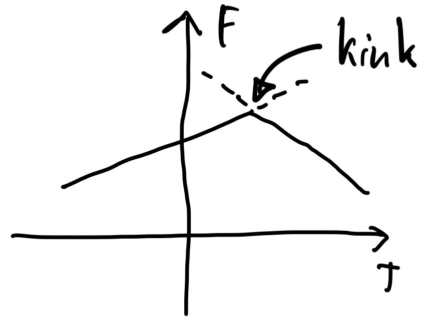
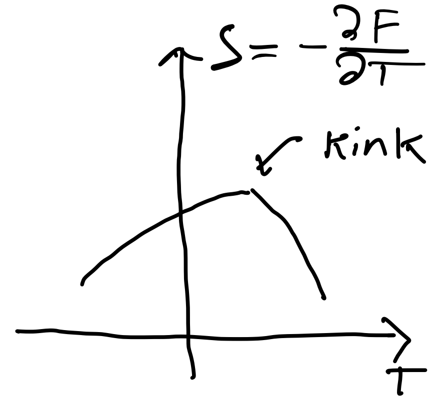
Landau Theory

A phase transition occurs when thermo-potential, e.g. $F(T, N, V)$, has non-analytic behavior in $T, N, V, \dots$





1st Order:
$\partial_g F$ discontinuous

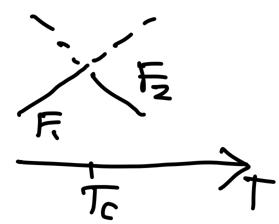
2nd Order
$\partial_g F$ continuous,

Since $S = -\frac{\partial F}{\partial T}$, $P = -\frac{\partial F}{\partial V}$, $\kappa^{-1} = -\frac{1}{V}\frac{\partial^2 F}{\partial V^2}$ etc

$\hookrightarrow$ jumps (1st) / kinks (2nd) in observables

= First order behaviour:

- metastability
- hysteresis
- Latent heat



$$S_1 = -\frac{\partial F_1}{\partial T} \leq S_2 = -\frac{\partial F_2}{\partial T}$$

Since $F_1 = F_2$ at transition

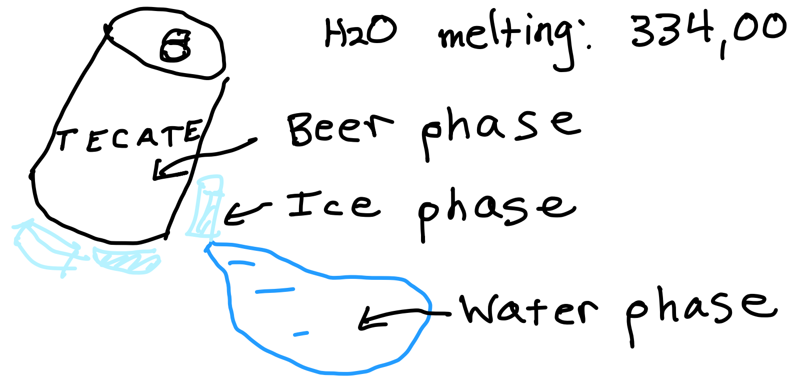
$$F_1 = E_1 - S_1 T_c = E_2 - S_2 T_c$$

$$(S_2 - S_1) T_c = E_2 - E_1 \cong \Delta Q \geq 0$$

So if system heats up $T_c - \epsilon \longrightarrow T_c + \epsilon$ it must absorb extensive "Latent Heat ΔQ"

Like a $C = \frac{dE}{dT} = \infty$

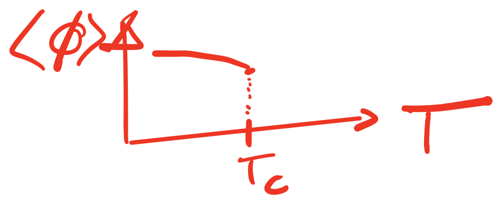
Latent Heat is useful:



H_2O melting: $334{,}000\ J/Kg = \Delta Q$

Liquid $\rightarrow$ steam: $2.2\ 10^6\ J/Kg = \Delta Q$

Can also show SSB (rare).
Ex.: Potts model w/ $q > 4$

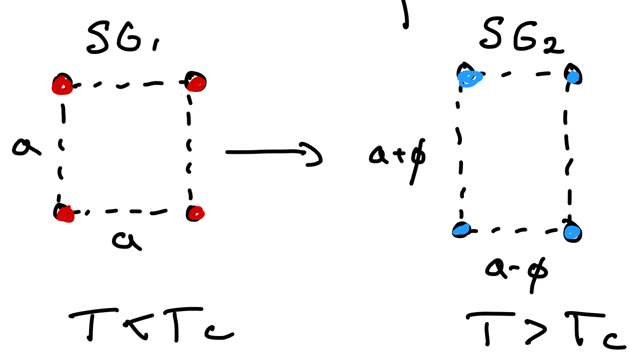


but, maybe, it's not really spontaneous. There must be an effective non-zero "field"

1st: Discontinuous change in order param.

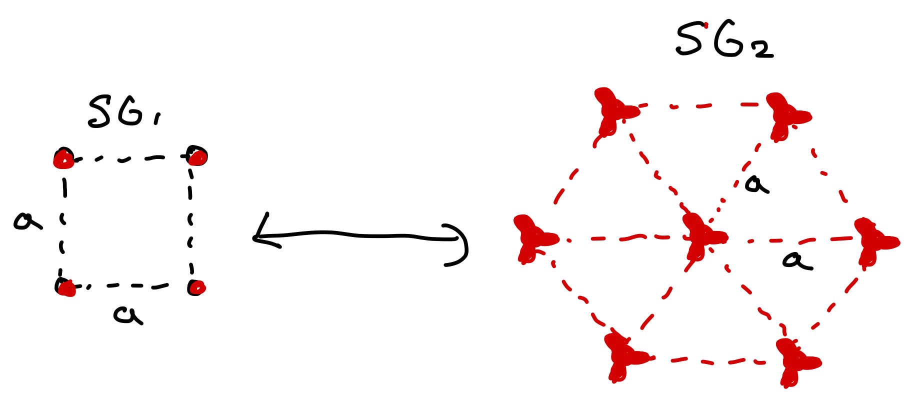
2nd: cont. " "

Continuous Phase transitions, on the otherhand, are found to occur between certain "allowed" pairs of phases. For example, consider a transition between two structural phases of crystal:



On both sides there is a "space group", SG_1, SG_2, describing symmetry of crystal (230 in 3D). In this case $SG_2 \subset SG_1$ and we will
subgroup

find continuous allowed. But for

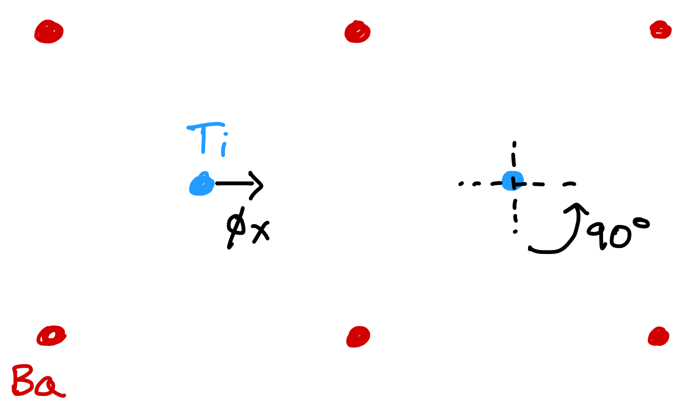


no continuous critical point observed; "forbidden". Can be related to group-theoretic considerations, e.g. $SG_2 \not\subset SG_1$

Order parameters

Symmetry breaking always implies a phase transition. If $g\hat{H}g^{-1} = \hat{H}$ for $g \in G$ (e.g. $\sigma \Leftrightarrow -\sigma$ for $H = \sum \sigma_i \sigma_j$)

and "ϕ" is an observable with $g\phi g^{-1} \neq \phi$, we call ϕ an "order parameter" for g. Ex:



The cubic crystal has various symmetries including $M_{x/y}$ and C_4 ($R_{90°}$)

However in (say) $BaTiO_3$, above some T_c, the Ti displace by

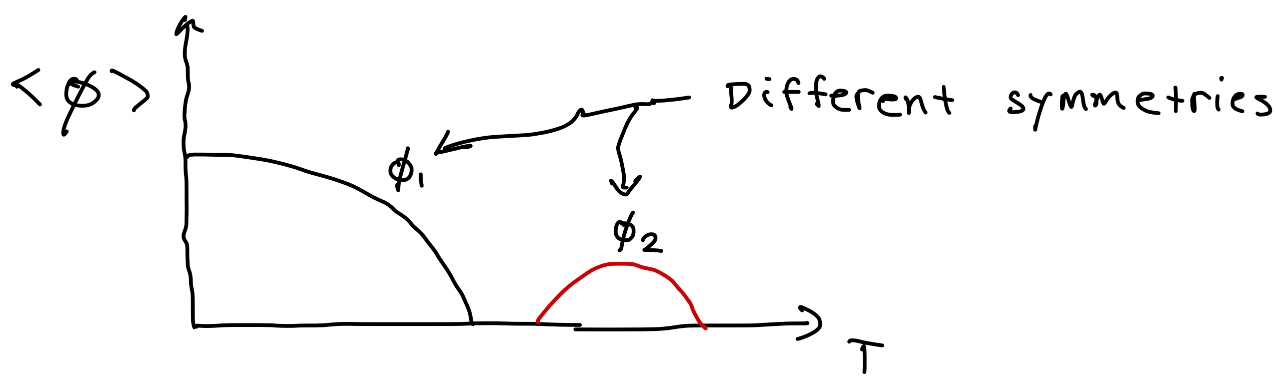
$$\vec{\phi} = (\phi_x, \phi_y)$$

Since $R_{90°} : (\phi_x, \phi_y) \longrightarrow (-\phi_y, \phi_x) \neq \vec{\phi}$,

$\vec{\phi}$ is "order parameter" for $R_{90°}$

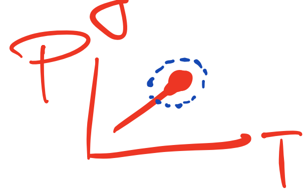
Formally, order parameters carry an "irreducible representation" (irrep) of the symmetry group.

If $\langle \phi \rangle \neq 0$, the symmetry is (spontaneously) broken. So $\langle \phi \rangle = 0$ vs $\langle \phi \rangle \neq 0$ is sharp distinction which must be separated by phase transition:



Landau theory is a phenomenological framework for deriving when its possible to have ~~direct~~, continuous transitions between different orders (and there are some "beyond Landau" exceptions).

+ neighborhood of continuous transitions.



The "effective" Hamiltonian / Free energy

Suppose we have identified an order parameter/s $\{\phi_i\}$, e.g., $\phi = \frac{1}{N}\sum_{i=1}^{N} \sigma_i$.

How do we understand transition? Of course if we can compute

$$\langle \phi \rangle = \frac{1}{Z}\sum_{\nu} e^{-\beta \mathcal{H}(\nu)} \phi(\nu),$$

we're good, but that's usually hard! Landau introduced idea of "effective" $\mathcal{H}_{eff}(\phi)$.

Key is trivial identity:

$$\int d\phi \; \delta(\phi - x) = 1$$

We can write

$$e^{-\beta F} = \sum_{\nu} e^{-\beta \mathcal{H}[\nu]} = \int d\Phi \; \underbrace{\sum_{\nu} e^{-\beta \mathcal{H}[\nu]} \delta(\Phi - \phi(\nu))}_{\equiv e^{-\beta \cdot V \cdot \mathcal{H}_{eff}(\Phi, \beta)}}$$

$$e^{-\beta F} = \int d\Phi \; e^{-\beta \cdot V \cdot \mathcal{H}_{eff}(\Phi, \beta)}$$

$$\langle \phi \rangle = \frac{\int d\Phi \; e^{-\beta \cdot V \cdot \mathcal{H}_{eff}(\Phi, \beta)} \; \Phi}{\int d\Phi \; e^{-\beta \cdot V \cdot \mathcal{H}_{eff}(\Phi, \beta)}}$$

As $V \to \infty$, dominated by max

$$\partial_{\Phi} \mathcal{H}_{eff}(\Phi, \beta) = 0$$

The solution then gives $\langle \phi \rangle$ and

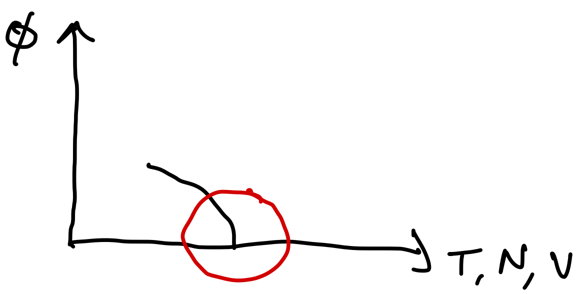
$$\frac{F}{V} = \mathcal{H}_{eff}(\phi, \beta)$$

So, <u>if</u> we could compute $\mathcal{H}_{eff}(\Phi, \beta)$, we could calculate any property ϕ, β, F, C_V, S etc from <u>one</u> variable stat-mech! Of course we've just swept problem under the rug:

$$e^{-\beta \cdot V \cdot \mathcal{H}_{eff}(\Phi, \beta)} = \sum_{\nu} e^{-\beta \mathcal{H}[\nu]} \delta(\Phi - \phi(\nu))$$

is hard to compute. Here's where we go pheno! Near a (continuous) phase transition, ϕ is small:

key reason to look at 2nd order p.t.s!



So expand

$$\mathcal{H}_{eff} = \mathcal{H}_0 + \alpha \cdot \phi + A\phi^2 + C\phi^3 + B\phi^4 + \cdots$$

where $\mathcal{H}_0$, α, A etc depend on T, V, N etc.

If there are multiple order parameters, ϕ_i, then $\sum_i \alpha_i \cdot \phi_i + A_{ij} \phi_i \phi_j +$ etc.

Since $\mathcal{H}[g \cdot \nu] = \mathcal{H}[\nu]$ for $g \in G$, we know

$$\mathcal{H}_{eff}(g \cdot \Phi, T, N, V) = \mathcal{H}_{eff}(\Phi, T, N, V)$$

This constrains the expansion. In particular, since $g \Phi \neq \Phi$ for some $g \in G$ (order parameter) $\boxed{\alpha = 0}$

$$\mathcal{H}_{eff} = \mathcal{H}_0 + A\phi^2 + C\phi^3 + B\phi^4 + \cdots$$

In general, $A_{ij} \phi_i \cdot \phi_j$ (etc) can only have $A_{ij} \neq 0$ if decomposing the tensor product

$$\phi \otimes \phi = \Gamma_1 + \Gamma_2 + \cdots$$

contains irrep $\Gamma_1 = \mathbb{1}$ (trivial).

This is just complicated way of saying $\mathcal{H}_{eff}$ is symmetric under G.

Ising Example: $g(\sigma) = -\sigma$ $\quad g^2 = 1$

$G = \mathbb{Z}_2$

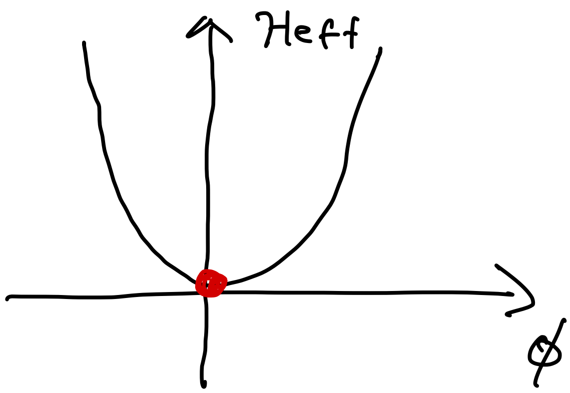
$$\phi = \frac{1}{N}\sum \sigma_i, \quad g(\phi) = -\phi$$

So ϕ^3 is forbidden:

$$\mathcal{H}_{eff}(\beta) = \mathcal{H}_0 + A\phi^2 + B\phi^4 + \dots$$

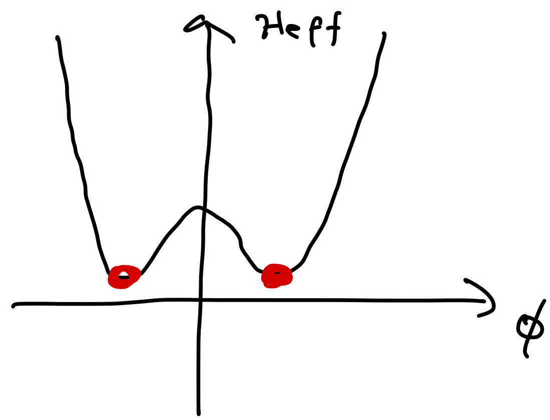
Let's assume (for now) $B > 0$, so $D\phi^6$ won't be important. Two cases:

$A > 0$



$\langle \phi \rangle = 0$

$A < 0$



$\langle \phi \rangle \neq 0$

$$0 = \frac{\partial \mathcal{H}_{eff}}{\partial \phi} = \phi(2A + 4B\phi^2) = 0$$

$$\phi = \pm\sqrt{\frac{|A|}{2B}} \quad \text{for } A < 0$$

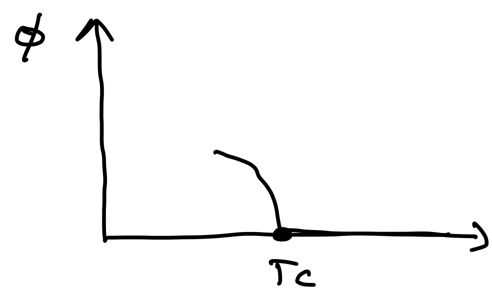
The critical point is $A=0$, so we can expand

$$A = \alpha_0 (T-T_c) + \alpha_1 (T-T_c)^2 + \cdots$$

To leading $T-T_c$,

$$\langle \phi \rangle = \pm \sqrt{\frac{\alpha_0 |T-T_c|}{2B}} \propto \pm |T-T_c|^{1/2}$$

for $T < T_c$



Predicts critical exponent

$$\boxed{\text{“}\beta = 1/2\text{''}}$$

We can then compute F:

$$F(T) = F_0(T) + A\phi^2$$

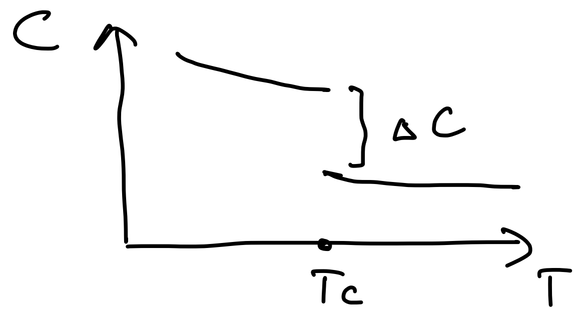
$$= \begin{cases} F_0(T) - \dfrac{\alpha_0^2 (T-T_c)^2}{4B} + \cdots, & T < T_c \\ F_0(T), & T > T_c \end{cases}$$

$F_0(T) = f_0 + (T-T_c)\cdot f_1 + \cdots$ is "smooth" across transition, but $A\phi^2 + B\phi^4$ gives kink

$$S = -\frac{\partial F}{\partial T} = \begin{cases} S_0(T) + \dfrac{\alpha_0^2 (T-T_c)}{2B} + \cdots, & T < T_c \\ S_0(T), & T > T_c \end{cases}$$

$$C = T\frac{\partial S}{\partial T} = \begin{cases} C_0(T) + T\cdot\dfrac{\alpha_0^2}{2B} \\ C_0(T) \end{cases}$$

So heat capacity (but not F, S, ϕ) jumps:



Field Dependence

If $H[\mu] \rightarrow H(\mu) - h\cdot\sum \sigma_i$, then we <u>exactly</u> have

$$\mathcal{H}_{eff} = \mathcal{H}_0 - h\phi + A\phi^2 + B\phi^4 + \cdots$$

We can then use same analysis near T_c!

$$h = 2\alpha_0(T-T_c)\phi + 4B\phi^3$$

We now have $\phi \neq 0$ for <u>any</u> $\boxed{t = T - T_c}$: transition is "rounded out". The width of the rounding (in t) is

$$\alpha_0 t \phi^2 \sim h \phi$$

$$\phi t \sim \frac{h}{\alpha_0}$$

With $\phi \sim \sqrt{\alpha_0 t / 2B}$ ($h = 0$ result)

Width of h-induced rounding:

$$\boxed{\Delta t \sim h^{2/3} B^{1/3} / \alpha_0}$$

Susceptibility

$$h = 2 \alpha_0 t \phi + 4 B \phi^3$$

<u>For $t > 0$</u>, to leading order

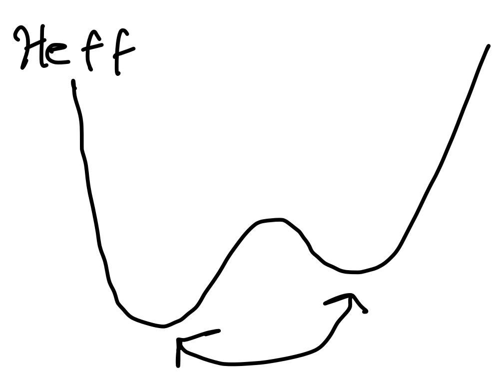
$$\phi = \frac{h}{2 \alpha_0 t} \Rightarrow \chi \Big|_{h=0} = \frac{1}{2 \alpha_0 t}$$

Diverges as $1/t$.

<u>For $t = 0$:</u>

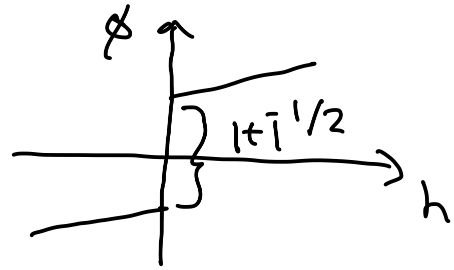
$$\phi = \left(\frac{h}{4B} \right)^{1/3} \qquad \text{"}\delta = 3\text{"}$$

For $t < 0$:



Jumps!

For $t<0$



However, we can calculate

$$\chi(t,h) = \partial_h \phi \quad \text{at} \quad h = 0 \pm \epsilon;$$

From $h = 2\alpha_0 t \phi + 4B\phi^3$, we expand

$$\phi = \sqrt{-\frac{\alpha_0 t}{2B}} + \delta\phi$$

$$\hookrightarrow h = 2\alpha_0 t\, \delta\phi + 12B\,\delta\phi\left(-\frac{\alpha_0 t}{2B}\right) + O(\delta\phi^2)$$

$$\delta\phi = \frac{h}{-4\alpha_0 \cdot t} \sim t^{-1}$$

Summary of "Exponents"

- "Heat capacity exponent" $\boxed{\alpha}$

$$C \sim \begin{cases} A_+ \, t^{-\alpha}, & t>0 \\ A_- \, (-t)^{-\alpha}, & t<0 \end{cases} \quad : \alpha = 0$$

- "order parameter exponent" $\boxed{\beta}$

$$\langle\phi\rangle(t, h=0) \propto \begin{cases} 0, & t>0 \\ \mathrm{sgn}(h)(-t)^{\beta}, & t<0 \end{cases} \quad : \beta = \tfrac{1}{2}$$

- "susceptibility exponent" $\boxed{\gamma}$

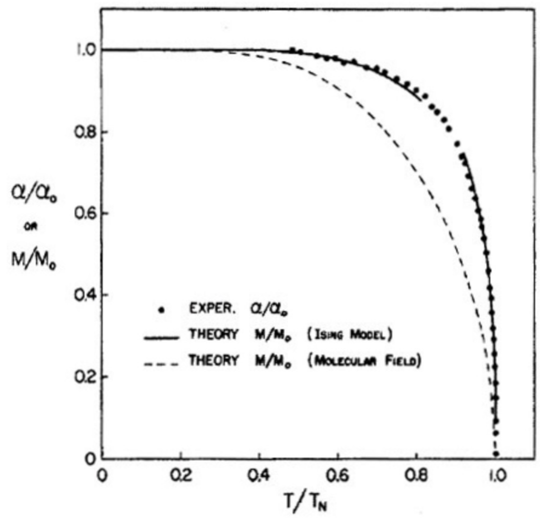
$$\chi(t\neq 0, h=0) \propto \begin{cases} C_+ |t|^{-\gamma} \\ C_- |t|^{-\gamma} \end{cases}, \quad \gamma = 1$$

- "Isotherm exponent" $\boxed{\delta}$

$$\langle\phi\rangle(t=0, h) \propto \mathrm{sgn}(h)\cdot|h|^{1/\delta} \qquad \delta = 3$$

Experiment: ferromagnetism in $DyPO_4$

$\langle \phi \rangle$



As predicted, $\langle \phi \rangle \sim t^{-\beta}$ is a perfect power law near $t \sim 0$. But $\beta \simeq 0.32$ vs prediction $\beta = 0.5$!

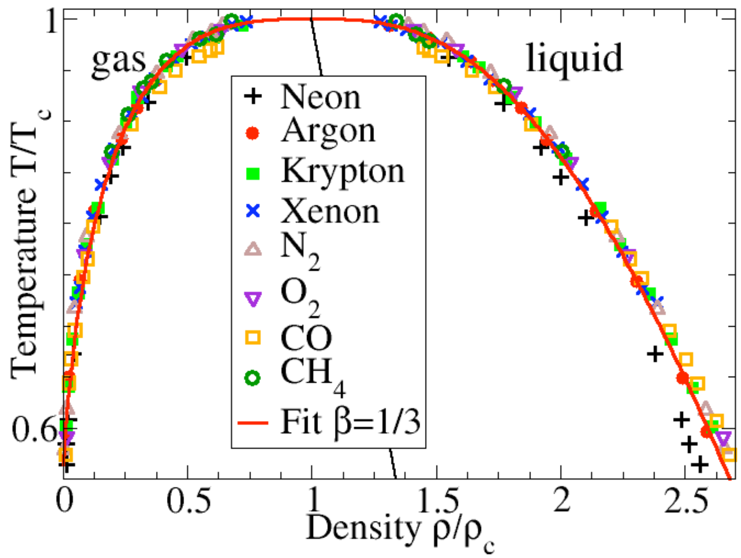
Remarkably, all 3D magnets with Ising-like order parameter are found to have the same exponents to within a couple digits:

	α	β	γ	δ
MFT:	0	0.5	1	3
Exp:	0.11	0.32	1.24	4.8

This surprising "universality" is subject of PH212.

Universality: Shared Critical Behavior

Ising Model and Liquid-Gas Critical Point

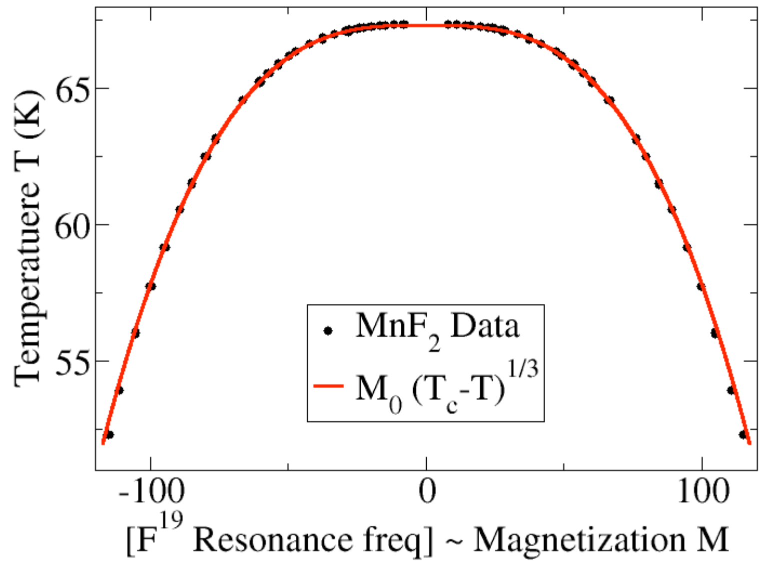


Liquid-Gas Critical Point

$$\rho - \rho_c \sim (T_c - T)^\beta$$

$$\rho^{Ar}(T) = A\, \rho^{CO}(BT)$$

Same critical exponent β=0.332!



Ising Critical Point

$$M(T) \sim (T_c - T)^\beta$$

$$\rho^{Ar}(T) = A(M(BT),T)$$

Universality: Same Behavior up to Change in Coordinates

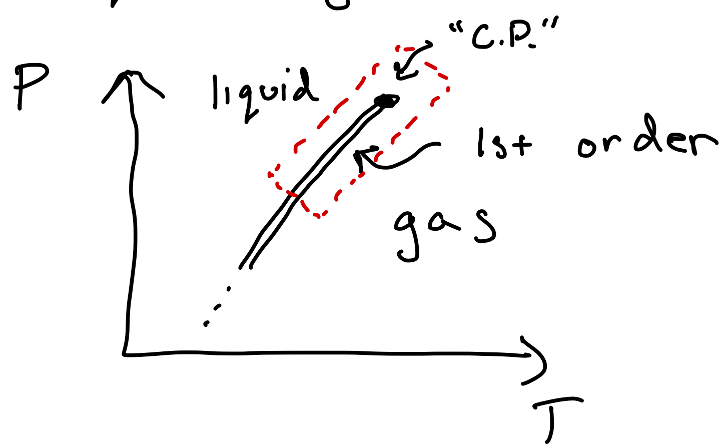
$$A(M,T) = a_1 M + a_2 + a_3 T + \textit{(other singular terms)}$$

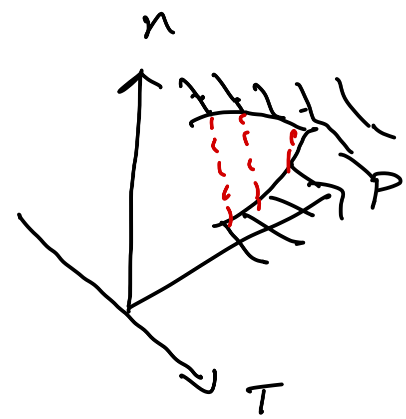
Nonanalytic behavior at critical point (not parabolic top)

All power-law singularities (χ, c_v, ξ) are shared by magnets, liquid/gas

(Non-symmetric Models: ϕ^3)

The Ising symmetry allowed us to eliminate odd terms in $\mathcal{H}_{eff}$, but that doesn't mean the formalism can't be applied more generally. Recall the liquid-gas transition:





Across the transition, the density "n" jumps. This suggests we consider

$$e^{-\beta V \mathcal{H}_{eff}(n)} \equiv \sum_{\nu} e^{-\beta \mathcal{H}(\nu)} \, \delta(n - n(\nu))$$

Now n is not small, so we can't immediately Taylor expand in n. But define $n = n_{c.p.} + \delta n$, $\frac{\delta n}{n} \ll 1$, so

$$\mathcal{H}_{eff}[\delta n] = E^\circ + \alpha_1 \delta n + \alpha_2 \delta n^2 + \alpha_3 \delta n^3 + \alpha_4 \delta n^4 + \dots$$

with $\alpha_i(P,T)$, and $\alpha_1, \alpha_3 \neq 0$

Now let's make one more shift. For each P, T, we can shift by $\delta n^*(P,T)$

$$\delta n = [\phi + \delta n^*(P,T)].$$

why possible?

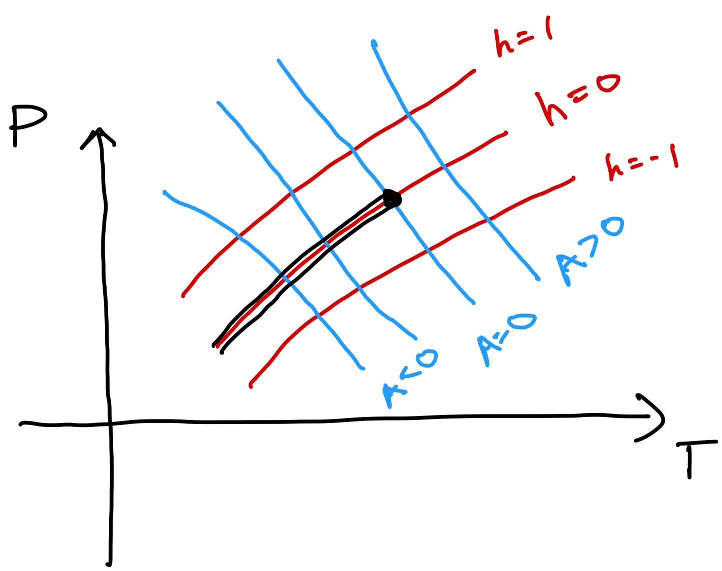
chosen such that $\alpha_3 \longrightarrow 0$:

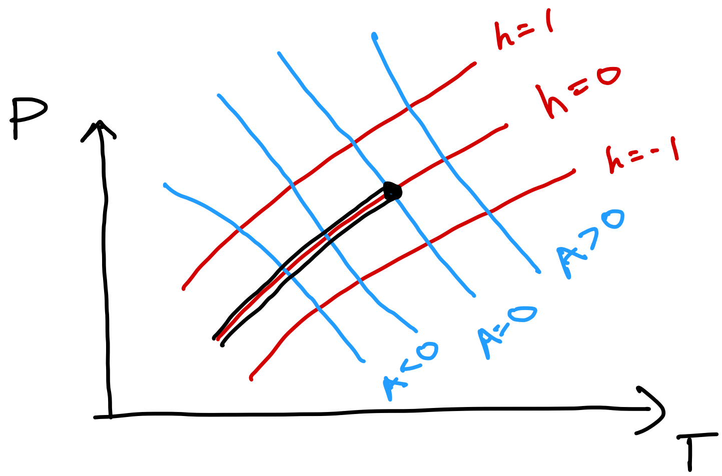
$$\mathcal{H}_{eff}\{\phi\} = E^\circ + h(P,T)\phi + A(P,T)\phi^2 + B(P,T)\phi^4$$

However, we can't get rid of h.

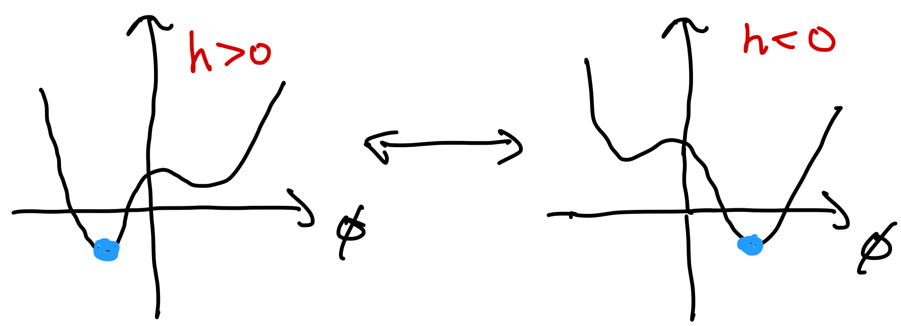
$A(P,T)$, $h(P,T)$ vary smoothly in P, T,

so they are like "change of coordinate" from $P, T \longrightarrow A, h$ space:





In terms of ϕ, h, A, now no different than Ising: system minimizes $\mathcal{H}_{eff}[\phi]$, which lead to phase transition for all $A<0$, $h=0$:



However, this is first order. The continuous critical point occurs only at special $A=h=0 \longleftrightarrow (T_*, P_*)$

This illustrates general principle in Landau theory. A critical transition requires both $A=h=0$, so we need to control two knobs (P, T) to "tune" to this point. So generically transition is 1st order. With symmetry, however, $h=0$ "for free", so only need 1 knob (T) $\rightarrow$ generically continuous.