Phase Transitions and Universality Coefficients

Statistical Mechanics, Spring 2016

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Outline

This class summarize Chapter 1 and 2 of Yeomans “Statistical Mechanics of Phase Transitions” Oxford Science Publications

The chapters, as well as all other chapters of the book will be uploaded online, the book is excellent and you should consider having it for your own reference

Note that the content in Chapter 1 are just a general introduction to the whole book, read it with ease, we will come back to each single one of them.

In general this and next class cover the first half of Chapter 5 of your book, the rest will be covered after the Lab on Ising Model

Scope of this first class is to bridge what you know on classical mechanics with what you have learned on Statistical Mechanics

Where are we with the course?

- Key assumptions in stat mech
- All of the ensembles
- The formulas for entropy

$$\boxed{S = k_B \ln \Omega} \rightarrow S = k_B \, p_\nu \ln p_\nu$$

- The distribution functions

What is the main link between the two thermodynamics treatment?

$$\boxed{\beta A = \ln Q}$$

$$G = A - PV$$

The importance of Helmoltz free energy

Table 2.1. The relation of the thermodynamic variables pertinent to a magnetic system to the partition function

Thermodynamic variables for a magnet

First law: $\mathrm{d}U = T\mathrm{d}S - M\mathrm{d}H$

Partition function

$$Q \longleftarrow \mathcal{Z}(T,H) = \sum_r e^{-\beta E_r}$$

$$\downarrow$$

Free energy

$$A \longleftarrow \mathcal{F} = -kT \ln \mathcal{Z}$$

Internal energy	*Entropy*	*Magnetization*
$U = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}$	$S = -\left(\frac{\partial \mathcal{F}}{\partial T}\right)_H = (U - \mathcal{F})/T$	$M = -\left(\frac{\partial \mathcal{F}}{\partial H}\right)_T$
↓	↓	↓
Specific heat (constant H)	*Specific heat (constant X = H, M)*	*Isothermal susceptibility*
$C_H = \left(\frac{\partial U}{\partial T}\right)_H$	$C_X = T\left(\frac{\partial S}{\partial T}\right)_X$	$\chi_T = \left(\frac{\partial M}{\partial H}\right)_T$

The importance of Helmoltz free energy

Table 2.2. The relation of the thermodynamic variables pertinent to a fluid system to the partition function

Thermodynamic variables for a fluid

First law: $dU = T dS - P dV$ (1)

Partition function

$$\mathcal{Z}(T, V) = \sum_r e^{-\beta E_r}$$

$\downarrow$

Free energy

$$\mathcal{F} = -kT \ln \mathcal{Z}$$

$\swarrow \quad \downarrow \quad \searrow$

Internal energy	*Entropy*	*Pressure*
$U = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}$	$S = -\left(\frac{\partial \mathcal{F}}{\partial T}\right)_V = (U - \mathcal{F})/T$	$P = -\left(\frac{\partial \mathcal{F}}{\partial V}\right)_T$
$\downarrow$	$\downarrow$	$\downarrow$
Specific heat (constant V)	*Specific heat (constant $X = V, P$)*	*Isothermal compressibility*
$C_V = \left(\frac{\partial U}{\partial T}\right)_V$	$C_X = T\left(\frac{\partial S}{\partial T}\right)_X$	$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

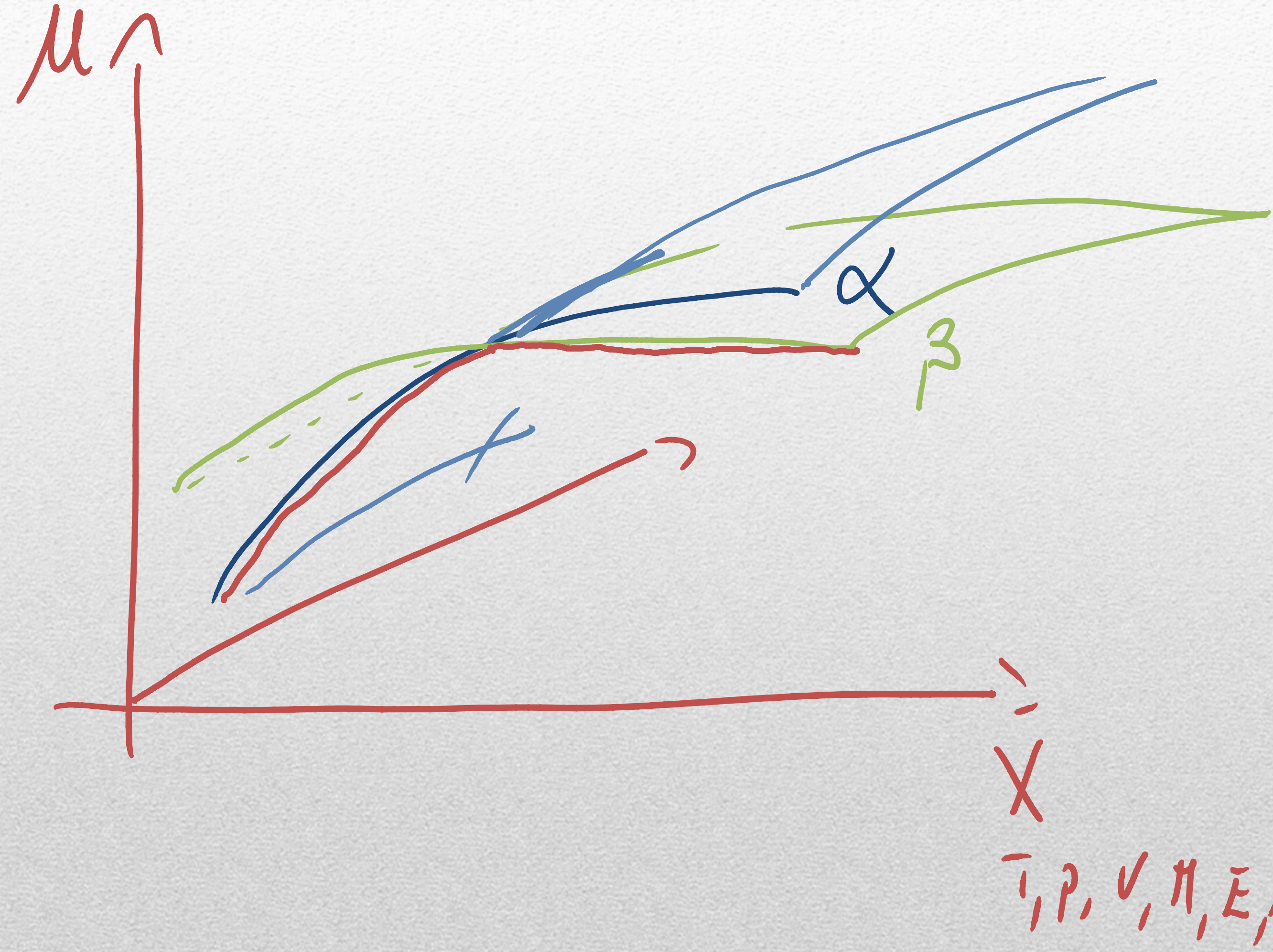
Why are we here?

- Modern Science is atomistic
- The of Stat mech bridges
  Q.M. ⟶ classical T.D.
- Same phenomenon the
  stat. mech. explains
- Simulations are key in
  modern science

What is a phase transition?

A Phase Transition is a thermodynamic transformation that occurs in a system when a transformation is induced across two states via a path that at least in the reversible limits passes through a singularity in the free energy (Helmoltz or Gibbs) or in one of its derivatives

In a graphical form this means:

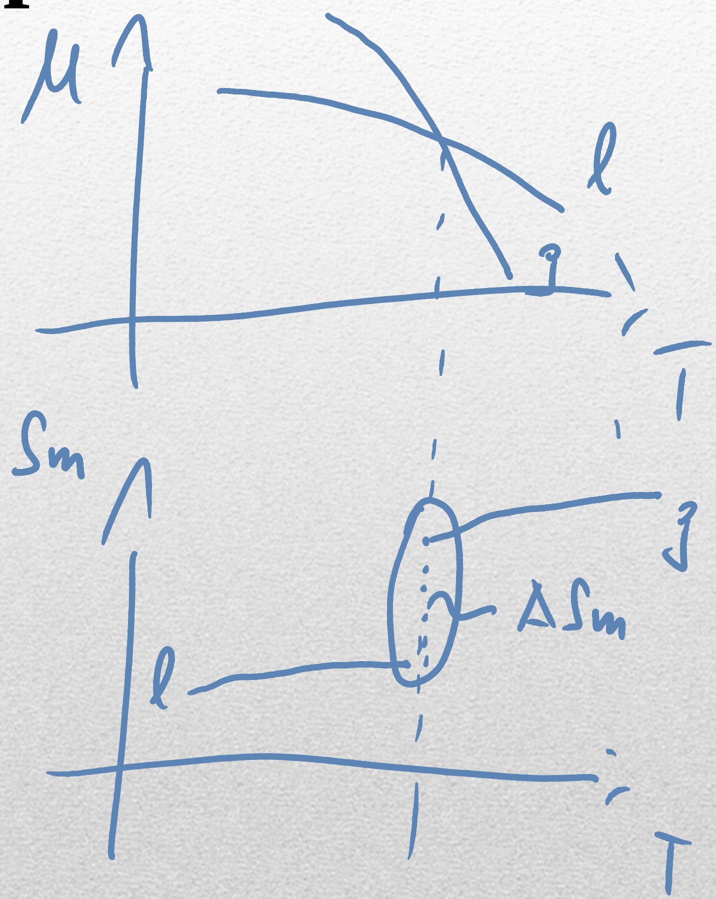


How many types of phase transitions are there?

first order $\left(\frac{\delta \mu}{\delta x_i}\right)_{x_{j, j \neq i}}$ is discontinuous

Continuous phase transitions $\left(\frac{\delta^n \mu}{\delta^n x_{i,j}}\right)_{x_{k \neq i,j}}$ is discontinuous

What happens during a first order phase transition?



$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$$

$$\Delta G_{s\text{-}l} = 0 = \Delta H - T\Delta S$$

constant p

$$Q = \Delta H_m = T\Delta S_m$$

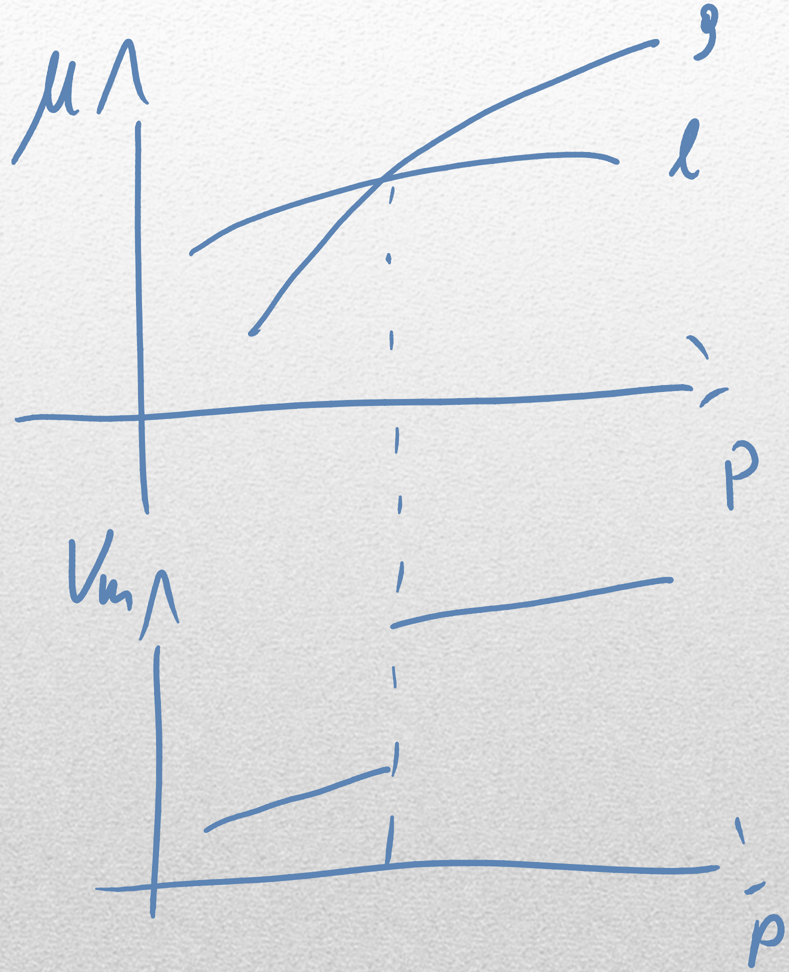
latent heat

What changes during a phase transition?

- symmetry (subset)

- order parameter
  - → density
  - correlation function (Co-Pt)

Order Parameter in Phase Transitions



$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m$$

p

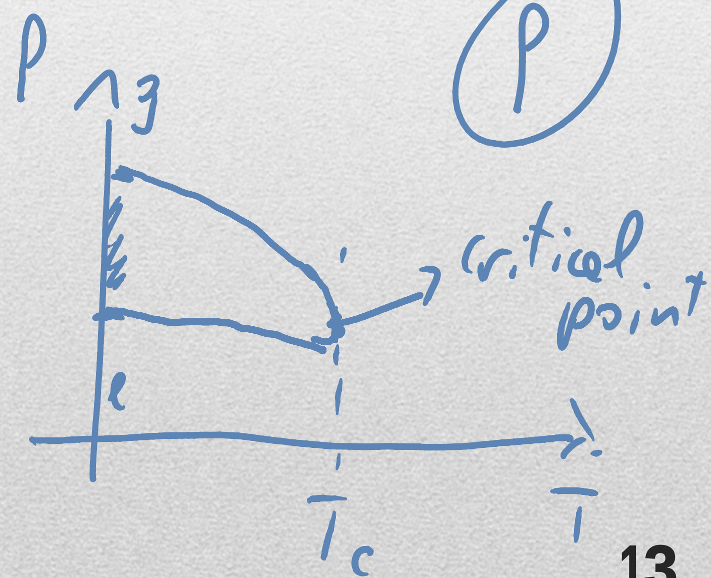
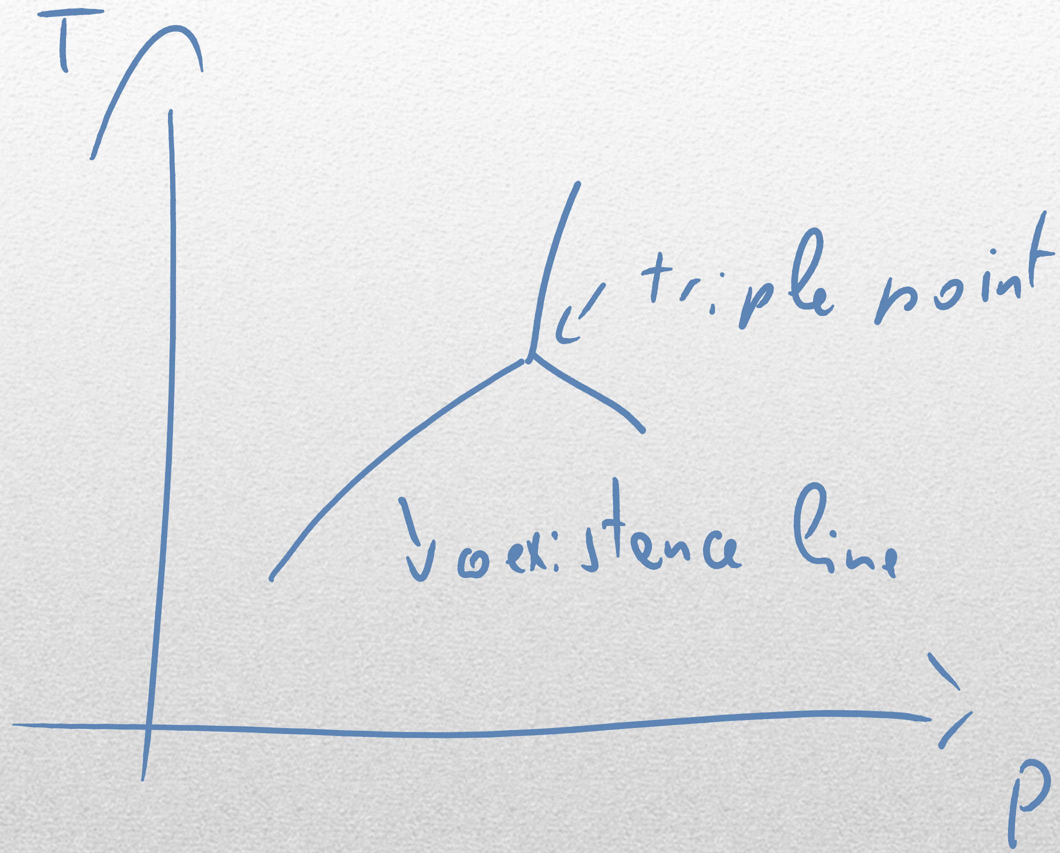


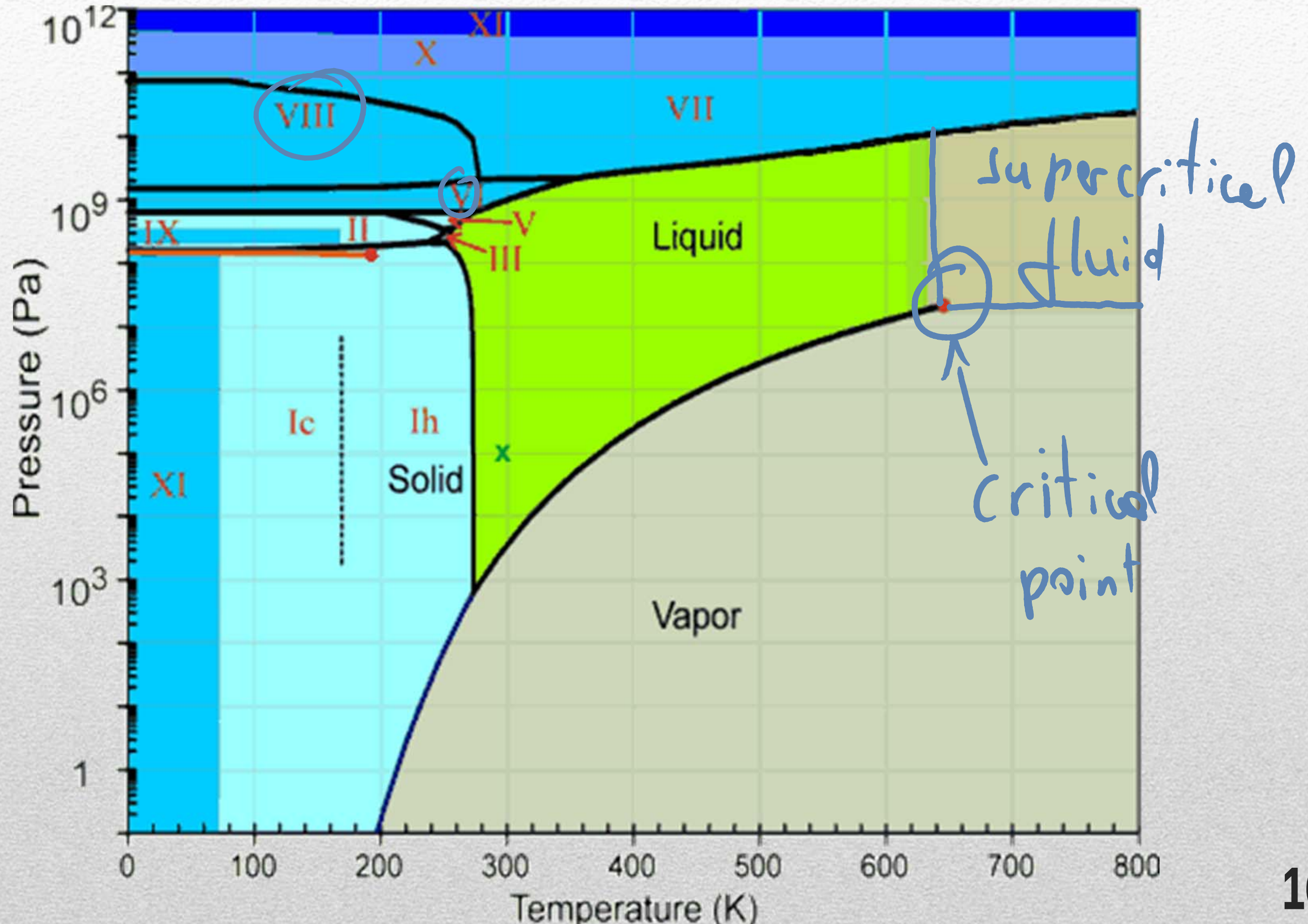
Table 1.1. Examples of the diversity of phase transitions found in nature

Transition	Example	Order parameter
ferromagnetic[a]	Fe	magnetization
antiferromagnetic[a]	MnO	sublattice magnetization
ferrimagnetic[a]	Fe_3O_4	sublattice magnetization
structural[b]	$SrTiO_3$	atomic displacements
ferroelectric[b]	$BaTiO_3$	electric polarization
order-disorder[c]	CuZn	sublattice atomic concentration
phase separation[d]	$CCl_4+C_7F_{16}$	concentration difference
superfluid[e]	liquid ^4He	condensate wavefunction
superconducting[f]	Al, Nb_3Sn	ground state wavefunction
liquid crystalline[g]	rod molecules	various

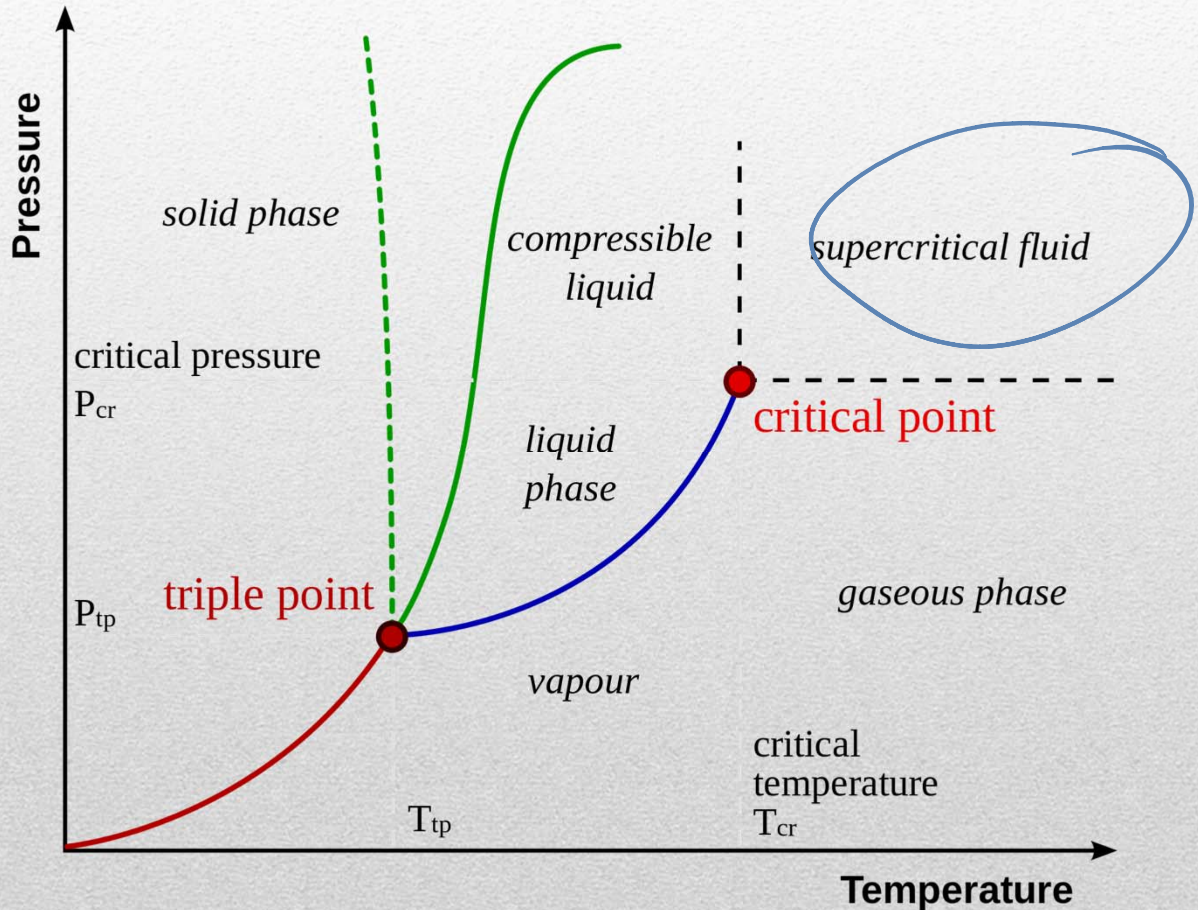
Phase Diagrams



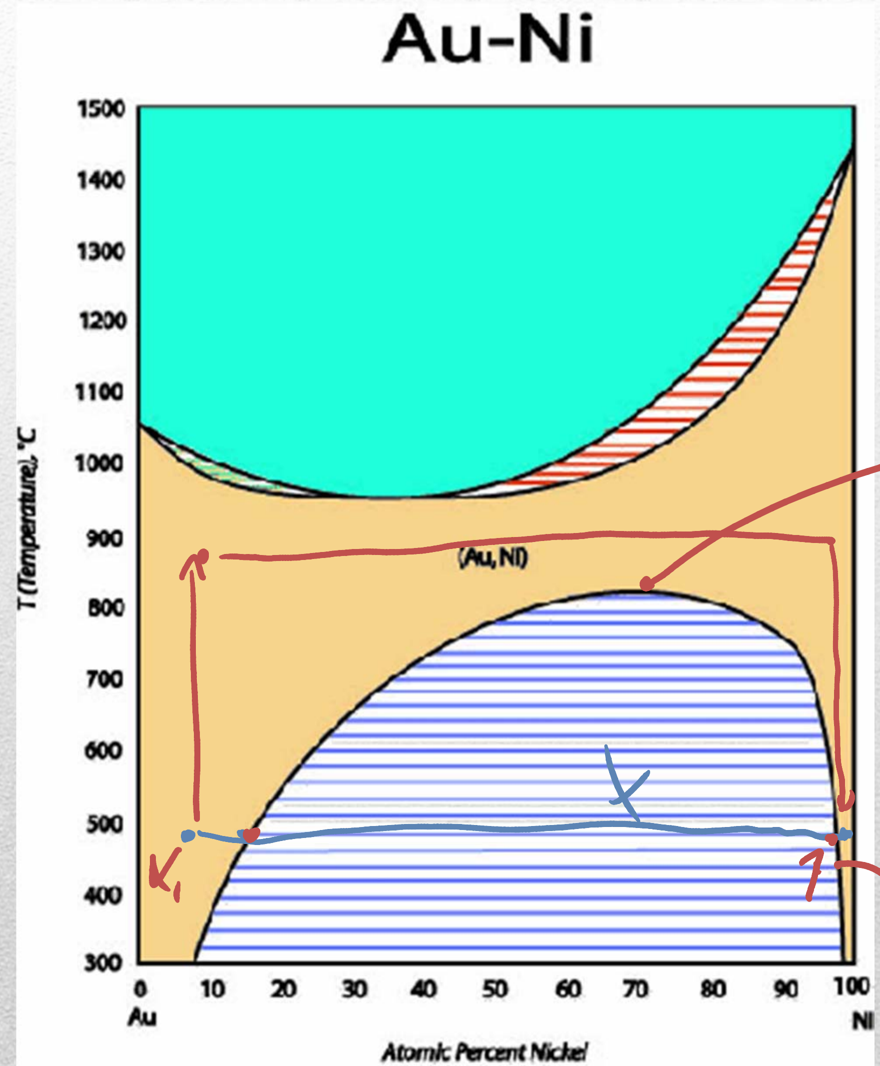
Phase Diagram of Water

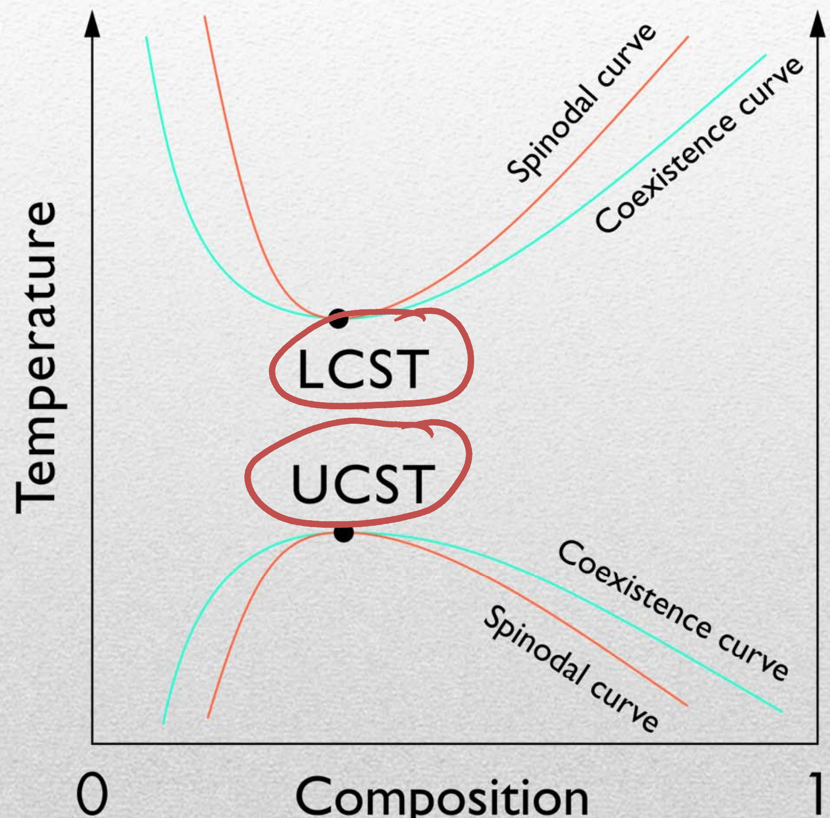


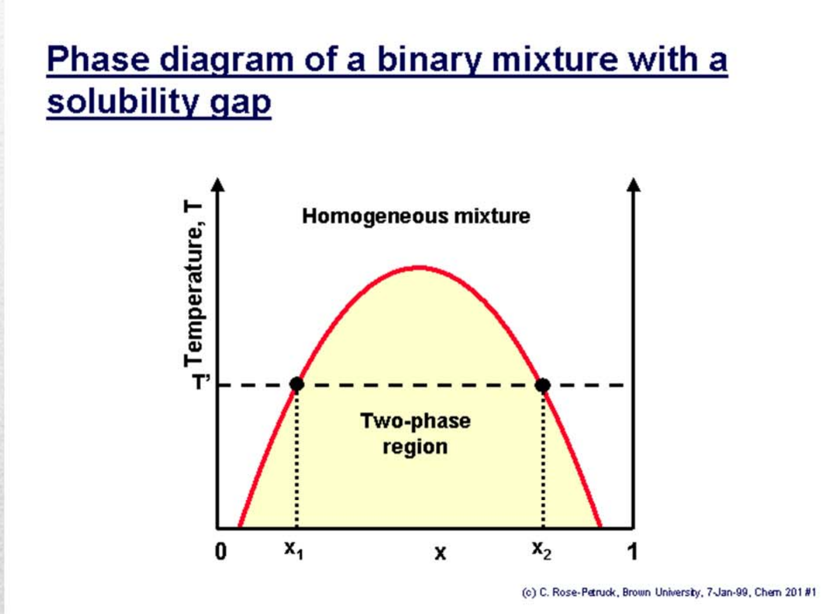
Phase Diagram of Water



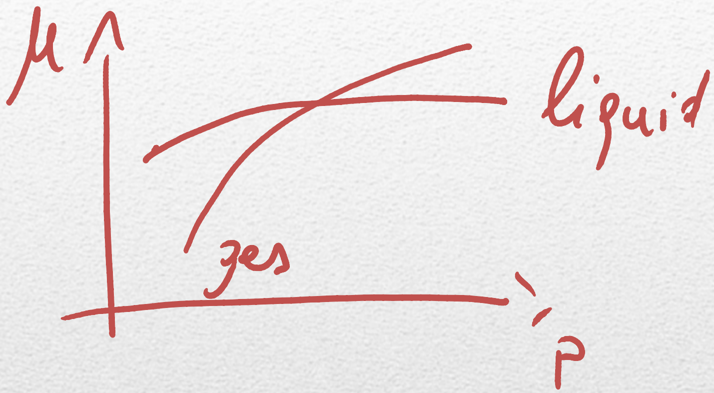
Solubility-Gap Phase Diagram




Temperature
Spinodal curve
Coexistence curve
LCST
UCST
Coexistence curve
Spinodal curve
0
Composition
1

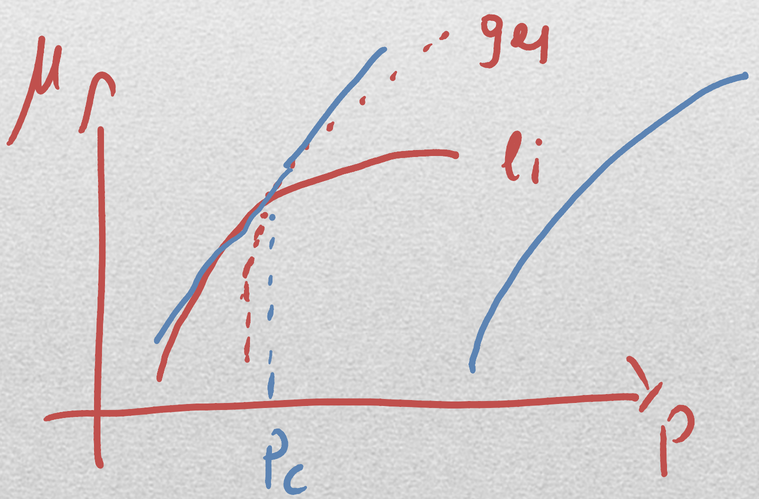

Phase diagram of a binary mixture with a solubility gap
Temperature, T
Homogeneous mixture
T'
Two-phase region
0
x_1
x
x_2
1
(c) C. Rose-Petruck, Brown University, 7-Jan-99, Chem 201 #1

Free energy curve for a liquid-gas phase transition

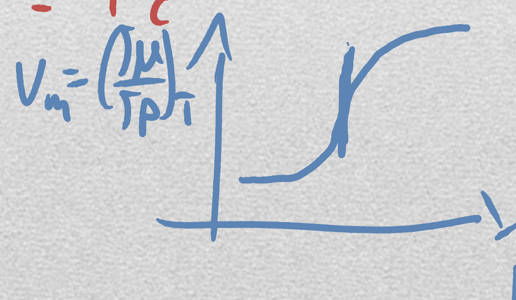


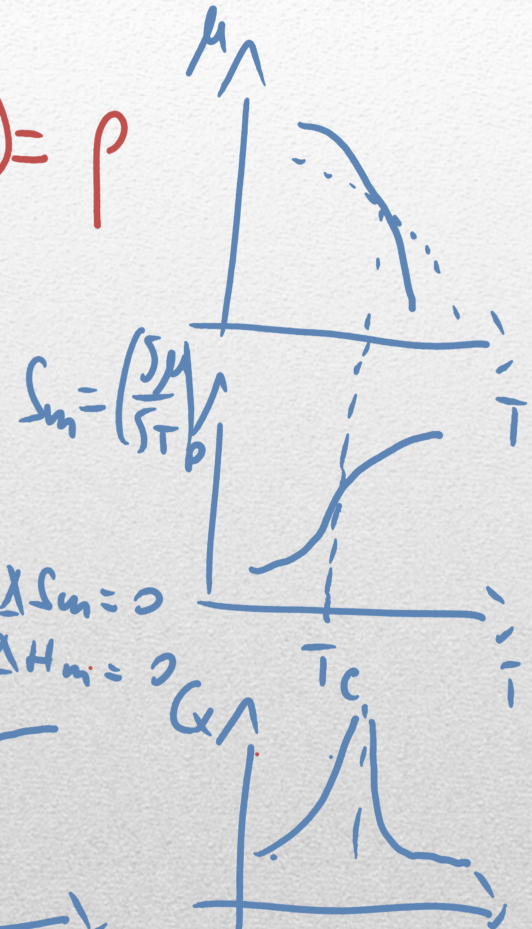
$$\left(\frac{\delta\mu}{\delta p}\right)_T = V_m(p) = \rho$$

$T < T_c$

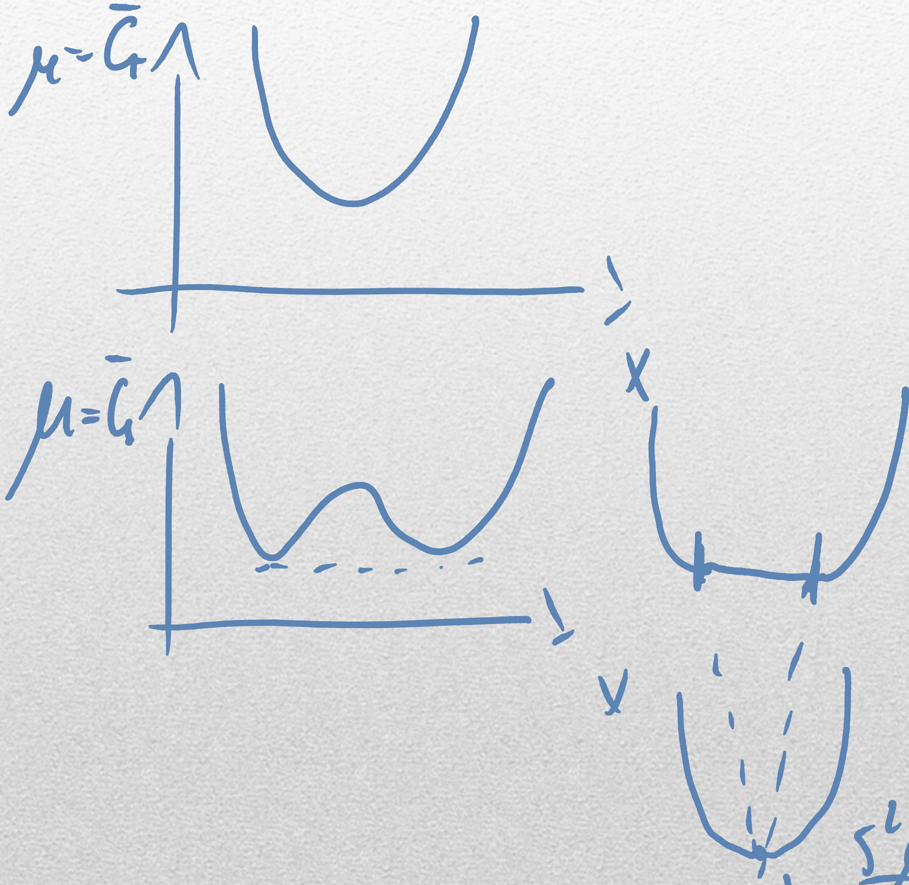


$T = T_c$





Free energy curve for solubility-gap phase diagram



$\frac{\delta^2 \mu}{\delta x^2} = 0$

$\Delta S^{mix} = x_A \ln x_A + x_B \ln x_B$

↳ consistent with $S = k_B \ln \Omega$

$\Delta H = \Omega \, x_A x_B$

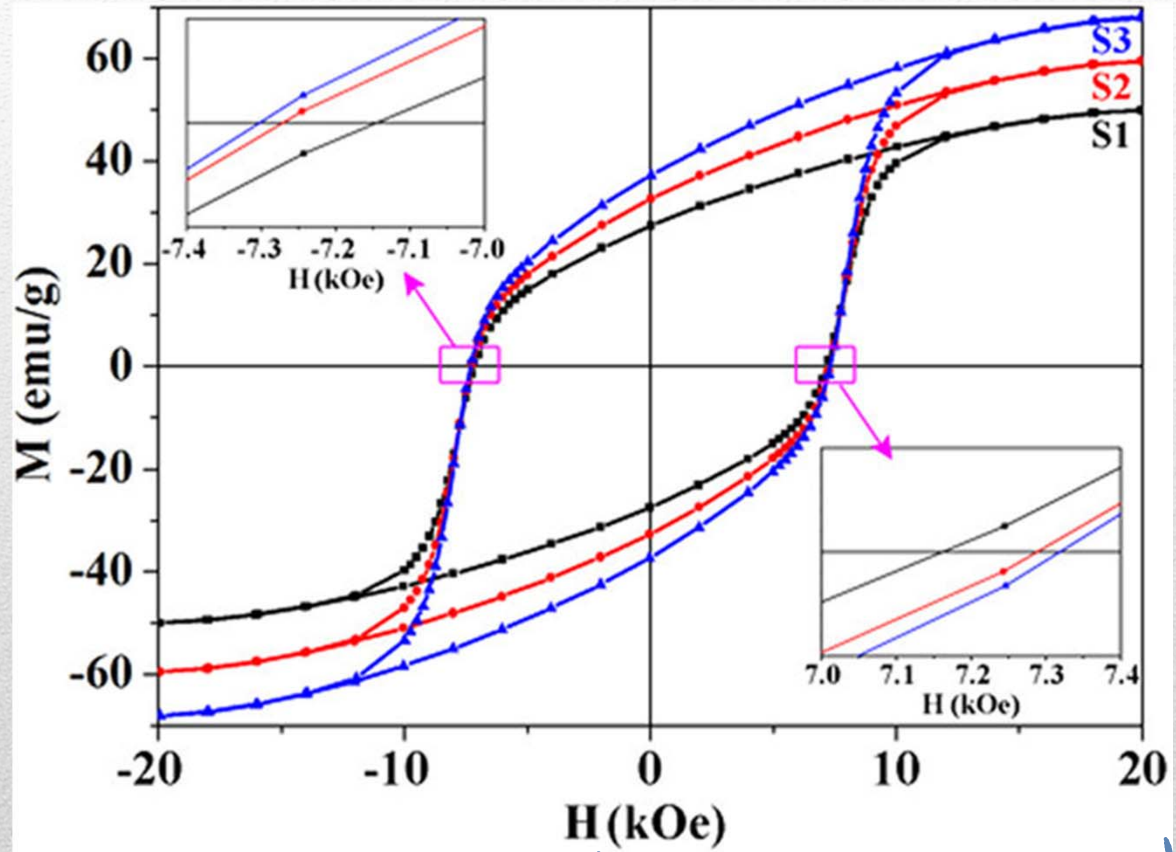
$\Omega > 0$

nothing to do

Magnetism in Materials

diamagnetic $\chi <$
peremagnetic $\chi >$
ferromagnetic $\chi \gg$

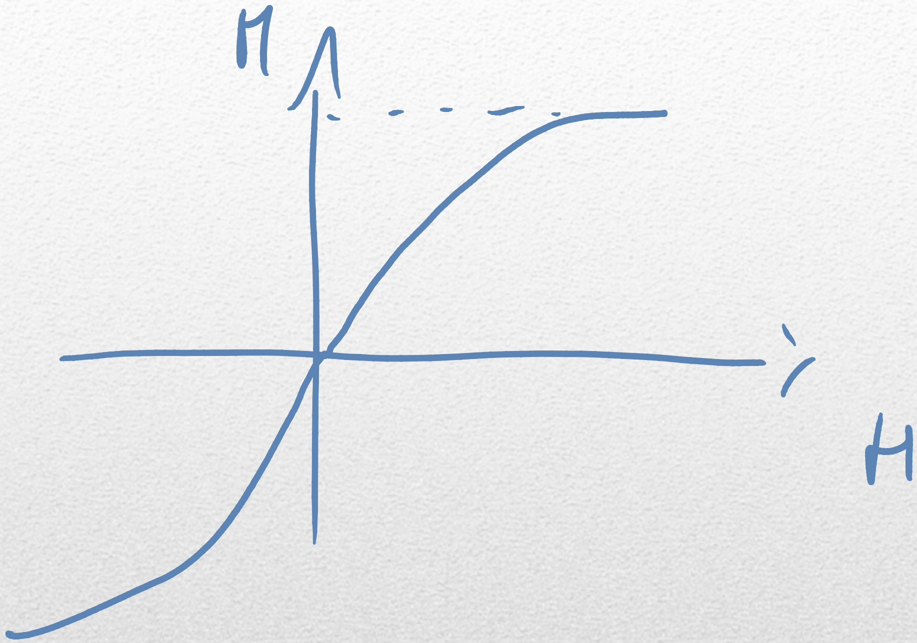
$$\left(\frac{\delta M}{\delta H}\right)_T = \chi_T$$



J

$\vec{B}$ external field $\quad \vec{M}$ 'spin' field $\quad \vec{H} = \vec{B} + \vec{M}$ internal field

Idealized Magnetic Materials



small

2D

μ magnetization x atom

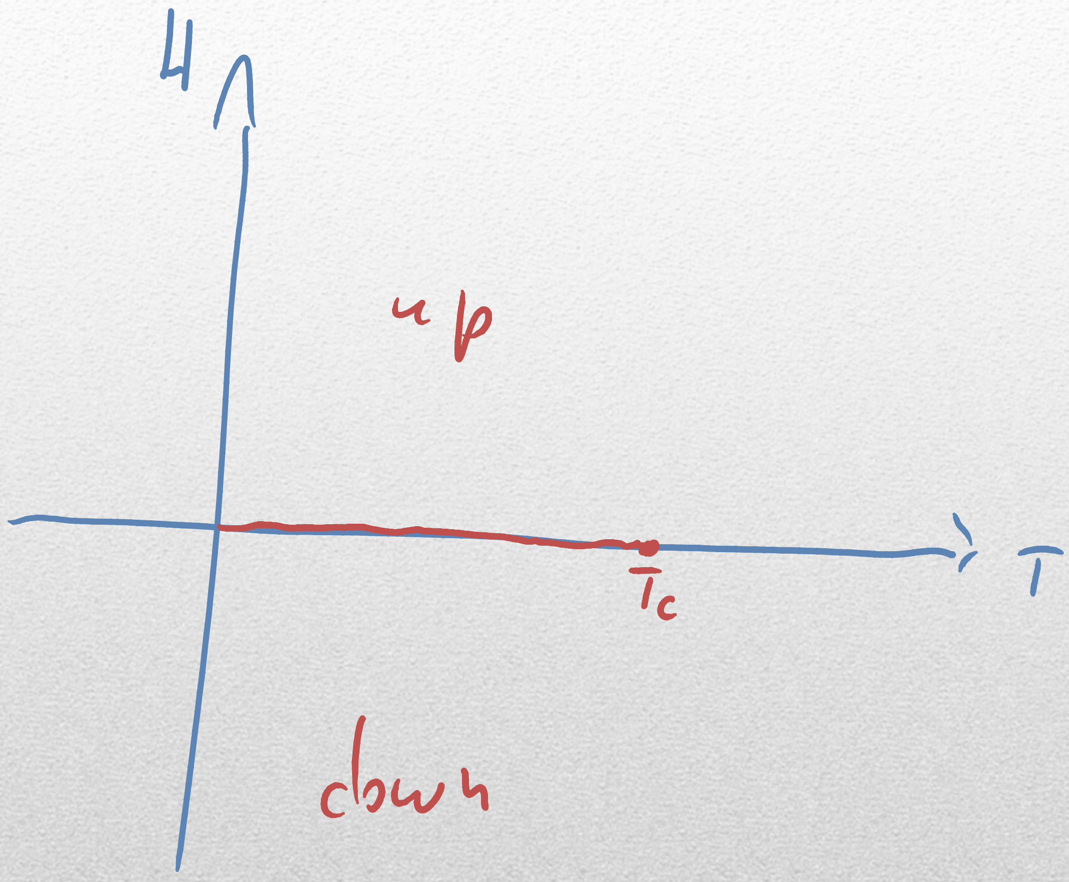
$N\mu$

$\langle M \rangle = \mu \langle S_i \rangle$

$S_i = 1$ alligned

$S_i = -1$ opposite

Ferroelectric Phase Diagram



Free energy curve for a ferroelectric phase diagram

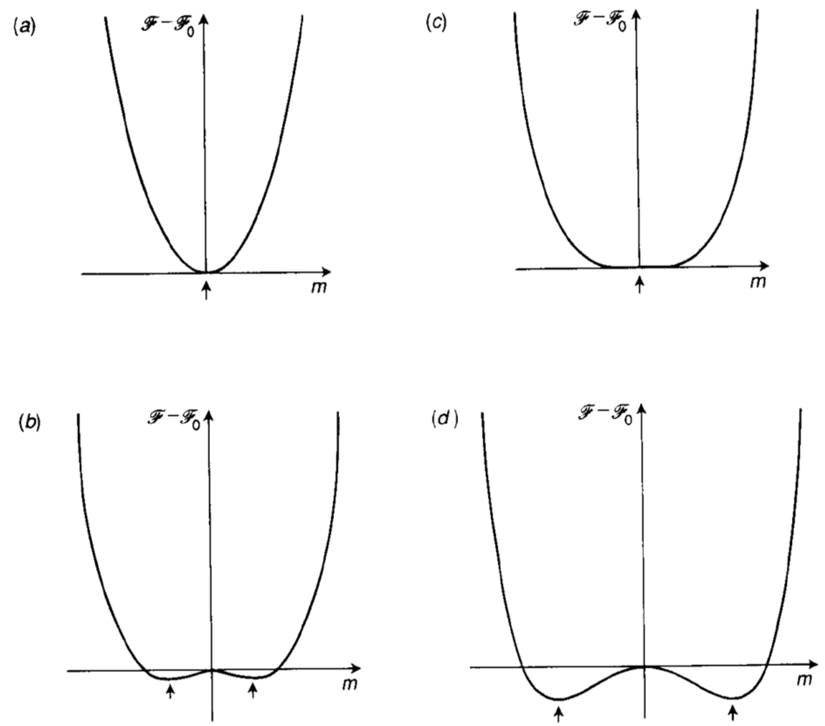
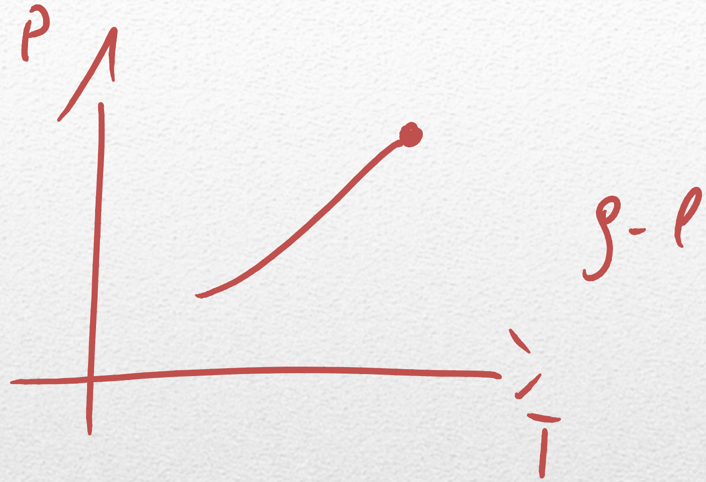
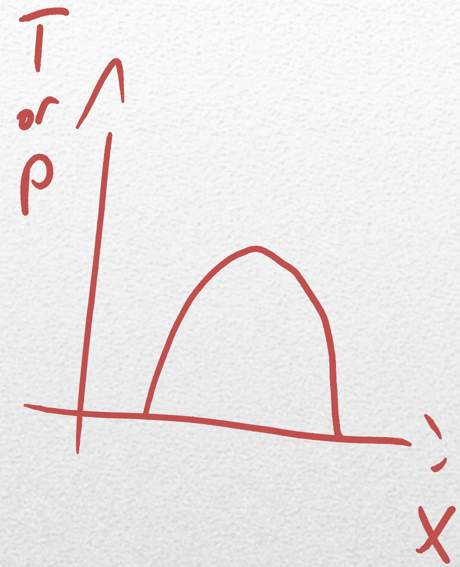
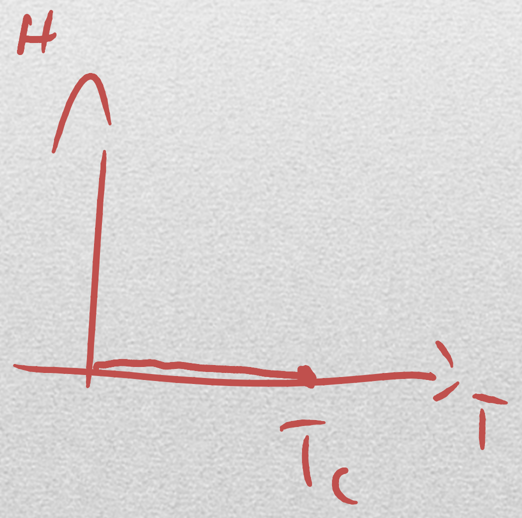


Fig. 4.2. Variation of the Landau free energy with magnetization for decreasing values of a_2. (a) $a_2 > 0$, (b) $a_2 = 0$, (c) $a_2 \lesssim 0$, (d) $a_2 < 0$.

Critical Points in Phase Diagrams







Consequences of Critical Points

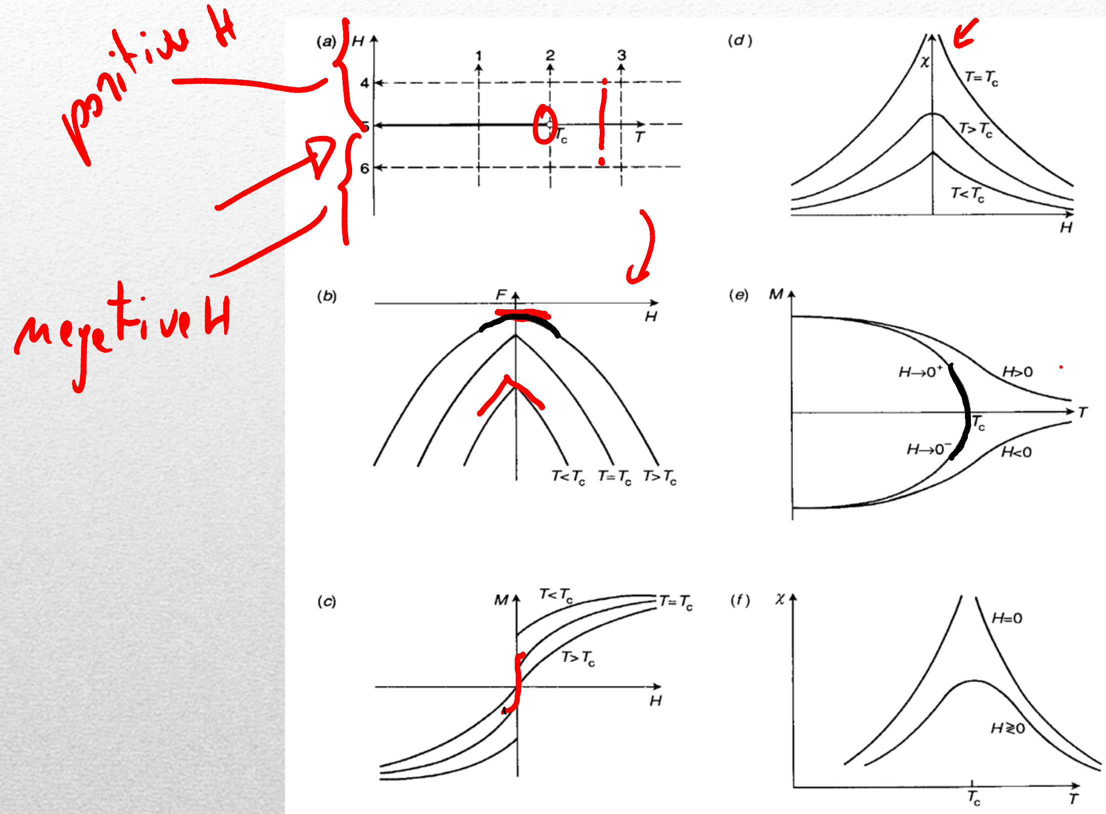


Fig. 2.1. (*a*) Phase diagram of a simple ferromagnet. There is a line of first-order transitions along $H = 0$ which ends at a critical point at $T = T_c$. (*b*) Field dependence of the free energy. (*c*) Field dependence of the magnetization. (*d*) Field dependence of the susceptibility. (*e*) Temperature dependence of the magnetization. (*f*) Temperature dependence of the susceptibility.

3

Consequences of Critical Points

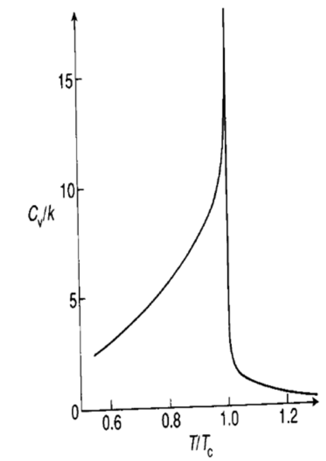


Fig. 1.3. Specific heat at constant volume of argon measured on the critical isochore, $\rho = \rho_c$. After Fisher, M.E. (1964). *Physical Review*, **136A**, 1599.

signature of a critical point

4

Correlation Functions

$$C(r,0) = \langle \mathbf{s_1}(R,t) \cdot \mathbf{s_2}(R+r,t) \rangle - \langle \mathbf{s_1}(R,t) \rangle \langle \mathbf{s_2}(R+r,t) \rangle$$

For the spin-spin correlation function (time invariant)

$$\Gamma(\vec{r}_i, \vec{r}_j) = \langle (s_i - \langle s_i \rangle)(s_j - \langle s_j \rangle) \rangle$$

s_i s_j

ith jth

$s = \pm 1$

For a translationally invariant system

$$\Gamma(\vec{r}_i - \vec{r}_j) \equiv \Gamma_{ij} = \langle s_i s_j \rangle - \langle s \rangle^2.$$

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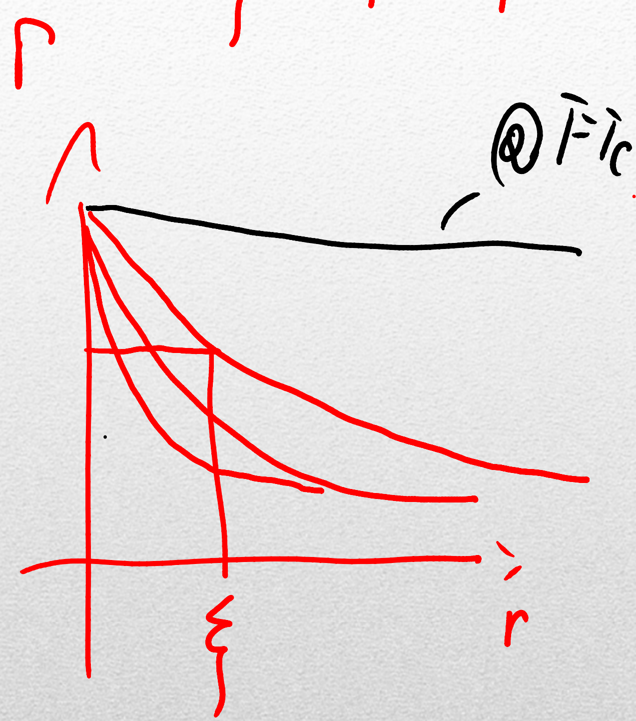
Correlation Length

$r^{-\tau} e^{-r/\xi}$

$\xi \propto |T-T_c|^{-\alpha}$



$$\Gamma(\vec{r}) \sim r^{-\tau} \exp^{-r/\xi}$$

$$\Gamma(\vec{r}) \propto \frac{1}{r^{d-2+\eta}} \exp\left(-\frac{r}{\xi}\right)$$

At the critical point

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

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

6

$$\langle M - \langle M \rangle \rangle^2 = \langle M^2 \rangle - \langle M \rangle^2 = \delta^2 M = \chi_T$$

$$\left(\frac{\delta^2 M}{\delta H^2} \right)_T = \chi_T$$

$$\langle M - \langle M \rangle \rangle^2 = \underbrace{\sum_i (s_i - \langle s_i \rangle) \sum_j (s_j - \langle s_j \rangle)}_{\text{by definition}} = \sum_{ij} \Gamma_{ij}$$

$$\sum_{ij} \Gamma_{ij} = N \sum_j \Gamma_{1j} \sim N \int \Gamma(r)\, r^{d-1}\, dr$$

$$\chi_T \sim N \int \Gamma(r)\, r^{d-1}\, dr$$

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$$\mathcal{H}_i = \mu^2 \sum_j c_{ij}$$

below T_c $\quad H^+ \quad \langle \Pi \rangle = + N m_0 \mu$

$\quad H^- \quad \langle \Pi \rangle = - N \mu m_0$

above T_c $\quad H^+$ or $H^- \quad \langle \Pi \rangle = 0$

@ T_c $\quad H^+ \quad \langle \Pi \rangle = + N m_0 \mu$

$\quad H^- \quad \langle \Pi \rangle = - N m_0 \mu$

Critical Points Exponents

$t = \frac{T - T_c}{T_c}$ $\lambda = \lim_{t \to 0} \frac{\ln|F(t)|}{\ln|t|}$ $F(t) \sim t^{\lambda}$

Table 2.3. Definitions of the most commonly used critical exponents for a magnetic system

Zero-field specific heat	$C_H \sim \mid t \mid^{-\alpha}$
Zero-field magnetization	$M \sim (-t)^{\beta}$
Zero-field isothermal susceptibility	$\chi_T \sim \mid t \mid^{-\gamma}$
Critical isotherm ($t = 0$)	$H \sim \mid M \mid^{\delta} \mathrm{sgn}(M)$
Correlation length	$\xi \sim \mid t \mid^{-\nu}$
Pair correlation function at T_c	$G(\vec{r}) \sim 1/r^{d-2+\eta}$

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$F(t) = t^{\alpha}\left(1 + b\,t^{\lambda_1} + c\,t^{\lambda_2} + \dots\right)$

Table 2.4. Definitions of the most commonly used critical exponents for a fluid system

Specific heat at constant volume V_c	$C_V \sim \mid t \mid^{-\alpha}$
Liquid–gas density difference	$(\rho_l - \rho_g) \sim (-t)^{\beta}$
Isothermal compressibility	$\kappa_T \sim \mid t \mid^{-\gamma}$
Critical isotherm ($t = 0$)	$P - P_c \sim \mid \rho_l - \rho_g \mid^{\delta} \operatorname{sgn}(\rho_l - \rho_g)$
Correlation length	$\xi \sim \mid t \mid^{-\nu}$
Pair correlation function at T_c	$G(\vec{r}) \sim 1/r^{d-2+\eta}$

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The concept of Universality

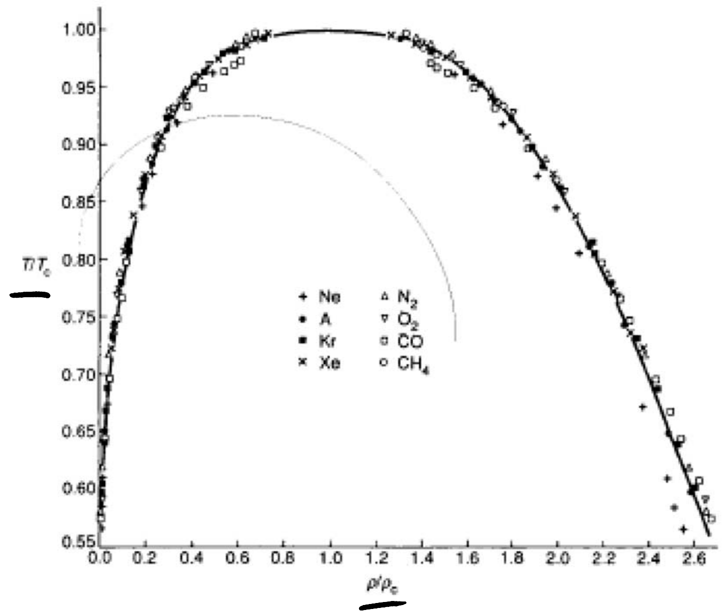

Fig. 2.2. The coexistence curve of eight different fluids plotted in reduced variables. The fit assumes an exponent $\beta = 1/3$. After Guggenheim, E. A. (1945). *Journal of Chemical Physics*, **13**, 253.

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Exponent Inequalities

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

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

$$C_H \sim (-t)^{-\alpha}, \quad \chi_T \sim (-t)^{-\gamma}, \quad \left(\frac{\partial M}{\partial T}\right)_H \sim (-t)^{\beta-1}.$$

$$\alpha + 2\beta + \gamma \geq 2.$$

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Exponent Inequalities

$$\alpha + \beta(1 + \delta) \geq 2,$$

$$\gamma \leq (2 - \eta)\nu; \quad d\nu \geq 2 - \alpha; \quad \gamma \geq \beta(\delta - 1),$$

The Ising Model (Spin ½ Ising model)

lattice model in N dimensions
with 2 allowed states @ each
lattice point spin ± 1
Chandler $\pm \mu$
and with J as interaction parameter

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What is special in the Ising Model

is a model for interacting particles

→ it is applicable to most interacting system

for dimension $d > 1$ ($d=2$ $H=0$) there is no analytical solution

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The Hamiltonian in the Ising Model

Yeomans

$J > 0$

$\uparrow\uparrow$ $\downarrow\downarrow$

$$\mathcal{H} = -J \sum_{\langle ij \rangle} s_i s_j - H \sum_i s_i .$$

nearest neighbours

In Chandler

$$E_\nu = -H\mu \sum_i s_i - J \sum_{ij} s_i s_j$$

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Equivalent Models: Order Disorder Transitions in Binary Alloys (Cu - Zn)

$S_i = 1$ Cu

$S_i = -1$ Zn

J_{CuCu}, J_{CuZn}, J_{ZnZn}

$$\mathcal{H} = \frac{1}{4}\sum_{ij} J_{CuCu}(1+S_i)(1+S_j) + \frac{1}{4}\sum_{ij} J_{ZnZn}(1-S_i)(1-S_j) + \frac{1}{4}\sum_{ij} J_{CuZn}\left[(1-S_i)(1+S_j) + (1+S_i)(1-S_j)\right] + H\sum_i S_i$$

$$J = \frac{1}{4}\left\{J_{CuCu} + J_{ZnZn} - 2J_{CuZn}\right\} \rightarrow \mathcal{H} = -J\sum_{ij} S_i S_j + H\sum_i S_i$$

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The gas model

$n_i = 1$ liquid state

$n_i = 0$ gas state

$$-\varepsilon \sum_{ij} n_i n_j$$

$$\Xi = \sum_{\substack{n_1, n_2, \dots \\ n_j = 0,1}} \exp\left\{ \beta\mu \sum_{i=1}^{N} n_i + \beta\varepsilon \sum_{ij} n_i n_j \right\}$$

$$H = -\varepsilon \sum n_i n_j - \mu \sum n_i$$

$$\boxed{S_i = 2n_i - 1}$$

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The 1D Ising Model

In general we can write:

$$Q(\beta, N, H) = \sum_{v} e^{-\beta E_v} = \sum_{s_1} \sum_{s_2} \dots \sum_{s_N = \pm 1} exp\left[\beta \mu H \sum_{i=1}^{N} s_i + \beta J \sum_{ij} s_i s_j\right]$$

$\uparrow\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow\uparrow\downarrow\uparrow\downarrow$

In 1D for H=0 this reduces to:

$$Q(\beta, N, 0) = \sum_{v} e^{-\beta E_v} = \sum_{s_1} \sum_{s_2} \dots \sum_{s_N = \pm 1} exp\left[\beta J \sum_{ij} s_i s_j\right]$$

$H=0$

$$= \sum_{s_1} \sum_{s_2} \dots \sum_{s_N = \pm 1} exp\left[\beta J \sum_{i=1}^{N} s_i s_{i+1}\right]$$

The 1D Ising Model

$$Q(\beta, N, 0) = [2cosh(\beta J)]^N$$

for N large enough there is no phase transition

for T > 0 the disordered phase is favored

$$T_c = \frac{J}{N k_B}$$

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The 2D Ising Model

for $H = 0$ 1944 Onsager

$$Q(\beta, N, 0) = \left[2\cosh(\beta J) \cdot e^{I}\right]^{N}$$

$$I = (2\pi)^{-1} \int_0^{\pi} d\phi \, \ln\left\{\frac{1}{2}\left[1 + \left(1 - \kappa^2 \sin^2 \phi\right)^{\frac{1}{2}}\right]\right\}$$

$$\kappa = 2\sinh(2\beta J) / \cosh^2(2\beta J)$$

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there is a T_c $\Rightarrow$ $\sinh \frac{2J}{k_B T_c} = 1$

$$T_c = \frac{2.269\, J}{k_B}$$

below wich the stable state is ordered

$$C = \left(\frac{\delta \langle E \rangle}{\delta T} \right)_{H=0}$$ is singular (diverges)

$$\frac{C}{N} \sim \frac{8 k_B}{\pi} (\beta J)^2 \ln \left(\frac{1}{T - T_c} \right)$$

$$\frac{M}{N} \sim \text{const} \, (T - T_c)^{\beta} \qquad \beta = \frac{1}{8}$$

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Other Models

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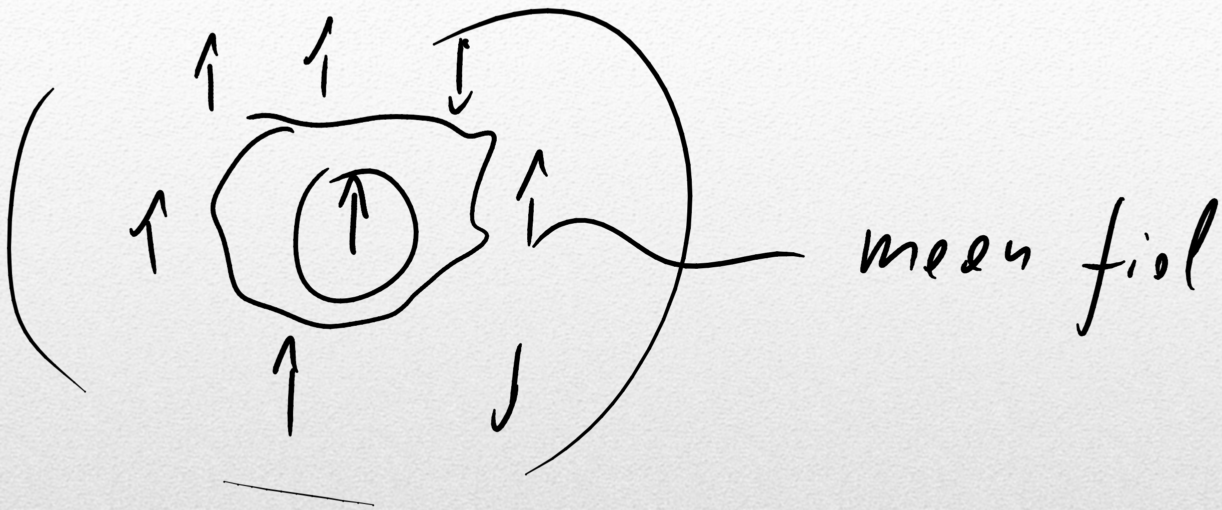
The mean field approach



The result for 2D Ising Model