exercise**: Take $T \to T_c^-$ where $m \neq 0$ and convince yourself that you get $\gamma=1$ as when $T \to T_c^+$.

* **Exercise**: Show that $C_{H=0}$ has a jump discontinuity (so there is no α-value) at $T=T_c$.

Comments: 1.) Note that MFT predicts long-range order indep. of d, while we know from exact solutions that $T_c>0$ only occurs for $d=2$ & higher. This is a general feature, that MFT tends to predict a T_c that is higher than the exact solutions. This is because MFT neglects fluctuations, which tend to destroy long-range order.

2.) Related to this, notice the critical exponents have no dependence on d. When we get to Landau-Ginzburg theory, we'll see this is a general feature of MFT. I.e., the Universality is "too strong".