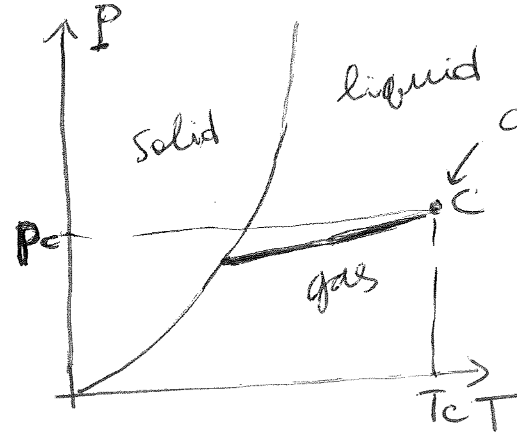
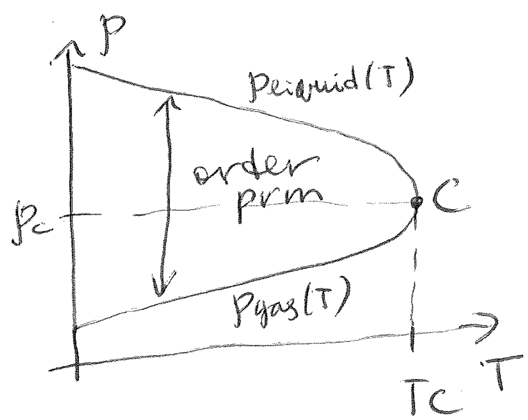
Phase transitions

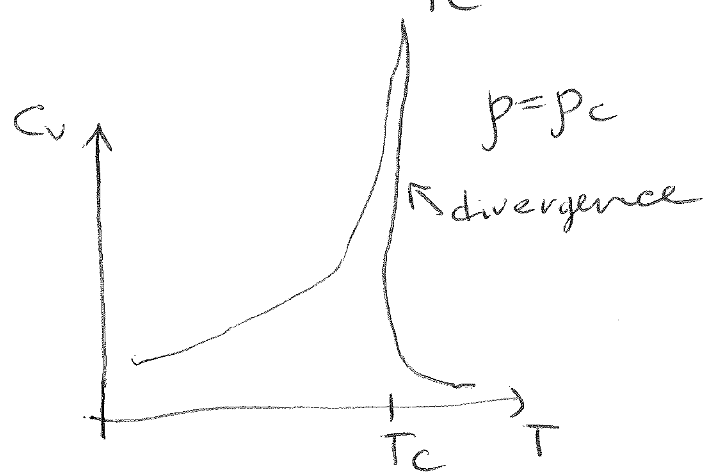
Sharp change in the properties of the substance. Liquid ⇔ gas, metal ⇔ SC, etc.



critical point,
diff. in density = 0 @ C
order parameter of the liquid-gas transition

Liquid-gas transition:





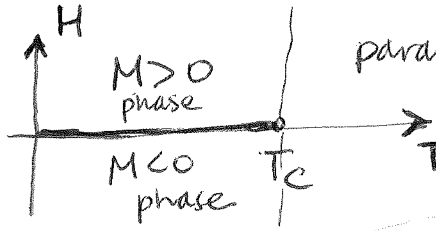
$\rho = \rho_c$ [argon]

Magnetic phase transitions:

$\vec{M}$ is magnetic dipole moment per unit volume

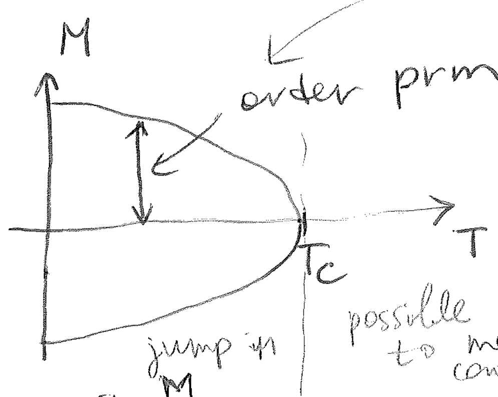
magnetic field

$$\vec{B} = \mu_0 (\vec{H} + \vec{M})$$



paramagnetic phase [M=0 when H=0]

$\vec{M} = \chi_m \vec{H}$ but not in ferro-magnets



Spontaneous magnet'n $\pm M(T)$ below T_c, even @ H=0

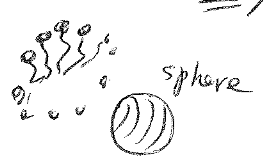
Surfactants in solution

molecules with polar (hydrophylic) head groups & hydrophobic (hydrocarbon) tails

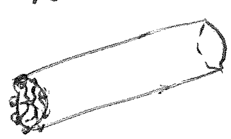
As surfactant concentr'n goes up,

molecules

=> micelles

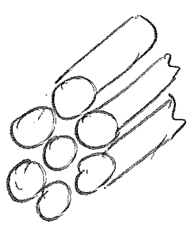


=> cylindrical micelles

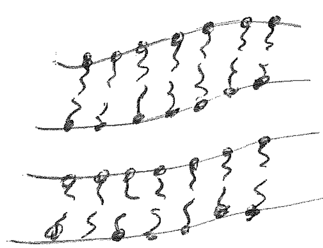


=>

=> Hexagonal phase



=> Lamellar phase



OR Cubic phase

fcc(?)

[2D Ising model on a square lattice]

$s_i = \pm 1$

$\mathcal{H} = -J \sum_{\langle ij \rangle} s_i s_j$ [favors parallel alignment]

Phase diagram as above...

<u>$T > T_c$</u>: finite correlation (~cluster size) length, short-range order

group spins together: $b = 3, 3^2, 3^3, \ldots$ by majority rule → correlation between new cells decrease; $T_r \uparrow$. As $T \to T_c$ from above, corr'n length increases

<u>$T = T_c$</u>: $\underline{\underline{\infty}}$ correlation length; ordered structures exist on every length scale

The system remains @ T_c under renormalization →

→ self-similarity

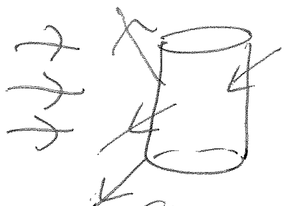
<u>$T < T_c$</u>: $M = \sum_i s_i \neq 0$ "spontaneously"

Clusters of spins of the same sign → long-range order

as $T \to 0$, all spins get aligned; as $T \uparrow$ from 0, the correl'n length $\uparrow$ & becomes ∞ at T_c, destroying all long-range order

Renormalization: flow toward $T=0$ from $T < T_c$.

Density fluct's in fluids →
→ critical opalescence



Strong reflection, fluid appears milky white

Happens @ a range of λ's → fluct's on many length scales. Also, happens at fixed λ and a range of T → fluct's at a given length scale persist as T is changed.

Correlation functions

spin-spin $\Gamma(\vec{r}_i, \vec{r}_j) = \langle (S_i - \langle S_i \rangle)(S_j - \langle S_j \rangle) \rangle$

position of i site ↑ ; ↑ thermal average

Translational invariance: $\langle S_i \rangle = \langle S_j \rangle = \langle S \rangle$

$$\Gamma(\vec{r}_i, \vec{r}_j) = \Gamma(\underbrace{|\vec{r}_i - \vec{r}_j|}_{= r}) = \langle S_i S_j \rangle - \langle S \rangle^2$$

$$\Rightarrow \Gamma(0) = \langle S^2 \rangle - \langle S \rangle^2 = 1 - \langle S \rangle^2$$

So, at $T > T_c$: $\langle S \rangle = 0$ $\quad \Gamma(r) \sim \frac{1}{r^{\tau}} e^{-r/\xi}$, $r > 0$ (ξ: corr'n length)

$T < T_c$: $\langle S \rangle \neq 0$

no magnetic field

$T = T_c$: $\Gamma(r) \sim \frac{1}{r^{d-2+\eta}}$ (d: # dims; η: critical exp)

Note that

$$\langle (M - \langle M \rangle)^2 \rangle = \langle M^2 \rangle - \langle M \rangle^2$$

$$Z_{(T,H)} = \sum_{\underset{\text{sum over all states}}{r}} e^{-\beta E_r}$$

$$E_r = -J \sum_{\langle ij \rangle} s_i s_j - \underbrace{\left(\sum_i s_i \right)}_{M} \cdot H$$

Then $\langle M^2 \rangle - \langle M \rangle^2 = (k_B T)^2 \dfrac{\partial^2}{\partial H^2} \log Z$

But $\underset{\substack{\uparrow \\ \text{isothermal} \\ \text{susceptibility}}}{\chi_T} = \left(\dfrac{\partial \langle M \rangle}{\partial H} \right)_T = - \left(\dfrac{\partial^2}{\partial H^2} \underset{\substack{\text{free en.} \\ \| \\ -k_B T \log Z}}{F} \right)_T =$

$= (k_B T) \left(\dfrac{\partial^2 \log Z}{\partial H^2} \right)_T$, so that

$$\langle M^2 \rangle - \langle M \rangle^2 = (k_B T)^2 \chi_T / (k_B T) = (k_B T) \chi_T.$$

On the other hand,

$$\langle (M - \langle M \rangle)^2 \rangle = \left\langle \left(\sum_i (s_i - \langle s_i \rangle) \right) \left(\sum_j (s_j - \langle s_j \rangle) \right) \right\rangle =$$

$$= \sum_{i,j} \left[\langle s_i s_j \rangle - \langle s \rangle^2 \right] = \sum_{i,j} \Gamma(|\vec{r}_i - \vec{r}_j|) =$$

$$= \underset{\substack{\uparrow \\ \# \text{spins}}}{N} \sum_i \Gamma(r_i) \sim N \int_0^\infty dr\, r^{d-1} \Gamma(r)$$

(choose $\vec{r}_0 = 0$)

Finally,

$$\chi_T \sim N \int_0^\infty dr\, r^{d-1} \underbrace{\Gamma(r)}_{\sim \frac{1}{r^{d-2+\eta}}}$$

$\rightarrow$ the $\int$ diverges at the upper limit if $\eta < 2$

$\uparrow$ diverges at $T=T_c$ [implies divergent fluct's in M]

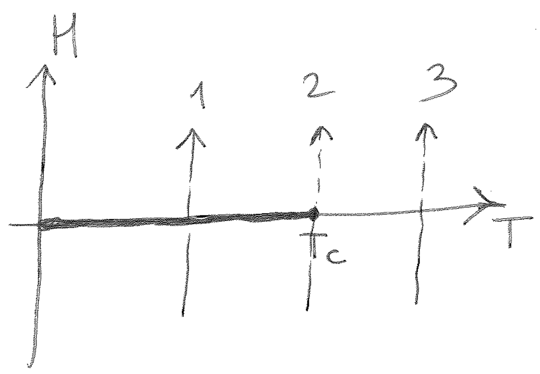
Ising model: consider $F = U - TS$

<u>1st order transition</u>: finite discontinuity in one or more of 1st derivative of F

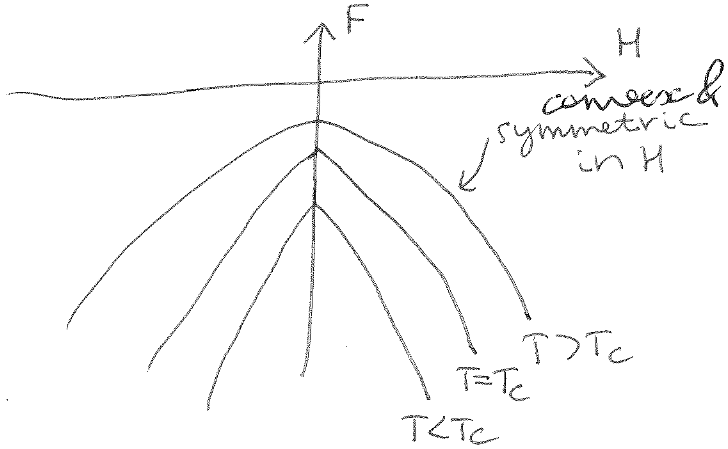
<u>Continuous (2nd order) transition</u>:

1st derivatives continuous but 2nd derivatives discont. <u>or</u> infinite

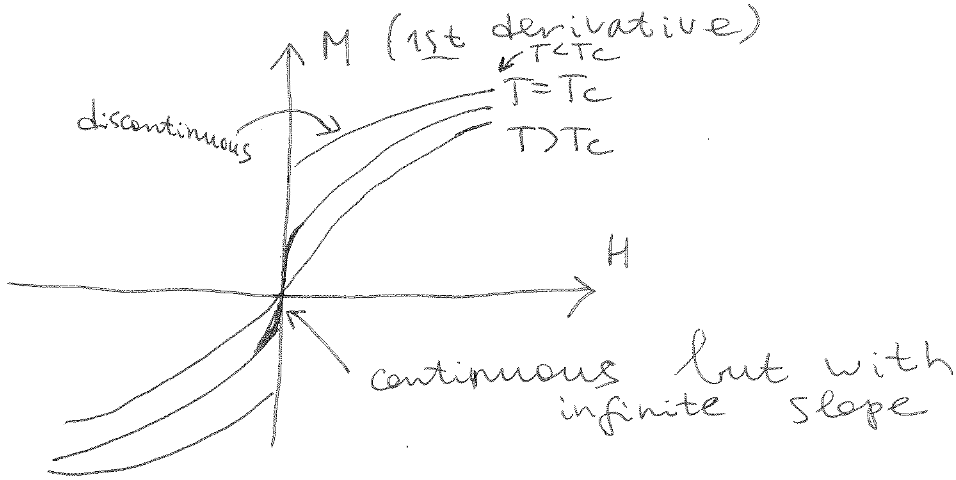
eg. divergent susceptibility $\Rightarrow$
$\Rightarrow$ divergent fluct's of M $\Rightarrow$
$\Rightarrow$ infinite corr'n length (i.e., power-law decay of correlations)

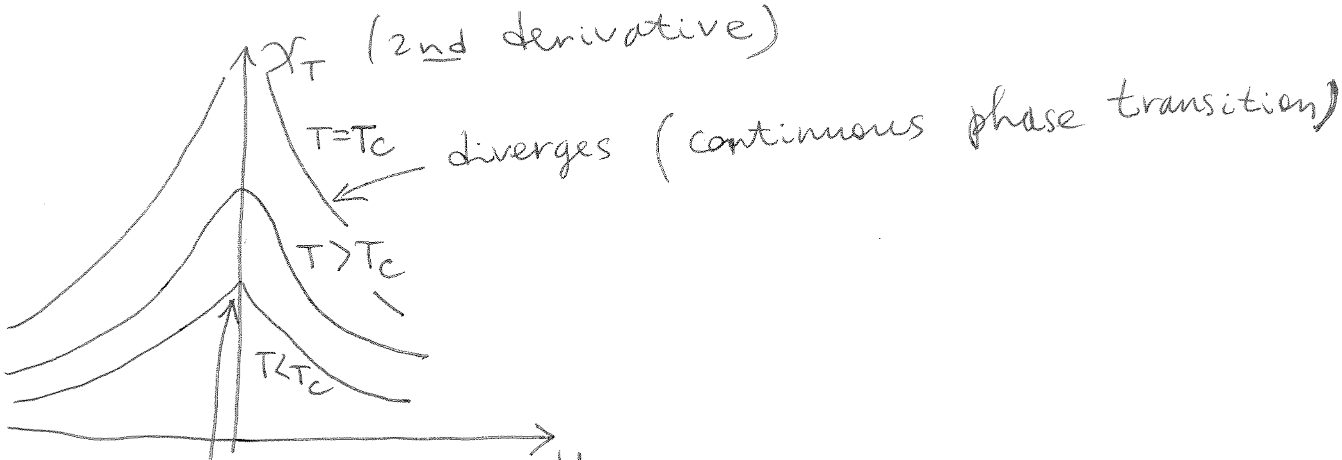


As a function of H:



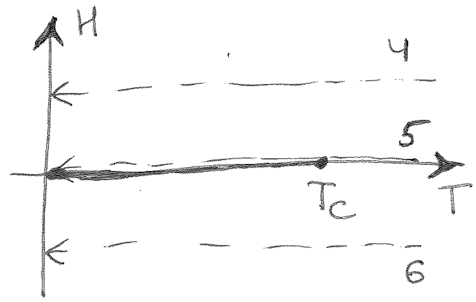
Cusp develops at $T=T_c$ and stays at $T<T_c$

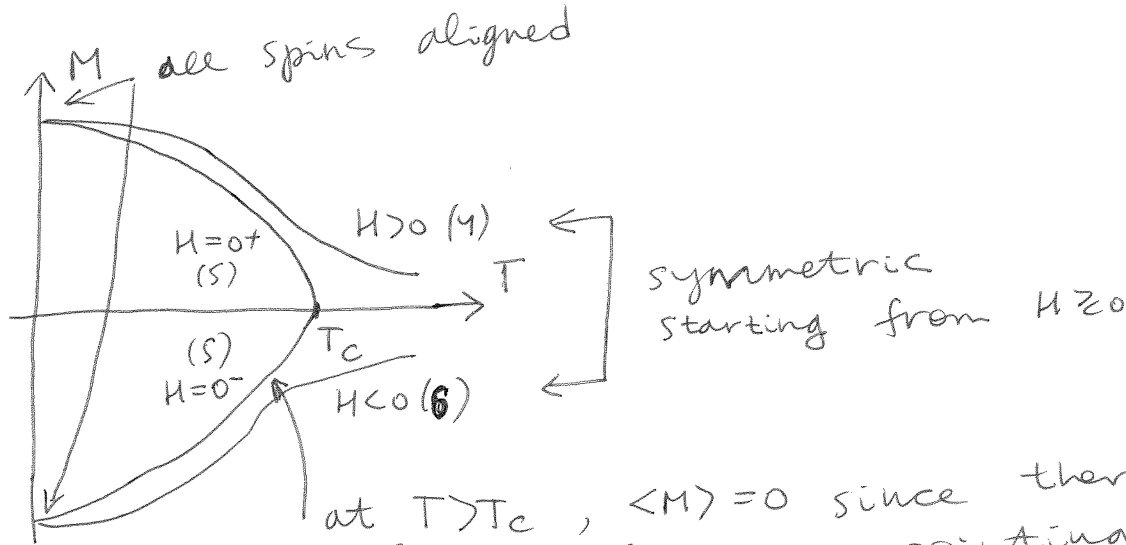




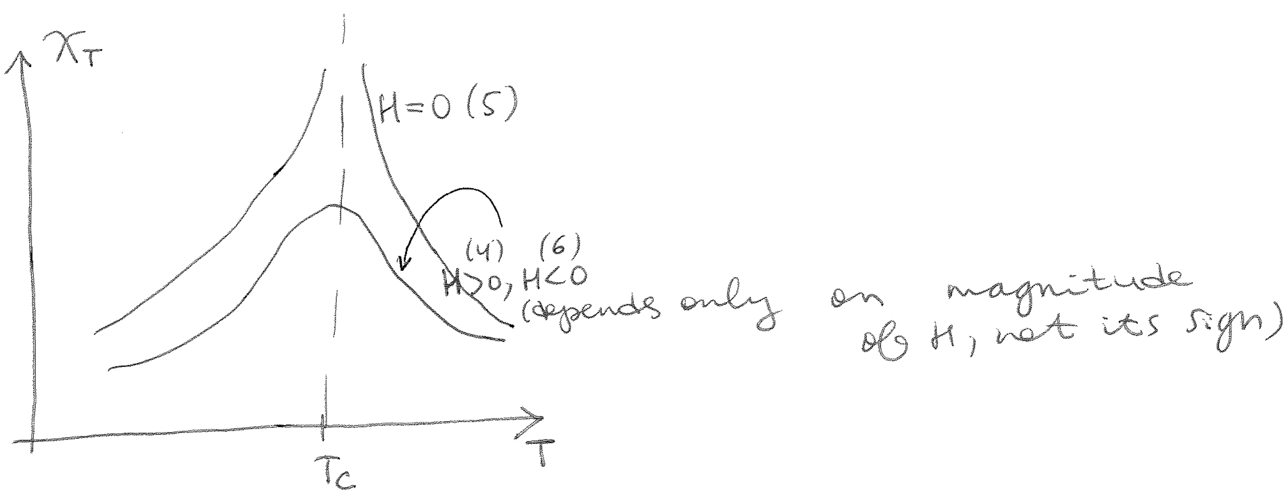
cusp at 1st order phase transition ($H=0$)

As a function of T:





at $T > T_c$, $\langle M \rangle = 0$ since there're clusters of spins pointing up and down, & no preference between them. At $T = T_c$, one cluster "takes over" by chance, & then reaches saturation as T↓



Critical exponents

Consider $t = \frac{T - T_c}{T_c}$

Critical exp. definition $\lambda = \lim_{t \to 0} \frac{\log |G(t)|}{\log |t|} \Rightarrow |G(t)| \sim |t|^\lambda$, or $G(t) \sim |t|^\lambda$.

For example,

$M \sim (-t)^\beta \quad [H=0] \quad \Rightarrow \beta \simeq \frac{1}{2}$ from the plot

$\chi_T \sim |t|^{-\gamma} \quad [H=0] \quad \Rightarrow \gamma > 0$ (χ_T diverges)

$\Gamma(r) \sim \frac{1}{r^{d-2+\eta}}$

Note that the same exponent works for χ_T above & below T_c (non-trivial!)

Corr'n length $\xi \sim |t|^{-\nu} \Rightarrow \nu > 0$

Universality

T_c depends on the system, but critical exponents are much more universal.

For example, in the 3D Ising model:

sc, bcc, fcc $\quad K_c = \frac{k_B T_c}{J} = 0.22, 0.16, 0.10$ respectively

But $\beta = 0.327$ is the same in all cases. So systems fall into universality classes $\Rightarrow$ can work with the simplest system of its class

Consider

$$C_H = T\left(\frac{\partial S}{\partial T}\right)_H = T\,\frac{\partial(S,H)}{\partial(T,H)} = T\,\frac{\dfrac{\partial(S,H)}{\partial(T,M)}}{\dfrac{\partial(T,H)}{\partial(T,M)}} \; (=)$$

$$\frac{\partial(S,H)}{\partial(T,H)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial H} \\ \frac{\partial H}{\partial T} & \frac{\partial H}{\partial H} \end{vmatrix} = \left(\frac{\partial S}{\partial T}\right)_H \qquad \leftarrow (H,T) \text{ variables}$$

$$\frac{\partial(T,H)}{\partial(T,M)} = \begin{vmatrix} \frac{\partial T}{\partial T} & \frac{\partial T}{\partial M} \\ \frac{\partial H}{\partial T} & \frac{\partial H}{\partial M} \end{vmatrix} = \left(\frac{\partial H}{\partial M}\right)_T \qquad \leftarrow (M,T) \text{ variables}$$

$$\frac{\partial(S,H)}{\partial(T,M)} = \begin{vmatrix} \frac{\partial S}{\partial T} & \frac{\partial S}{\partial M} \\ \frac{\partial H}{\partial T} & \frac{\partial H}{\partial M} \end{vmatrix} = \qquad \leftarrow (M,T) \text{ variables}$$

$$= \left(\frac{\partial S}{\partial T}\right)_M \left(\frac{\partial H}{\partial M}\right)_T - \left(\frac{\partial S}{\partial M}\right)_T \left(\frac{\partial H}{\partial T}\right)_M$$

$$(=)\; T\,\frac{\left(\frac{\partial S}{\partial T}\right)_M \left(\frac{\partial H}{\partial M}\right)_T - \left(\frac{\partial S}{\partial M}\right)_T \left(\frac{\partial H}{\partial T}\right)_M}{\left(\frac{\partial H}{\partial M}\right)_T} =$$

$$= \underbrace{T\left(\frac{\partial S}{\partial T}\right)_M}_{C_M} - T\,\frac{\left(\frac{\partial S}{\partial M}\right)_T \left(\frac{\partial H}{\partial T}\right)_M}{\left(\frac{\partial H}{\partial M}\right)_T}$$

Note that $Z(H,T) = \sum_r e^{-\beta E_r}$

$$F_{(H,T)} = -k_B T \log Z(H,T) = U - TS$$

Entropy: $S = -\left(\frac{\partial F}{\partial T}\right)_H$

Magnetization: $M = -\left(\frac{\partial F}{\partial H}\right)_T$ $\quad\Leftarrow$

$$dF = \underbrace{dU}_{} - TdS - SdT =$$
$$= \cancel{TdS} - MdH - \cancel{TdS} - SdT =$$
$$= -MdH - SdT$$

$$\hookrightarrow \left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H$$

OK, so $(C_H - C_M)\left(\frac{\partial H}{\partial M}\right)_T = -T\left(\frac{\partial S}{\partial M}\right)_T \left(\frac{\partial H}{\partial T}\right)_M$ (*)

Likewise, $d\tilde{u} = TdS + HdM = TdS - MdH + MdH + HdM = du + d(\underbrace{HM}_{\text{energy stored in magnetic field}})$

$$d\tilde{F} = d\tilde{u} - TdS - SdT = HdM - SdT \Rightarrow \begin{cases} H = \left(\frac{\partial \tilde{F}}{\partial M}\right)_T, \\ S = -\left(\frac{\partial \tilde{F}}{\partial T}\right)_M \end{cases}$$

$$\Leftarrow \quad \left(\frac{\partial H}{\partial T}\right)_M = -\left(\frac{\partial S}{\partial M}\right)_T$$

(*) gives $(C_H - C_M)\left(\frac{\partial H}{\partial M}\right)_T = T\left(\frac{\partial H}{\partial T}\right)_M^2$

$$\frac{\left(\frac{\partial H}{\partial T}\right)_M^2}{\left(\frac{\partial H}{\partial M}\right)_T} \stackrel{?}{=} \frac{\left(\frac{\partial M}{\partial T}\right)_H^2}{\left(\frac{\partial M}{\partial H}\right)_T}$$

$$\left(\frac{\partial M}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_M \left(\frac{\partial H}{\partial T}\right)_M \stackrel{?}{=} \left(\frac{\partial H}{\partial M}\right)_T \left(\frac{\partial M}{\partial T}\right)_H \left(\frac{\partial M}{\partial T}\right)_H$$

$$\left(\frac{\partial M}{\partial H}\right)_T \left(\frac{\partial H}{\partial T}\right)_M \left(\frac{\partial T}{\partial M}\right)_H = -1$$

$$\left(\frac{\partial H}{\partial M}\right)_T \left(\frac{\partial M}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_M = -1$$

$$\Rightarrow -\left(\frac{\partial M}{\partial T}\right)_H \left(\frac{\partial H}{\partial T}\right)_M = -\left(\frac{\partial H}{\partial T}\right)_M \left(\frac{\partial M}{\partial T}\right)_H \quad 1=1$$

So, $$(C_H - C_M) = T\frac{\left(\frac{\partial M}{\partial T}\right)_H^2}{\underbrace{\left(\frac{\partial M}{\partial H}\right)_T}_{\chi_T}} \Rightarrow \chi_T(C_H - C_M) = T\left(\frac{\partial M}{\partial T}\right)_H^2$$

So, $\chi_T (C_H - C_M) = T \left(\frac{\partial M}{\partial T}\right)_H^2$

Since $C_M \geq 0$ $[S \uparrow \text{ as } T \uparrow]$, & $\chi_T \geq 0$

$$C_H \geq \frac{T}{\chi_T} \left(\frac{\partial M}{\partial T}\right)_H^2$$

as $t \to 0^-$ $(T \to T_c^-)$ in zero field, we have:

$C_H \sim (-t)^{-\alpha}$ $[H=0]$

$\chi_T \sim (-t)^{-\gamma}$

$\left(\frac{\partial M}{\partial T}\right)_H \sim (-t)^{\beta-1}$

$T = T_c + t T_c$,
$t \to 0^- \Rightarrow T \to T_c$,
Const

Then $(-t)^{-\alpha} \geq (-t)^{\gamma + 2(\beta-1)}$

$-\alpha \leq \gamma + 2(\beta - 1) \Rightarrow \alpha \geq -\gamma - 2\beta + 2$

$$\underbrace{(-\alpha)}_{\log(-t) < 0} \geq \underbrace{[\gamma + 2(\beta - 1)]}_{\log(-t)} \Rightarrow \alpha + \gamma + 2\beta \geq 2$$

0^+

2D Ising model: $\alpha = 0$, $\beta = \frac{1}{8}$, $\gamma = \frac{7}{4}$ $\Rightarrow$ equalities!

Auxiliary relations:

(1.) $f(x,y)$ $\qquad \left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_x \overset{?}{=} -1$ $\qquad$ [**]

$x(f,y)$

$y(f,x)$

Indeed,

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy =$$

$$= \left(\frac{\partial f}{\partial x}\right)_y \left[\left(\frac{\partial x}{\partial f}\right)_y df + \left(\frac{\partial x}{\partial y}\right)_f dy \right] + \left(\frac{\partial f}{\partial y}\right)_x dy$$

$$= \underbrace{\left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial f}\right)_y}_{=1} df + \underbrace{\left[\left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_f + \left(\frac{\partial f}{\partial y}\right)_x \right]}_{=0} dy$$

$\Downarrow$

[**] follows

(2.) $$\frac{\partial(u,v)}{\partial(x,y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix}$$

Note that $$\frac{\partial(u,v)}{\partial(x,y)} = -\frac{\partial(v,u)}{\partial(x,y)}$$

$$\frac{\partial(u,y)}{\partial(x,y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial y}{\partial x} & \frac{\partial y}{\partial y} \end{vmatrix} = \left(\frac{\partial u}{\partial x}\right)_y$$

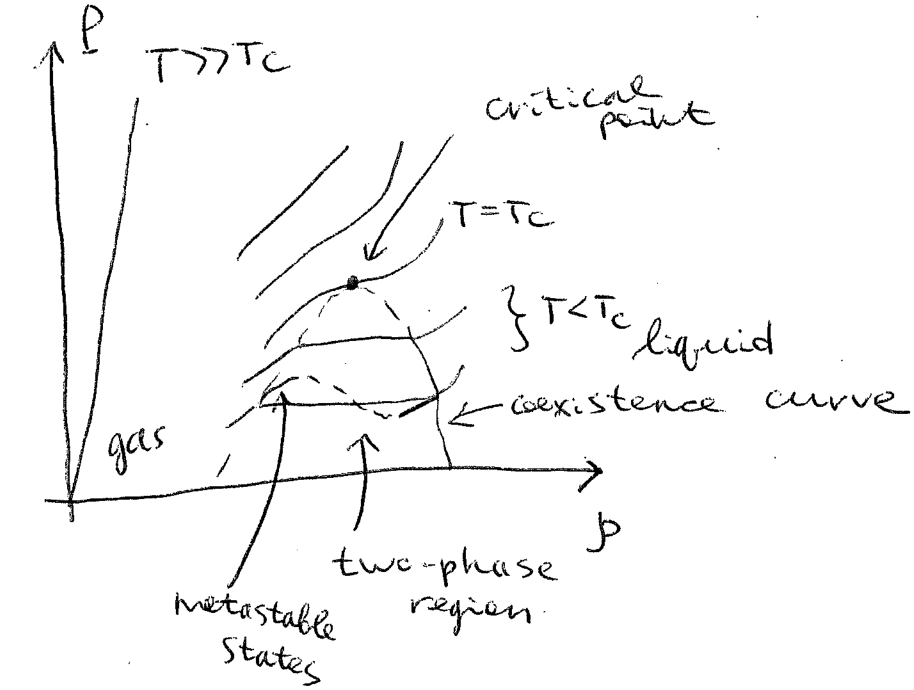
Finally, $$\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(t,s)} \frac{\partial(t,s)}{\partial(x,y)}$$

↑ can be checked by direct substitution

$\boxed{\text{Extra notes}}$

Eq'n of state: $f(P, \rho, T) = 0$

E.g. ideal gas: $P = \frac{\rho k_B T}{m} \sim \rho$, linear



$$C_H \geq \frac{T}{\chi_T}\left(\frac{\partial M}{\partial T}\right)_H^2$$

$$\begin{cases} C_H = a_1(-t)^{-\alpha} & a_1 > 0 \quad (C_H \geq 0) \\ \chi_T = a_2(-t)^{-\gamma} & a_2 > 0 \quad (\chi_T \geq 0) \\ \left(\frac{\partial M}{\partial T}\right)_H = \underbrace{a_3}_{<0 \text{ or } >0}(-t)^{\beta-1} & \end{cases}$$

$M \searrow$ as $t \nearrow$

$$t = \frac{T - T_c}{T_c} \qquad \underbrace{\overbrace{\left(\frac{T_c - T}{T_c}\right)}^{>0}{}^{\beta - 1}}_{>0}$$

$t \to 0^-$ $(T \to T_c^-)$: gives

$$a_1(-t)^{-\alpha} \geq \frac{T_c}{a_2}(-t)^{\gamma}\, a_3^2\, (\underbrace{-t}_{>0})^{2(\beta-1)}$$

$$(-t)^{-\alpha-\gamma-2(\beta-1)} \geq \underbrace{\frac{T_c}{a_1 a_2} a_3^2}_{\text{''}\, K > 0}$$

$$\underbrace{-\underbrace{\log(-t)}_{<0}}_{>0}\,[\alpha + \gamma + 2(\beta-1)] \geq \underbrace{\log K}_{\text{may be } <0 \text{ or } >0}$$

$$\alpha + \gamma + 2(\beta - 1) \geq \frac{\log K}{\underbrace{-\log(-t)}_{+\infty}} = 0$$