

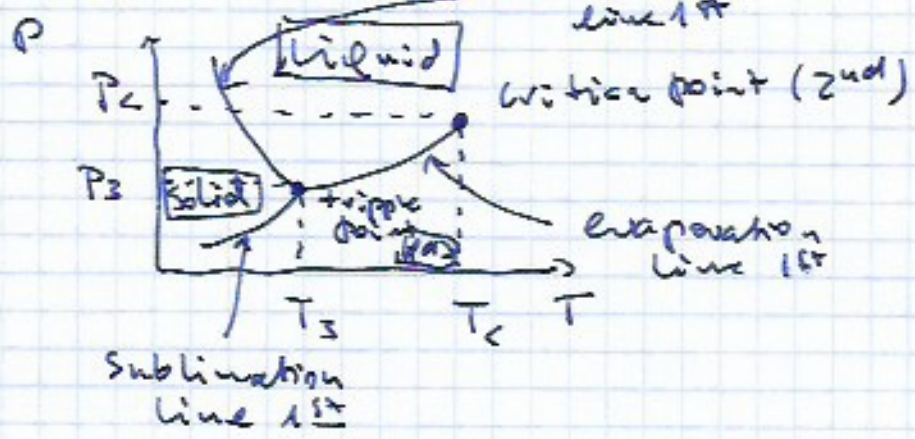
VI. PHASE TRANSITIONS

§ 1. PHASE AND PHASE DIAGRAM

Thermodynamical phase - a state of a matter characterized by distinct macroscopic properties.

e.g. gas, liquid, solid or magnet, superconductors, superfluid.

Phase diagram

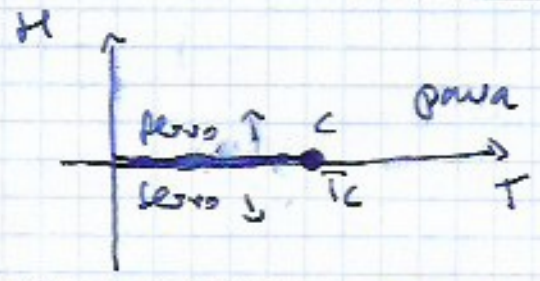


Phase boundary

triple point -
coexistence of 2 phases

critical point -
2 phase have equal densities and entropy densities

- the change is discontinuous for a first order transition
- the change is continuous for a second order transition



magn etc phase diagram

§2. FIRST ORDER PHASE TRANSITION

Each phase is characterized by well defined regular equation of state. When changing the phase this equation changes abruptly

Gibbs enthalpy

$U(S, V, N)$ + Legendre transf.

$$G(T, P, N) = U - PV - TS$$



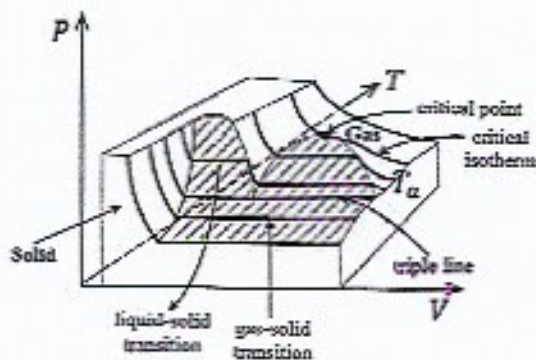
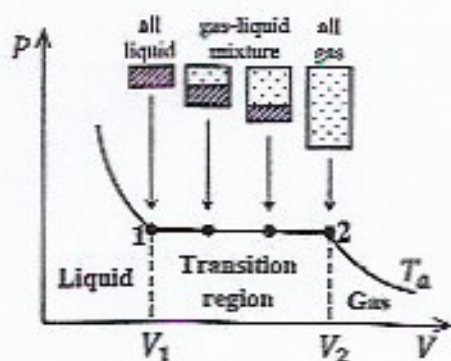
well suited to describe $P-T$ phase diagram.

$G(T, P, N)$ - changes continuously across the phase boundary of 1st order.

however, its derivatives are discontinuous!

$$dG = -SdT + VdP + \mu dN$$

$$S = - \left(\frac{\partial G}{\partial T} \right)_P, \quad V = \left(\frac{\partial G}{\partial P} \right)_T$$



Latent heat

Two phases coexist at a temperature T have different entropies S_1 and S_2 . The system must therefore absorb or release heat (latent heat)

$$\Delta Q_L = T (S_2 - S_1)$$

during a phase transition of 1st order.

Condition for phase coexistence

Let at a given T and p two phases coexist. The Gibbs potential is a sum of Gibbs potentials of the two phases

$$\begin{aligned} G(T, p, N) &= G_1(T, p, N_1) + G_2(T, p, N_2) = \\ &= N_1 \mu_1(T, p) + N_2 \mu_2(T, p) \end{aligned}$$

($G = \mu N$ - Gibbs - Duhem relation)

$$N = N_1 + N_2$$

μ_1, μ_2 - chemical potentials

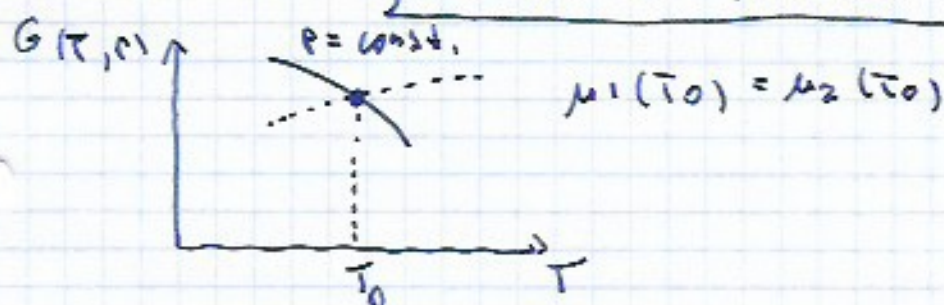
$$\mu_i = \left(\frac{\partial G_i}{\partial N_i} \right)_{T, p}$$

Minimizing the Gibbs potential

$$0 = dG = \mu_1 dN_1 + \mu_2 dN_2 = 0 \quad \text{but} \quad dN_1 = -dN_2$$

$$\Rightarrow \boxed{\mu_1(p, T) = \mu_2(p, T)}$$

coexistence condition



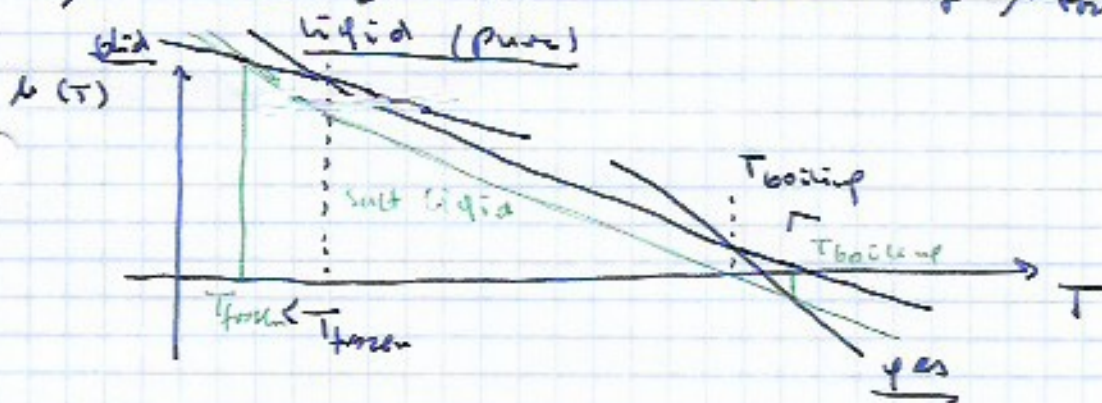
Why does the salt melt the ice?

Chemical potential for a solution $H_2O + NaCl$

$$\mu_{H_2O} = \mu_{H_2O}^{pure} + RT \ln \frac{n_{H_2O}}{n_{H_2O} + n_{NaCl}} \quad \text{mol concentrations}$$

$$\frac{n_{H_2O}}{n_{H_2O} + n_{NaCl}} < 1 \rightarrow RT \ln \frac{n_{H_2O}}{n_{H_2O} + n_{NaCl}} < 0$$

\Rightarrow increase of $n_{NaCl} \rightarrow$ decrease of μ_{H_2O}



Clausius - Clapeyron equation

Discontinuities across the phase boundary

$$\Delta S = S_2 - S_1 = - \left(\frac{\partial \Delta G}{\partial T} \right)_P > 0$$

$$\Delta V = V_2 - V_1 = \left(\frac{\partial \Delta G}{\partial P} \right)_T$$

$$\Delta G = G_2 - G_1 = 0$$

\uparrow
at equilibrium

$\Delta G, S, V$ are functions of V, T, P , which are related by the equation of state.

$$f(P, V, T) = 0.$$

Hence, there is a function

$$\tilde{f}(\Delta G, T, P) = 0$$

$$\Rightarrow \frac{\partial f}{\partial G} dG + \frac{\partial f}{\partial T} dT + \frac{\partial f}{\partial P} dP = df = 0$$

We find partial derivatives

$$\left(\frac{\partial P}{\partial T}\right)_G = - \frac{\frac{\partial f}{\partial T}}{\frac{\partial f}{\partial P}}, \quad \left(\frac{\partial T}{\partial G}\right)_P = - \frac{\frac{\partial f}{\partial G}}{\frac{\partial f}{\partial T}}, \quad \left(\frac{\partial G}{\partial P}\right)_T = - \frac{\frac{\partial f}{\partial P}}{\frac{\partial f}{\partial G}}$$

and we get $\left(\frac{\partial P}{\partial T}\right)_G \cdot \left(\frac{\partial T}{\partial G}\right)_P \cdot \left(\frac{\partial G}{\partial P}\right)_T = -1$ or

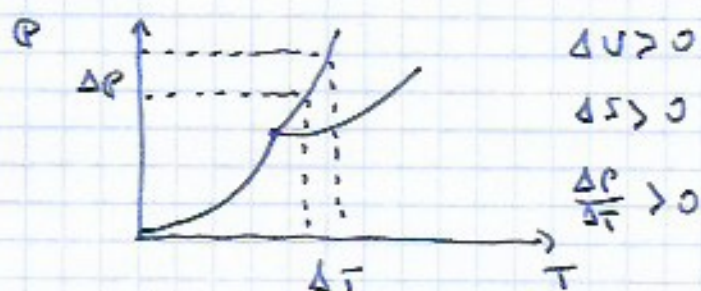
$$\underbrace{\left(\frac{\partial \Delta G}{\partial T}\right)_P}_{-\Delta S} \cdot \left(\frac{\partial T}{\partial P}\right)_{\Delta G} \cdot \underbrace{\left(\frac{\partial P}{\partial G}\right)_T}_{\frac{1}{\Delta V}} = -1 \quad \text{Euler chain rule}$$

Vapor pressure

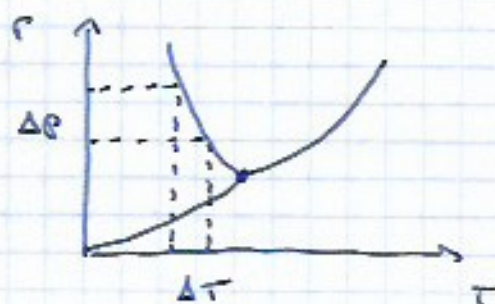
Let P - is the vapor-pressure for the gas-liquid transition. It changes along the phase transition line as

$$\frac{dP}{dT} = \left(\frac{\partial P}{\partial T}\right)_{\Delta G=0}$$

$\left(\frac{\partial P}{\partial T}\right)_{\Delta G}$ - slope on P-T diagram



typically a matter contracts under freezing $\Delta V > 0$



for water

$\frac{\Delta P}{\Delta T} < 0$ negative since $\Delta U < 0$.

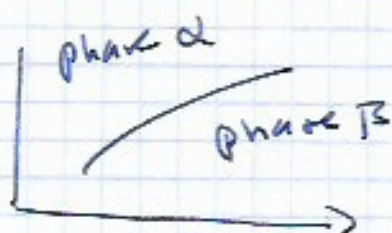
Clausius - Clapeyron relation

$$-\Delta S \left(\frac{\partial T}{\partial P} \right)_{\Delta G} \frac{1}{\Delta V} = -1$$

$$\Rightarrow \boxed{\left(\frac{\partial T}{\partial P} \right)_{\Delta G=0} = \frac{\Delta S}{\Delta V} = \frac{\Delta Q_L}{T \Delta V}}$$

In a second-order phase transition the difference of first derivatives of G vanishes and the Clausius - Clapeyron equation is replaced by a condition involving second order derivatives.

§ 3. EMBRENT CLASSIFICATION OF PHASE TRANSITIONS



Df. The order of the lowest derivative of the Gibbs enthalpy G showing a discontinuity ~~at~~ across the phase boundary is the order of a phase transition

Phase transition of the order n with

$$m=1, \dots, n-1 \quad \left(\frac{\partial^m G_\alpha}{\partial T^m} \right)_P = \left(\frac{\partial^m G_\beta}{\partial T^m} \right)_P, \quad \left(\frac{\partial^m G_\alpha}{\partial P^m} \right)_T = \left(\frac{\partial^m G_\beta}{\partial P^m} \right)_T$$

$$m=n, n+1, \dots \quad \left(\frac{\partial^m G_\alpha}{\partial T^m} \right)_P \neq \left(\frac{\partial^m G_\beta}{\partial T^m} \right)_P, \quad \left(\frac{\partial^m G_\alpha}{\partial P^m} \right)_T \neq \left(\frac{\partial^m G_\beta}{\partial P^m} \right)_T$$

1st order transition

1) $f(T, P)$ continuous

2) $S = - \left(\frac{\partial G}{\partial T} \right)_P$, $V = \left(\frac{\partial G}{\partial P} \right)_T$ discontinuous

3) there is a latent heat

2nd order phase transition

- 1) $G(T, p)$ continuous
- 2) $S(T, p), V(T, p)$ continuous
- 3) response functions discontinuous

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_p$$

heat capacity

$$\chi_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \left(\frac{\partial^2 G}{\partial p^2} \right)_T$$

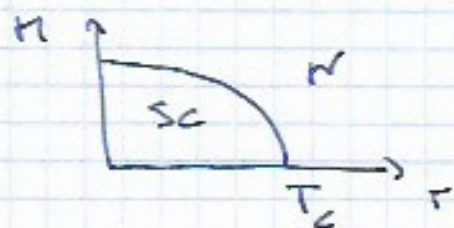
compressibility

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right) = \frac{1}{V} \left(\frac{\partial^2 G}{\partial T \partial p} \right)$$

thermal expansion coefficient

$$dG = -SdT + Vdp + \mu dN$$

Specific heat jump - Superconductors -



Diverging correlation length at criticality

The Ehrenfest classification is valid if correlation length is finite. It diverges at critical point in 2nd order phase transition leading to diverging response

$$\chi = \left(\frac{\partial M}{\partial H} \right)_T \sim \frac{1}{(T - T_c)^\nu}$$

ν - critical exponent

Entropy for a discontinuous transition

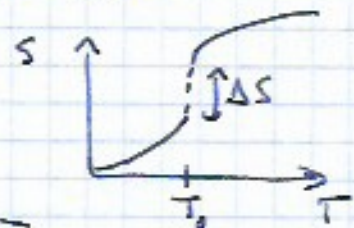
Another classification of phase transitions

For a discontinuous transition

1) $\Delta S \neq 0 \rightarrow$ latent heat

2) $C_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_p$ finite for $T \neq T_0$

at $T = T_c$ not defined

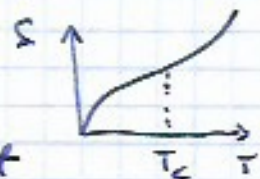


Entropy for a continuous transition

1) S continuous \rightarrow no latent heat

2) there is a critical point T_c

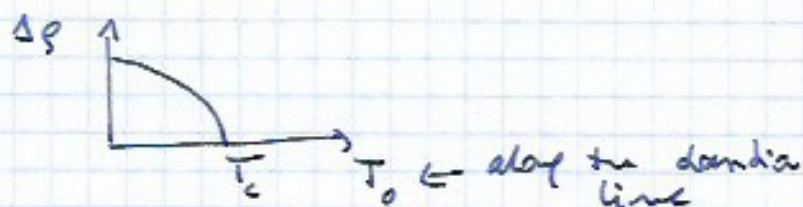
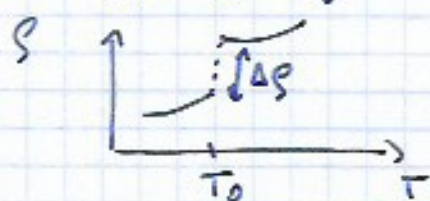
3) singularities in C_v, α_T, χ_T



Density jumps

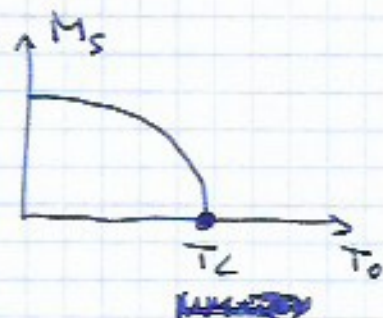
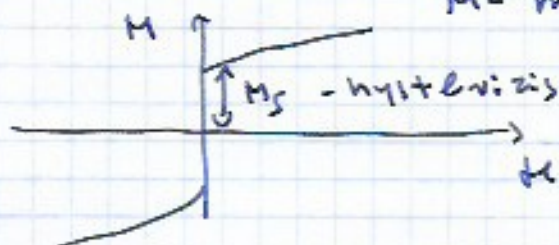
$v = \left(\frac{\partial G}{\partial p} \right)_T$, $\Delta v \neq 0$ at 1st order transition (liquid-gas)

density $\rho = \frac{N}{V}$ - discontinuous



Spontaneous magnetic order

M - magnetization



magnetic work $dU = SdS + dW$, $dW = HdM$, $U = U(S, M)$

$G(T, H) = U - TS + MH$

$M = - \left(\frac{\partial G}{\partial H} \right)_T$

$dG = -SdT - MdH$

At $T_0 < T_c$ - discontinuous

$T_0 = T_c$ - continuous

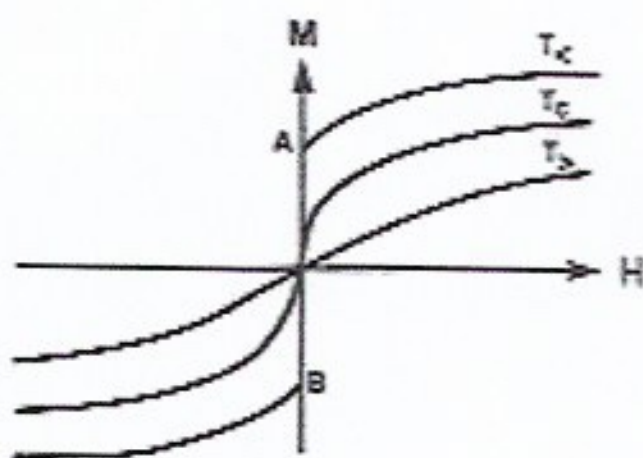
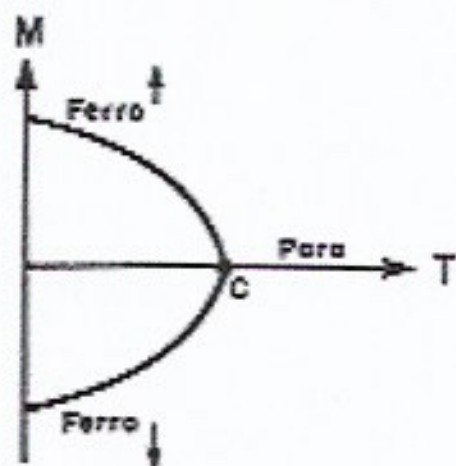
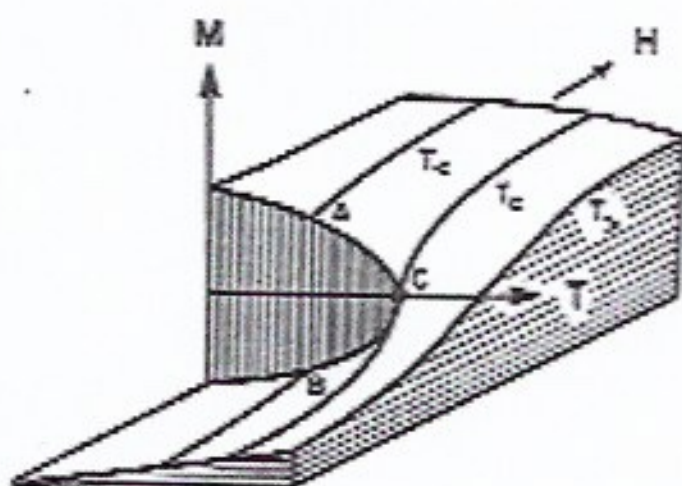
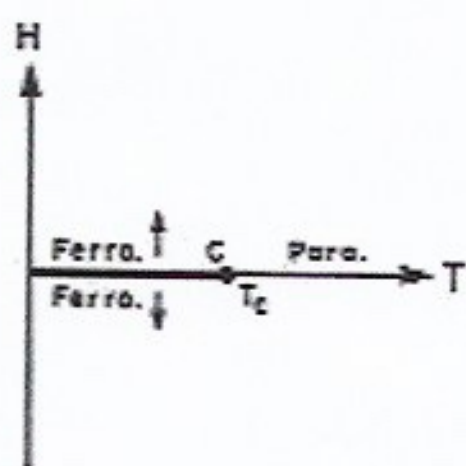


Fig. 4.1 Phase diagrams for a ferromagnet. The surface of the equation of state in the space of magnetization M , external magnetic field H , and temperature T is shown in the upper right. Projections of this surface are shown in the $H-T$, $M-T$, and $M-H$ planes. Isotherms are shown at the critical temperature T_c , at T_c below T_c , and at T_3 above T_c .

§4. MEAN-FIELD THEORY I

VAN DER WAALS EQUATION OF STATE

Ideal gas

$$pV = Nk_B T \quad \Leftrightarrow \quad pV = nRT, \quad z = 1$$

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

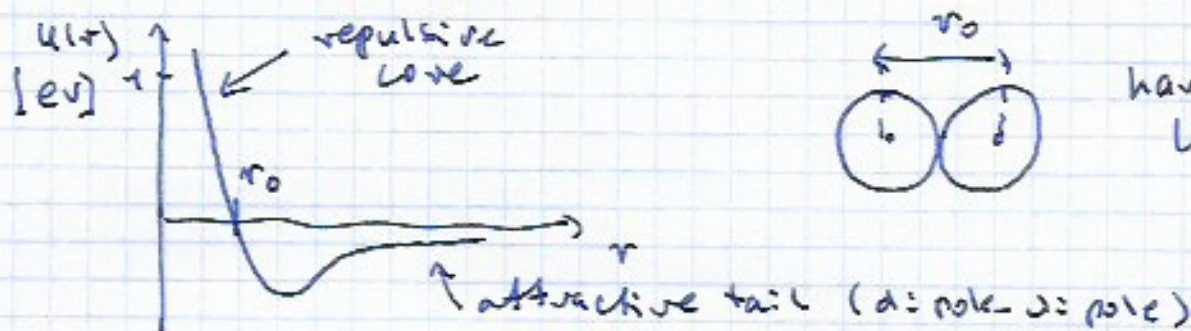
How to include interparticle interactions?

Heuristic (intuitive) approach

\rightarrow renormalized ideal gas

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

1) Interaction potential



2) Effective volume

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

\uparrow no double counting

3) Effective pressure

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

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_A - Avogadro's number

$$N = n N_A$$

$$\left(\underset{\substack{\uparrow \\ p_{\text{eff}}}}{p + a \left(\frac{n}{V} \right)^2} \right) \left(\underset{\substack{\uparrow \\ V_{\text{eff}}}}{V - b n} \right) = n R T$$

Microscopic approach - virial expansion

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

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

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

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

Configuration integral

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

Def. Mayer function

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

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

Mayer expansion

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

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.

Critical point

Write van der Waals equation

$$(pV^2 + an^2)(V - bn) = nRTV^2$$

$$V(p) = \alpha V^3 + \beta V^2 + \gamma V + \delta = 0 \quad \text{3rd order}$$

polynomial equation.

one real, two complex solutions

one threefold real solution

three different real solutions

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

At the critical point

$$(V - V_c)^3 = 0 \Leftrightarrow V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0$$

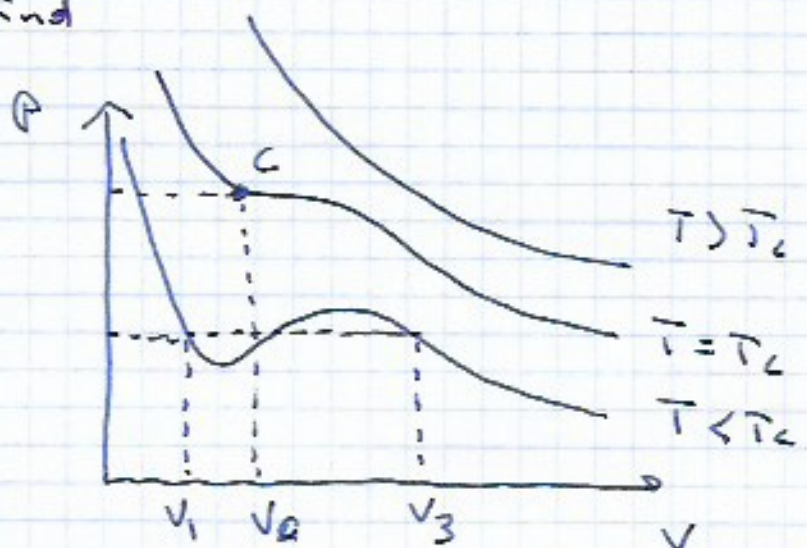
$$V^3 - n\left(b + \frac{RT}{p}\right)V^2 + \frac{an^2}{p}V - \frac{abn^2}{p} = 0$$

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

$$\begin{cases} 3V_c = nb + \frac{nRT_c}{p_c} \\ 3V_c^2 = \frac{an^2}{p_c} \\ V_c^3 = \frac{abn^3}{p_c} \end{cases}$$

Solving we get

$$\begin{aligned} V_c &= 3bn \\ p_c &= \frac{a}{27b^2} \\ RT_c &= \frac{8a}{27b} \end{aligned}$$



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

van der Waals gas $z_c = \frac{p_c V_c}{nRT_c} = \frac{3}{8} = 0,375$

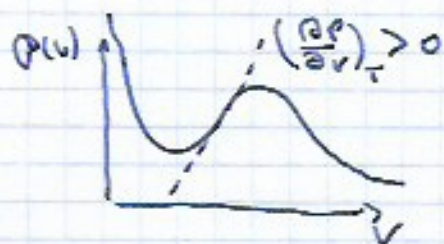
water $z_c = 0,226$
at $T_c = 374^\circ\text{C}$ (143)

Maxwell construction

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

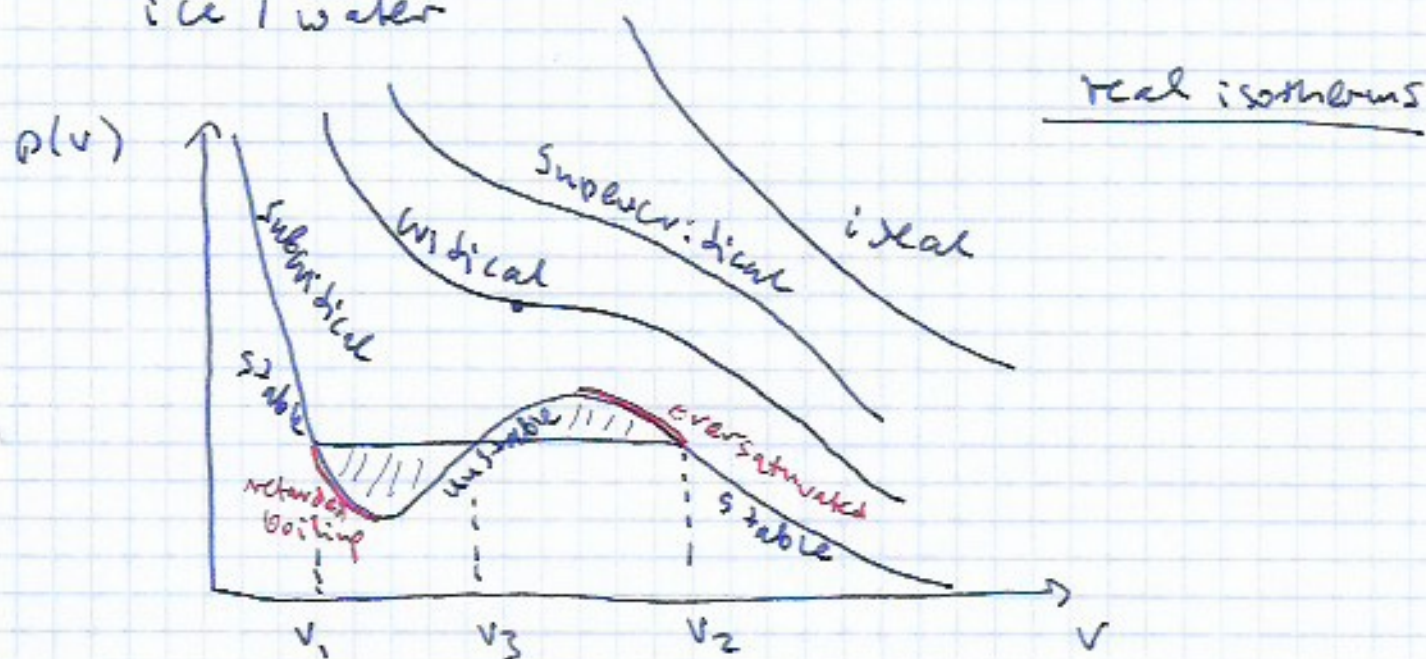
$T < T_c$ $p(v)$ has a "loop" with negative compressibility

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



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

$$dG_1(T, p_0, N_1) = dG_2(T, p_0, N_2)$$

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

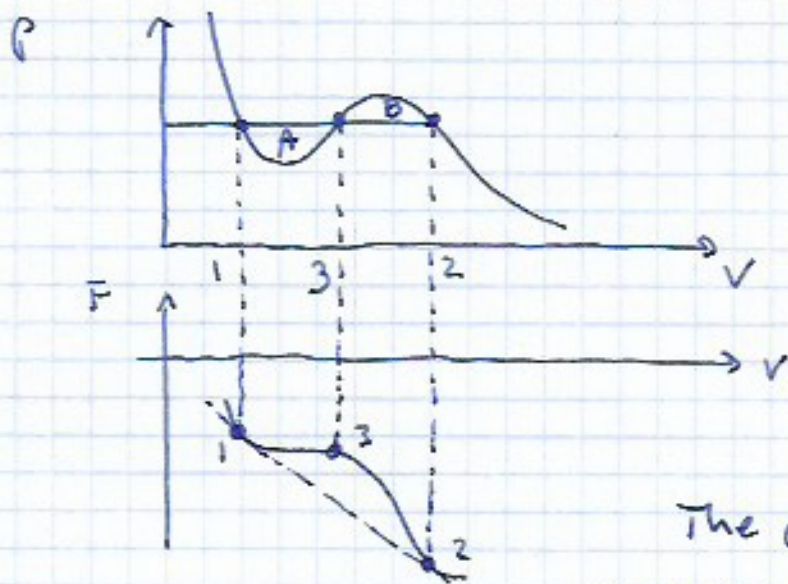
$$F(V, T) = - \int_{\text{isotherm}} p dV, \quad p = - \left(\frac{\partial F}{\partial V} \right)_{T, N}$$

(can be obtained as the area under the isotherm.)

Integrating (*)

$$F_1 - F_2 = p_0 (V_2 - V_1) \quad \text{coexistence condition}$$

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.