

§4. MEAN-FIELD THEORY I

VAN DER WAALS EQUATION OF STATE

Ideal gas

$$pV = Nk_B T \quad \hookrightarrow \quad pV = nRT, \quad n = \frac{N}{V}$$

valid at small density $\frac{N}{V} \rightarrow$ cannot describe phase transitions.

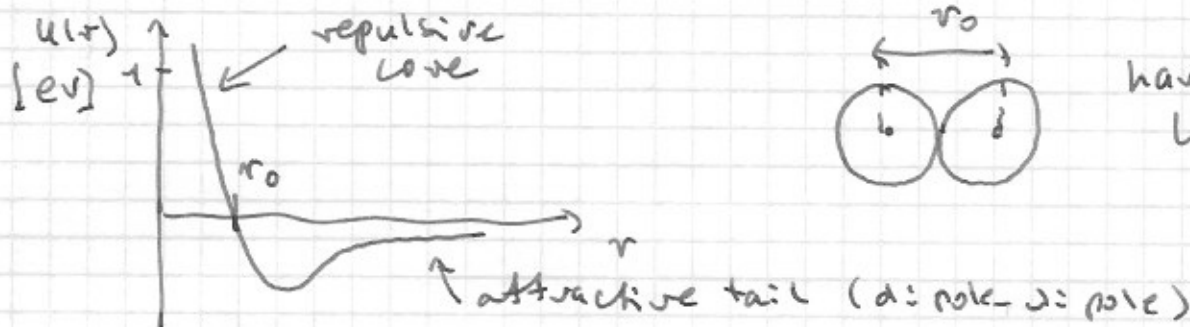
how to include interparticle interactions?

heuristic (intuitive) approach

\rightarrow renormalized ideal gas

$$p_{\text{eff}} V_{\text{eff}} = nRT$$

1) Interaction potential



2) Effective volume

$$V_{\text{eff}} = V - b'N, \quad b' = \frac{1}{2} \frac{4}{3} \pi (2r_0)^3 = \frac{16\pi r_0^3}{3}$$

\uparrow no double counting

3) Effective pressure

interaction is pairwise $\sim \left(\frac{N}{V}\right)^2$

van der Waals (dipole-dipole) interaction is attractive

physical pressure smaller $\rightarrow P = p_{\text{eff}} - a' \left(\frac{N}{V}\right)^2$

•) van der Waals equation

$$a \equiv N_A^2 a'$$

$$b \equiv N_A b'$$

$$N = n N_A$$

N_A - Avogadro's number

$$\boxed{\left(p + a \left(\frac{n}{V} \right)^2 \right) (V - bn) = nRT}$$

\uparrow \uparrow
 p_{eff} V_{eff}

Microscopic approach - virial expansion

$$\frac{p}{k_B T} = \frac{N}{V} \rightarrow \frac{p}{k_B T} = \sum_{l=1}^{\infty} B_l \left(\frac{N}{V} \right)^l = \frac{N}{V} + B_2 \left(\frac{N}{V} \right)^2 + B_3 \left(\frac{N}{V} \right)^3 + \dots$$

Applying to van der Waals equation

$$\frac{p}{k_B T} = \frac{\frac{N}{V}}{1 - b \frac{N}{V}} - \frac{a}{k_B T} \left(\frac{N}{V} \right)^2 = \sum_{l=1}^{\infty} b^{l-1} \left(\frac{N}{V} \right)^l - \frac{a}{k_B T} \left(\frac{N}{V} \right)^2$$

$$B_1 = 1, \quad B_2 = b - \frac{a}{k_B T}, \quad B_{l>2} = b^{l-1}$$

B_l virial coefficients

Statistical Physics

Ideal gas $H_0 = \sum_{i=1}^N \frac{p_i^2}{2m}$

$$Z_0 = \frac{1}{N! h^{3N}} \int \prod_{i=1}^N d^3 p_i d^3 r_i e^{-\beta H_0} = \frac{V^N}{N! h^{3N}} \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}}$$

$$F_0 = -k_B T \ln Z_0$$

Real gas $H = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i < j}^N u_2(r_{ij})$

$$Z = Z_0 \cdot Q \quad F = F_0 - k_B T \ln Q$$

$$Q = \frac{1}{V^N} \int \prod_i d^3 r_i e^{-\beta \sum_{i < j} u_2(r_{ij})}$$

Configuration integral

$$e^{-\beta \sum_{i < j}^N u_2(r_{ij})} = \prod_{i < j}^N e^{-\beta u_2(r_{ij})}$$

Def. Mayer function

$$e^{-\beta u(r_{ij})} = 1 + f_{ij}$$

$$Q = \frac{1}{V^N} \int \prod_i d^3 r_i \prod_{i < j}^N (1 + f_{ij})$$

Mayer expansion

$$\prod_{i < j}^N (1 + f_{ij}) = 1 + \sum_{i < j} f_{ij} + \sum_{i < j} \sum_{k < l} f_{ij} f_{kl} + \dots$$

hence $Q = 1 + \frac{N}{V} a_1 + \frac{N(N-1)}{2V^2} a_2 + \dots$

$$pV = -F$$


$$\frac{p}{k_B T} = \frac{N}{V} + B_2(T) \left(\frac{N}{V} \right)^2 + B_3(T) \left(\frac{N}{V} \right)^3 + \dots$$

$B_2(T)$ - virial coefficients

e.g. $B_2(T) = -2\pi \int_0^\infty dr r^2 \left(e^{-\frac{u(r)}{k_B T}} - 1 \right)$, etc.

Mean field method I - Van der Waals gas

→ to take into account the effects of weak, long-range interactions among the particles

•) Let $V(r)$  interparticle interaction
b - hard-core

••) Let $n = \frac{N}{V}$ concentration of atoms / molecules

The average interaction of all other atoms acting on one at $r=0$ is

$$\int_b^\infty d\tau \tau V(\tau) n = -2na$$

$\underbrace{\hspace{10em}}_{2a}$ factor 2 - double

$n(r) = n = \text{const.}$

mean-field approximation - neglects correlation between molecules

The change of free / internal energy

$$\Delta F = \Delta U = -\frac{1}{2} (2Nna) = -\frac{N^2 a}{V}$$

to count the interaction once $N(N-1) \approx N^2$

•••) reduction of volume $V \rightarrow V - Nb$

$$F_{ideal} = -Nk_B T \left[\ln\left(\frac{na}{n}\right) + 1 \right] = -Nk_B T \left[\ln\left(\frac{naV}{N}\right) + 1 \right]$$

$$F_{vol} = -Nk_B T \left[\ln\left(na \frac{V-Nb}{N} \right) + 1 \right]$$

$$F_{vdw} = -Nk_B T \left[\ln\left(na \frac{V-Nb}{N} \right) + 1 \right] - \frac{N^2 a}{V}$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_{T,N} = \frac{k_B T N}{V - Nb} - \frac{N^2 a}{V^2}$$

$$\boxed{\left(P + \left(\frac{N}{V} \right)^2 a \right) (V - Nb) = Nk_B T}$$

(142a)

Critical point

$$N = n N_A$$

Write van der Waals equation

$$N_A a \rightarrow a$$

$$N_A b \rightarrow b$$

$$(p v^2 + a n^2)(v - b n) = n R T v^2$$

$$v(p) = \alpha v^3 + \beta v^2 + \gamma v + \delta = 0$$

3rd order
polynomial
equation.

⊕ one real, two complex solutions

⊕ one three fold real solution

⊕ three different real solutions

There exists a critical point (p_c, v_c, T_c)

At the critical point

$$(v - v_c)^3 = 0 \Leftrightarrow$$

$$v^3 - 3v_c v^2 + 3v_c^2 v - v_c^3 = 0$$

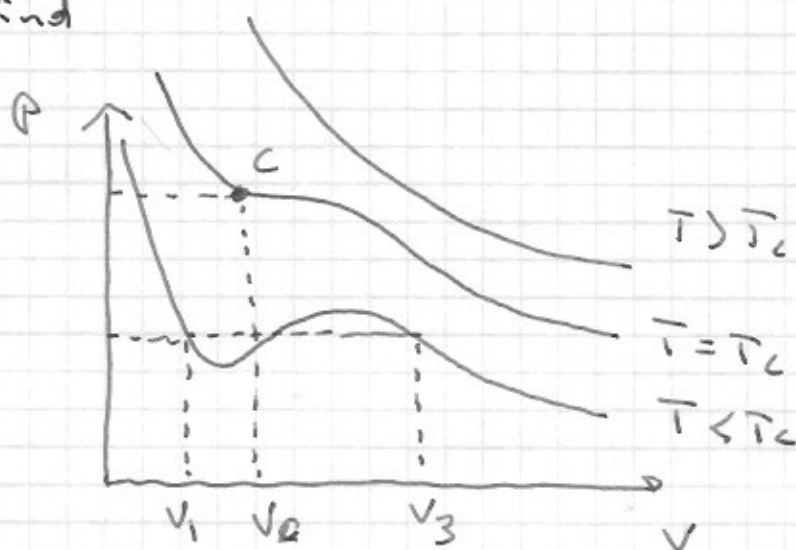
$$v^3 - n \left(b + \frac{R T}{p} \right) v^2 + \frac{a n^2}{p} v - \frac{a b n^2}{p} = 0$$

at $p = p_c, T = T_c$ we find

$$\begin{cases} 3v_c = nb + \frac{n R T_c}{p_c} \\ 3v_c^2 = \frac{a n^2}{p_c} \\ v_c^3 = \frac{a b n^3}{p_c} \end{cases}$$

Solving we get

$$\begin{aligned} v_c &= 3bn \\ p_c &= \frac{a}{27b^2} \\ R T_c &= \frac{8a}{27b} \end{aligned}$$



ideal gas $\frac{pv}{nRT} = 1$

van der Waals gas $z_c = \frac{p_c v_c}{n R T_c} = \frac{3}{8} = 0,375$

water $z_c = 0,226$

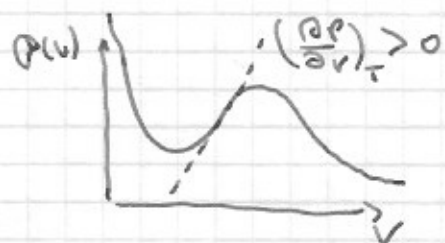
at $T_c = 324^\circ\text{C}$ (143)

Maxwell construction

$T > T_c$ $p(v)$ is monotonic

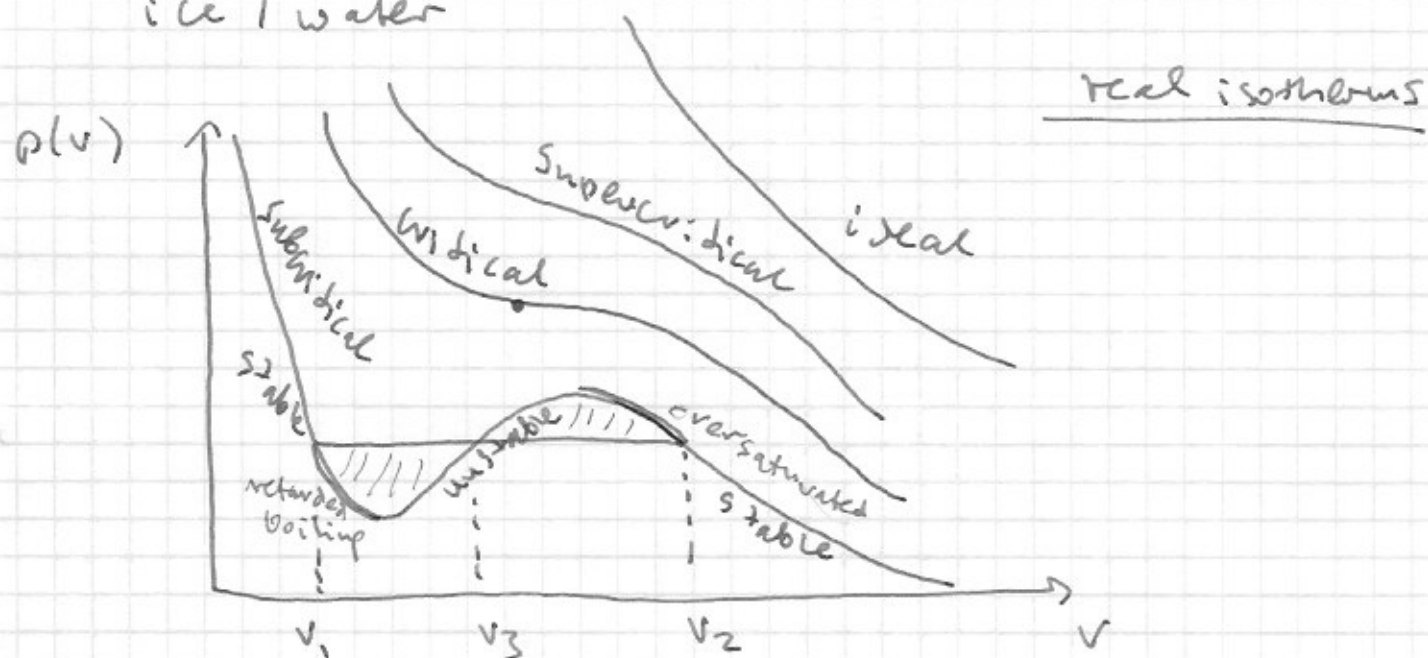
$T < T_c$ $p(v)$ has a "loop" with negative compressibility

$$\alpha_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T < 0, \quad \left(\frac{\partial p}{\partial v} \right)_T > 0$$



a system is unstable and would / should collapse

Phase separation - the system avoid this instability by separating into two phases
ice / water



Coexistence condition

The two phases 1 and 2 are in equilibrium at the vapor pressure p_v if for $N_1 + N_2 = N, V_1 + V_2 = V$
differentials of Gibbs enthalpy coincide

$$G = \mu N$$

$$dG_1(T, P_0, N_1) = dG_2(T, P_0, N_2)$$

or

$$dF_1(T, V_1, N_1) + P_0 dV_1 = dF_2(T, V_2, N_2) + P_0 dV_2 \quad (*)$$

$G = F + PV$ The free energy

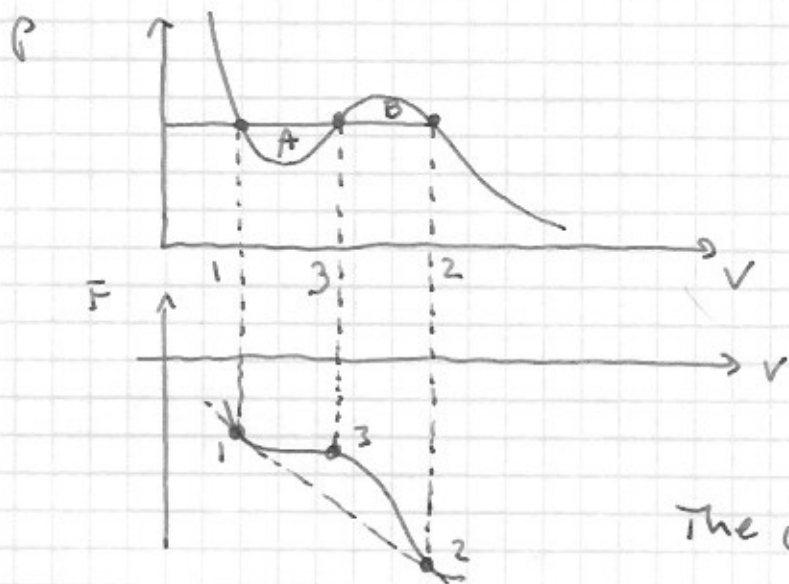
$$F(V, T) = - \int_{\text{isotherm}} P dV, \quad P = - \left(\frac{\partial F}{\partial V} \right)_{T, N}$$

can be obtained as the area under the isotherm.

Interpreting (*)

$$F_1 - F_2 = P_0 (V_2 - V_1) \quad \text{coexistence condition}$$

which implies that V_1 and V_2 are defined by a double tangent construction



The free energy is a weighted mixture of two phases 1 and 2 at any point along the tangent between 1 and 2.

The resulting non-uniform state has the same p and T as the uniform phase 3 but a lower free energy.

Maxwell construction:

$$F_2 - F_1 = \int_{V_1}^{V_2} (-p) dV = \int_{V_1}^{V_3} (-p) dV + \int_{V_3}^{V_2} (-p) dV$$

along the isotherm

From coexistence condition

$$F_2 - F_1 = P_V (V_1 - V_3 + V_3 - V_2)$$

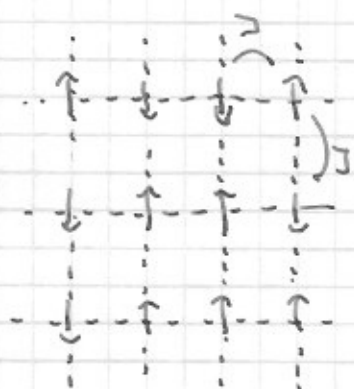
We then have

$$\underbrace{P_V (V_3 - V_1)}_{\text{area A}} - \int_{V_1}^{V_3} p dV = \int_{V_3}^{V_2} p dV - \underbrace{P_V (V_2 - V_3)}_{\text{area B}}$$

It determines the vapor pressure $p_V = p(V_3)$ as the pressure for which the areas A and B are the same.

§ 5. MEAN FIELD THEORY II — ISING MODEL

Ising model

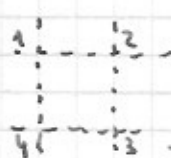


$$S_i = \{-1, +1\}$$

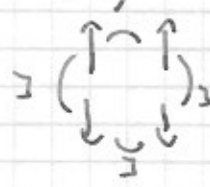
$$H = E(\{S_i\}) = -J \sum_{\langle ij \rangle} S_i \cdot S_j - h \sum_{i=1}^N S_i$$

$$J > 0 \quad (\text{FM})$$

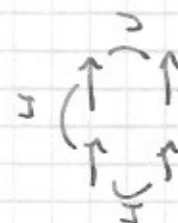
e.p.



$$E(S_1, S_2, S_3, S_4) = -J(S_1 \cdot S_2 + S_2 \cdot S_3 + S_3 \cdot S_4 + S_4 \cdot S_1) - h(S_1 + S_2 + S_3 + S_4)$$



$$E(1, 1, -1, -1) = -J(1 \cdot 1 + 1 \cdot (-1) + (-1) \cdot (-1) + (-1) \cdot 1) - h(1 + 1 - 1 - 1) = 0$$



$$E(1, 1, 1, 1) = -J(1 \cdot 1 + 1 \cdot 1 + 1 \cdot 1 + 1 \cdot 1) - h(1 + 1 + 1 + 1) = -4J - 4h$$

Partition function and averages

$$Z = \sum_{S_1=\pm 1} \dots \sum_{S_N=\pm 1} e^{-\beta E(S_1, \dots, S_N)}$$

a sum with 2^N elements

$$\langle S_i \rangle = \frac{1}{Z} \sum_{S_1} \dots \sum_{S_N} S_i e^{-\beta E(S_1, \dots, S_N)}$$

average moment at site i

magnetization

$$m = \frac{1}{N} \sum_i \langle S_i \rangle$$

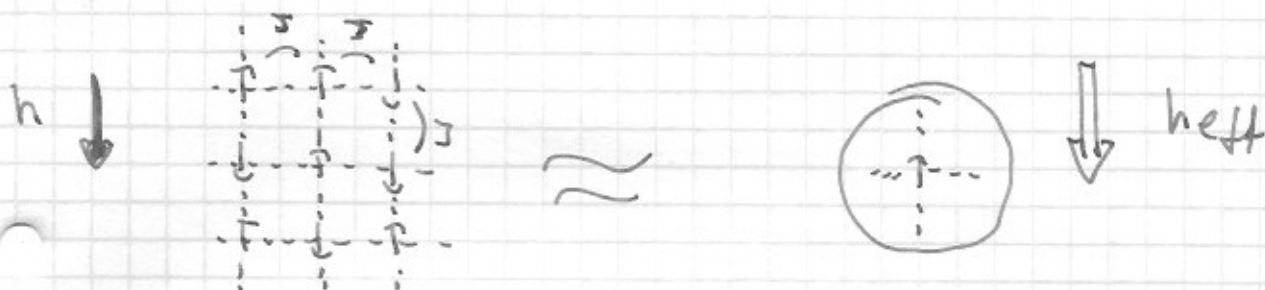
Exact solvable at $d=1$ (no phase transition) and $d=2$ (phase transition)

No exact solution in $d=3$ and higher

$$E_{MF}(\{s_i\}) = -h_{\text{eff}} \sum_i s_i + 2Jm^2 N$$

$$h_{\text{eff}} = h + 2Jm$$

"field" produced by other particles
 external field
 mean magnetic field



Self-consistency equation

$$\begin{aligned}
 Z_{MF} &= \sum_{s_1} \dots \sum_{s_N} e^{-\beta h_{\text{eff}} \sum_i s_i + 2Jm^2 N} = \left(\sum_s e^{-\beta h_{\text{eff}} \cdot s} \right)^N e^{2Jm^2 N} \\
 &= \left(e^{-\beta h_{\text{eff}}} + e^{\beta h_{\text{eff}}} \right)^N e^{2Jm^2 N} =
 \end{aligned}$$

$$Z_{MF} = e^{-\beta 2Jm^2 N} 2^N \left(\cosh \left(\frac{2Jm + h}{k_B T} \right) \right)^N$$

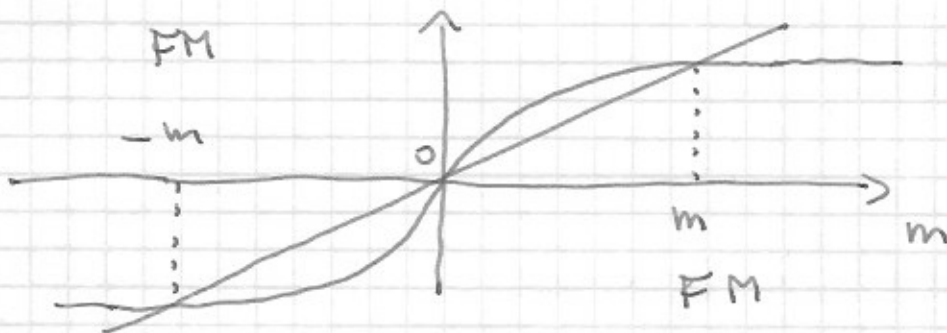
$$\begin{aligned}
 m &= \frac{1}{N} \sum_{i=1}^N \langle s_i \rangle = \frac{1}{N} \sum_{i=1}^N \frac{1}{Z_{MF}} \sum_{s_1} \dots \sum_{s_N} s_i e^{-\beta h_{\text{eff}} s_i} = \\
 &= \frac{1}{N} \sum_{s_1} e^{-\beta h_{\text{eff}} s_1} \dots \sum_{s_N} s_N e^{-\beta h_{\text{eff}} s_N} \dots \sum_{s_N} e^{-\beta h_{\text{eff}} s_N} \\
 &= \frac{\sum_{s_1} e^{-\beta h_{\text{eff}} s_1} \dots \sum_{s_N} e^{-\beta h_{\text{eff}} s_N}}{\sum_{s_1} e^{-\beta h_{\text{eff}} s_1} \dots \sum_{s_N} e^{-\beta h_{\text{eff}} s_N}}
 \end{aligned}$$

$$m = \frac{1}{N} \sum_{i=1}^N \frac{\sum_{j=1}^N s_i s_j e^{-\beta h_{eff} s_j}}{\sum_{s_j} e^{-\beta h_{eff} s_j}} = \frac{e^{\beta h_{eff}} - e^{-\beta h_{eff}}}{e^{\beta h_{eff}} + e^{-\beta h_{eff}}}$$

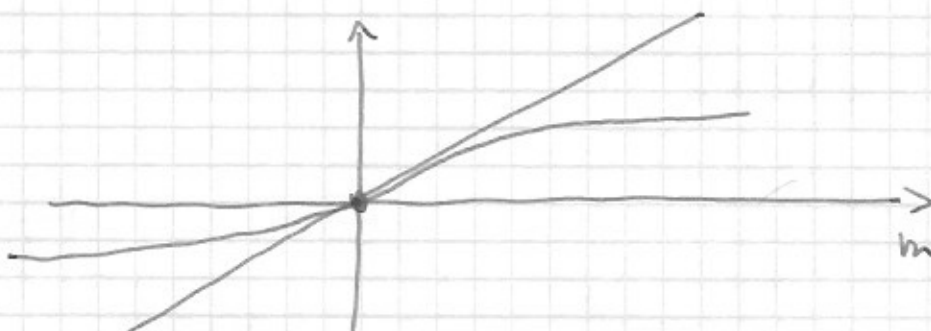
$$m = \tanh\left(\beta (2zJm + h)\right)$$

Solution at $h=0$

$$m = \tanh\left(\frac{2zJm}{k_B T}\right)$$



$\exists m \neq 0$
 $T < T_c$



only solution

$m = 0$
 $T > T_c$

Critical temperature

close to $T = T_c$

m is small

$$\tanh(x) \approx x$$

$$m = \frac{2zJ}{k_B T_c} m$$

\Rightarrow

$$T_c = \frac{2zJ}{k_B}$$

finite transition temperature.

Critical behavior at $h=0$

$$\tanh(x) = x - \frac{x^3}{3}$$

$$m = \frac{2zJm}{k_B T} - \frac{1}{3} \left(\frac{2zJ}{k_B T} \right)^3 m^3$$

$$m^2 \frac{1}{3} \left(\frac{2zJ}{k_B T} \right)^3 = \left(\frac{2zJ}{k_B T} \right) - 1$$

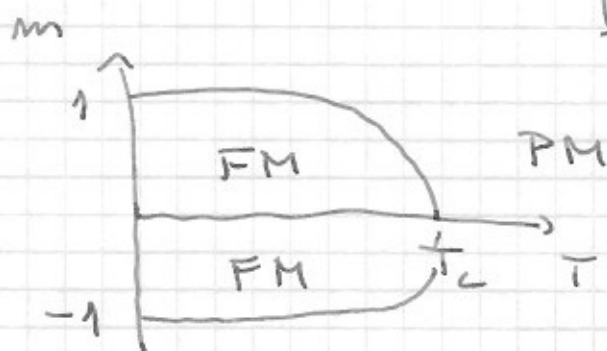
$$m^2 = 3 \left(\left| \frac{k_B T}{2zJ} \right|^2 - \left| \frac{k_B T}{2zJ} \right|^3 \right) = 3 \left(\frac{T}{T_c} \right)^2 \left(1 - \frac{T}{T_c} \right)$$

When $T \rightarrow T_c^-$

$$m = \sqrt{3} \sqrt{1 - \frac{T}{T_c}} = \sqrt{3} \left(1 - \frac{T}{T_c} \right)^{\frac{1}{2}}$$

$$\beta = 1/2$$

Critical exponent
mean-field



$$m(0,0) = \pm 1$$

order parameter

Susceptibility

$$\chi_T = \left(\frac{\partial m}{\partial h} \right)_T = \chi_T(T, h)$$

$$\chi_T = \frac{\beta \left(1 + 2zJ \left(\frac{\partial m}{\partial h} \right)_T \right)}{\cosh^2(\beta 2zJ m + h)} = \frac{\beta \left(1 + 2zJ \chi_T \right)}{\cosh^2(\beta (2zJ m + h))}$$

$$\chi_T = \frac{\beta}{\cosh^2(\beta (2zJ m + h)) - 2zJ \beta}$$

At $h=0$

$$\chi_T = \frac{\beta}{\cosh^2(\beta Z Z m) - Z Z \beta}$$

When $T \rightarrow T_c^+$ ($m \rightarrow 0$)

$$\chi_T = \frac{\beta}{1 - Z Z \beta} = \frac{1}{k_B T - \frac{Z Z J}{k_B T_c}} \sim \frac{1}{T - T_c}$$

$$\chi_T \sim \left(\frac{1}{T - T_c} \right)^{\gamma_+}$$

$$\gamma_+ = +1$$

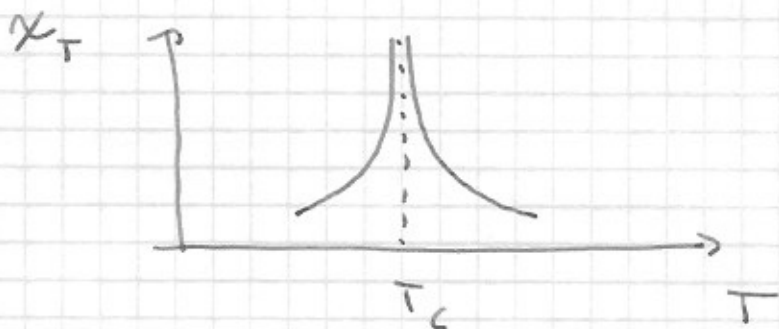
critical exponent

When $T \rightarrow T_c^-$ ($m \rightarrow 0^+$) $\cosh x = 1 + \frac{x^2}{2}$

$$\chi_T = \frac{\beta}{1 + \frac{1}{2} \beta^2 (Z Z J)^2 \beta (1 - \frac{T}{T_c}) - Z Z \beta} \approx \frac{1}{T_c - T}$$

$$\chi_T \sim \left(\frac{1}{T_c - T} \right)^{\gamma_-}$$

$$\gamma_- = 1$$



At the continuous transition the susceptibility diverges!

Free energy expansion

$$F_{MF} = -k_B T \ln Z_{MF} = -k_B T \left(-\beta \int m^2 N + N \ln 2 \right) +$$

$$+ N \ln \cosh \left(\frac{\beta \int m + h}{k_B T} \right) \approx$$

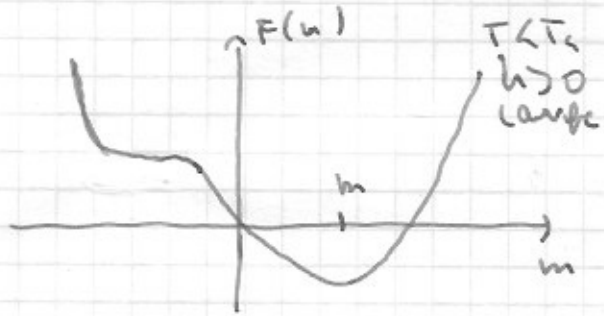
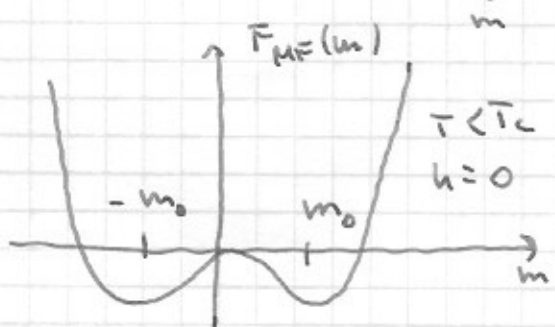
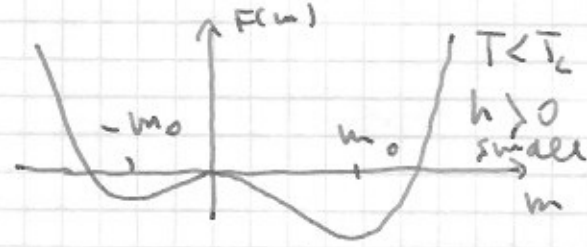
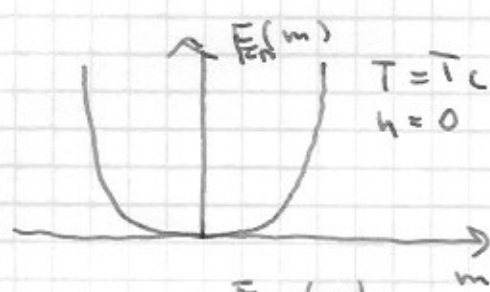
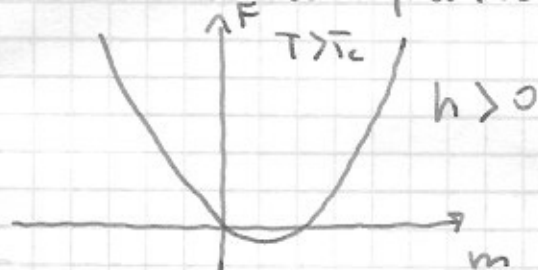
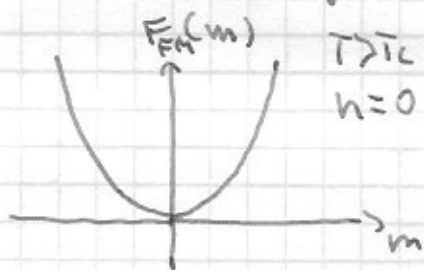
free spins
↓

$$\approx \underbrace{-k_B T N \ln 2}_{F_0} + \underbrace{\int m^2 N}_{\frac{b \bar{T}_c}{2}} - N k_B T \left(\frac{(\beta h_{eff})^2}{2} - \frac{(\beta h_{eff})^4}{12} + \dots \right)$$

$$F_{MF} \Big|_{h=0} \approx F_0 + N \frac{b \bar{T}_c}{2T} (T - T_c)^2 + \frac{N b \bar{T}_c^4}{12 T^3} m^4$$

$$\boxed{\tilde{F}_{MF}(m) = F_0 - h m + a (T - T_c)^2 + b m^4}$$

Landau free energy expansion vs order parameter



continuous transition

discontinuous

+ van der Waals (153)