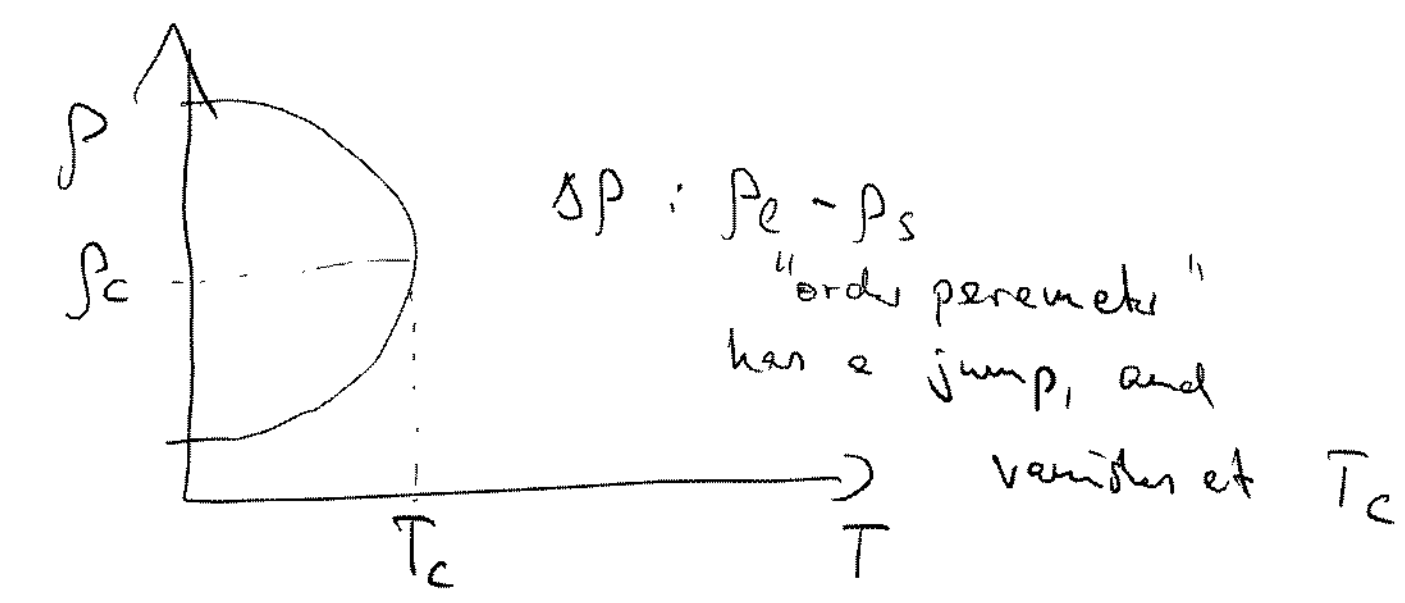
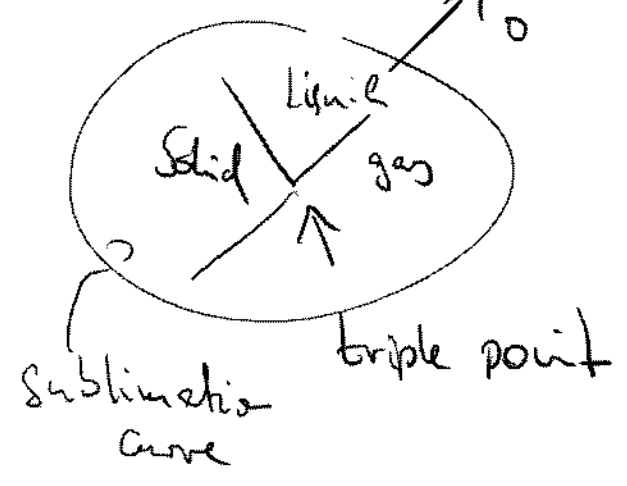
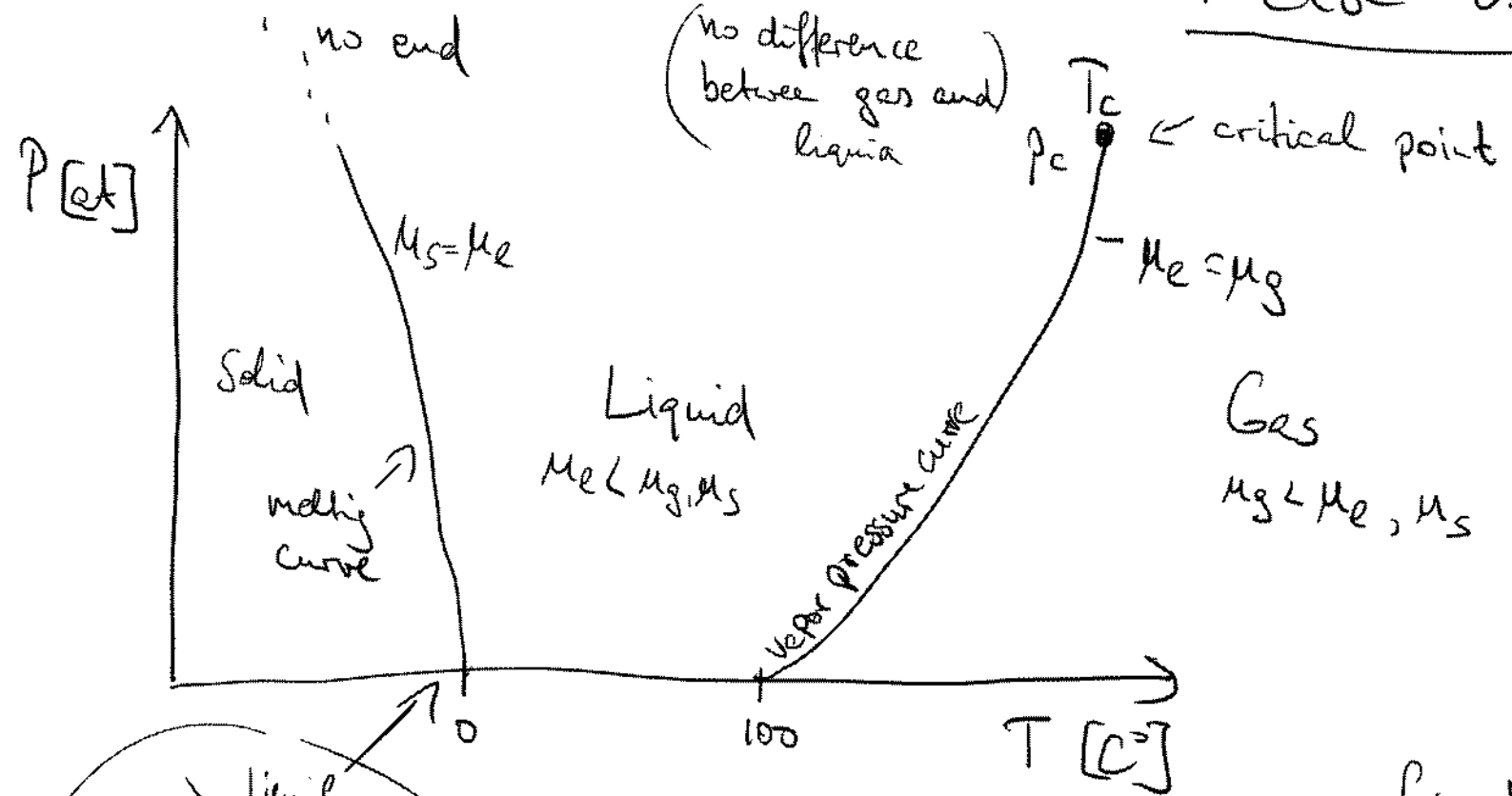


9.1.2014

Phase diagram of H₂O



first order phase transitions

order parameter jumps, existence latent heat

second order PT Like ferromagnetic transition

critical singularities can be described by critical exponents x with respect to the reduced temperature $t = |1 - T/T_c|^x$

Important concept : universality

Details of the short range interactions are not important

Relevant parameters

- spatial dimension D
- symmetry of the interaction

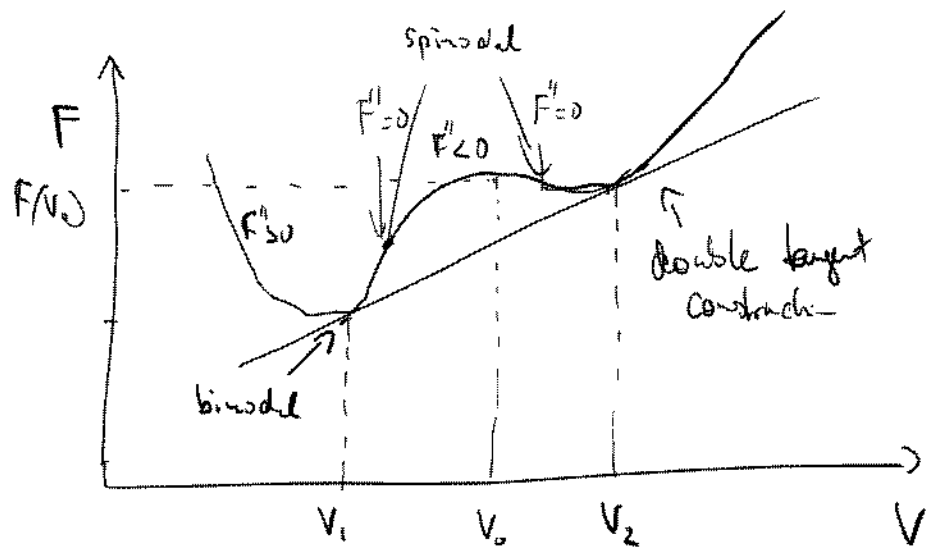
2D These are special : Mermin - Wigner Theorem

↳ Kosterlitz - Thouless transition (sometimes called PT of infinite order)

at low T this syst has a quasi-ordering, algebraic decay of correlation func

$F(N, V, T)$ is a minimum in equilibrium in the canonical ensemble

$\cup \approx$ convex $F'' > 0$



Let us split up the system into a fraction α_1 which occupies V_1 , and α_2 which occupies V_2

$$\left. \begin{aligned} \text{Evidently } \alpha_1 + \alpha_2 &= 1 \\ \alpha_1 V_1 + \alpha_2 V_2 &= V_0 \end{aligned} \right\} \begin{aligned} \alpha_1 &= \frac{V_0 - V_2}{V_1 - V_2} \\ \alpha_2 &= \frac{V_1 - V_0}{V_1 - V_2} \end{aligned}$$

$$\begin{aligned} F_{\text{split}} &= \alpha_1 F(V_1) + \alpha_2 F(V_2) + F_{\text{interface}} \\ &= \underbrace{\frac{V_0 - V_2}{V_1 - V_2} F(V_1) + \frac{V_1 - V_0}{V_1 - V_2} F(V_2)}_{\text{lines in } V_0} + F_{\text{interface}} \end{aligned}$$

lines in V_0
this is the line through $(V_1, F(V_1))$ and $(V_2, F(V_2))$

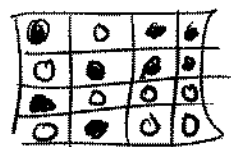
\Rightarrow the real free energy is the convex envelope (or Maxwell's construction)

- double tangent points (binodal) phase separates into the global minimum
- spinodal (metastable points)

Since for $V_0 = V_1 \rightarrow F(V_1)$
 $V_0 = V_2 \rightarrow F(V_2)$

Regular Solution model: (Flory-Huggins theory)

Binary mixture: two species A and B $\rightarrow r \neq 1$



The composition is measured ϕ
by volume fraction

$$\phi_A = \frac{\text{volume of A-molecules}}{\text{total volume}}$$

similar ϕ_B

assume incompressible

$$\phi_A + \phi_B = 1$$

{ also assume that A and B molecules have the same volume }

We are interested in the free energy of mixing

$$F_{\text{mix}} = F_{AB} - (F_A + F_B)$$



Entropy of mixing

S_{mix}

von-Neumann

$$S_{\text{mix}} = -k_B \sum p_i \ln p_i$$

p_i is the probability, that a site is occupied in state i

$$\rightarrow S_{\text{mix}} = k_B [\phi_A \ln \phi_A + \phi_B \ln \phi_B]$$

Note: if ϕ_A or ϕ_B is one,

Energy of mixtures: assume nearest-neighbor interactions, pairwise additive

$$A-A : \epsilon_{AA} \quad , \quad B-B : \epsilon_{BB} \quad , \quad A-B : \epsilon_{AB}$$

Assume ~~now~~ every particle has $z\phi_A$ neighbors, $z\phi_B$ B neighbors

The average energy per site is k_B

$$\frac{1}{2} \left[\phi_A (z\phi_A \epsilon_{AA} + z\phi_B \epsilon_{AB}) + \phi_B (z\phi_B \epsilon_{BB} + z\phi_A \epsilon_{AB}) \right]$$
$$= \frac{1}{2} z (\phi_A^2 \epsilon_{AA} + \phi_B^2 \epsilon_{BB} + 2\phi_A \phi_B \epsilon_{AB})$$

We have to subtract the energy of the unmixed state $\frac{z}{2} (\phi_A \epsilon_{AA} + \phi_B \epsilon_{BB})$

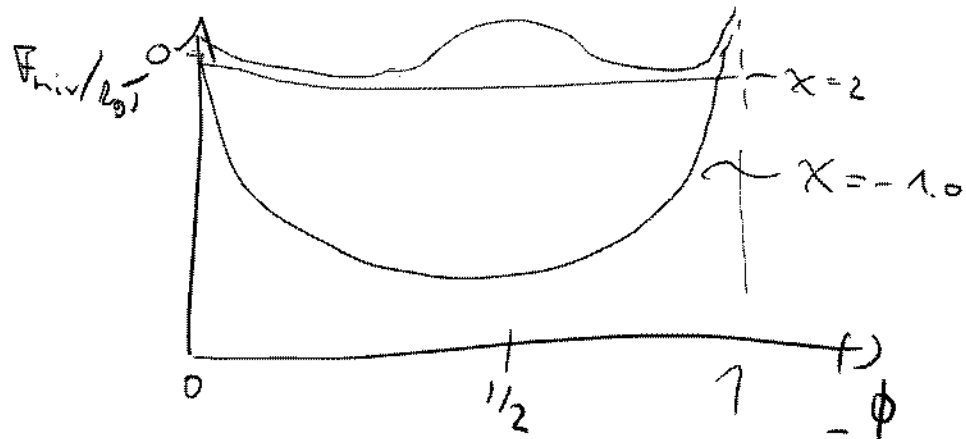
$$\rightarrow U_{\text{mix}} = \frac{z}{2} \left[\phi_A (\phi_A - 1) \epsilon_{AA} + \phi_B (\phi_B - 1) \epsilon_{BB} + 2\phi_A \phi_B \epsilon_{AB} \right]$$

Since $\phi_A + \phi_B = 1 \Rightarrow \phi_A - 1 = -\phi_B$, $\phi_B - 1 = -\phi_A$

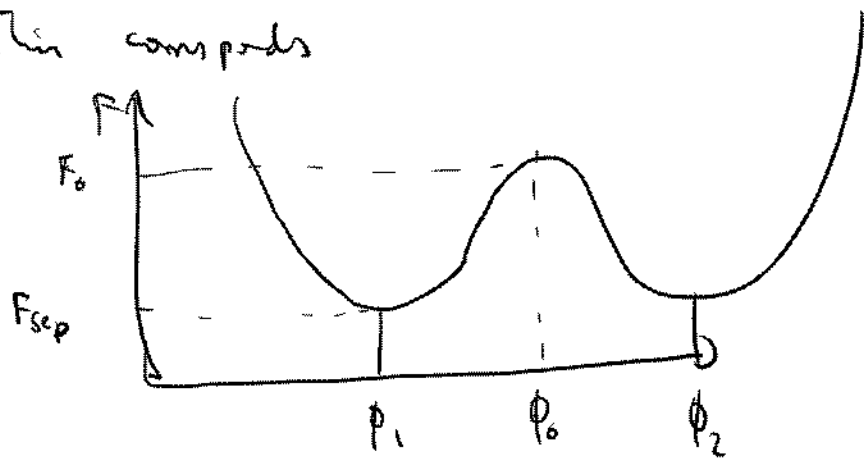
$$U_{\text{mix}} = \underbrace{\frac{z}{2} [2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB}]}_{\chi k_B T} \phi_A \phi_B = \chi k_B T \phi_A \phi_B$$

From $F = U - TS$

$$\frac{F_{mix}}{k_B T} = \chi \phi_A \phi_B + \phi_A \ln \phi_A + \phi_B \ln \phi_B$$



This corresponds



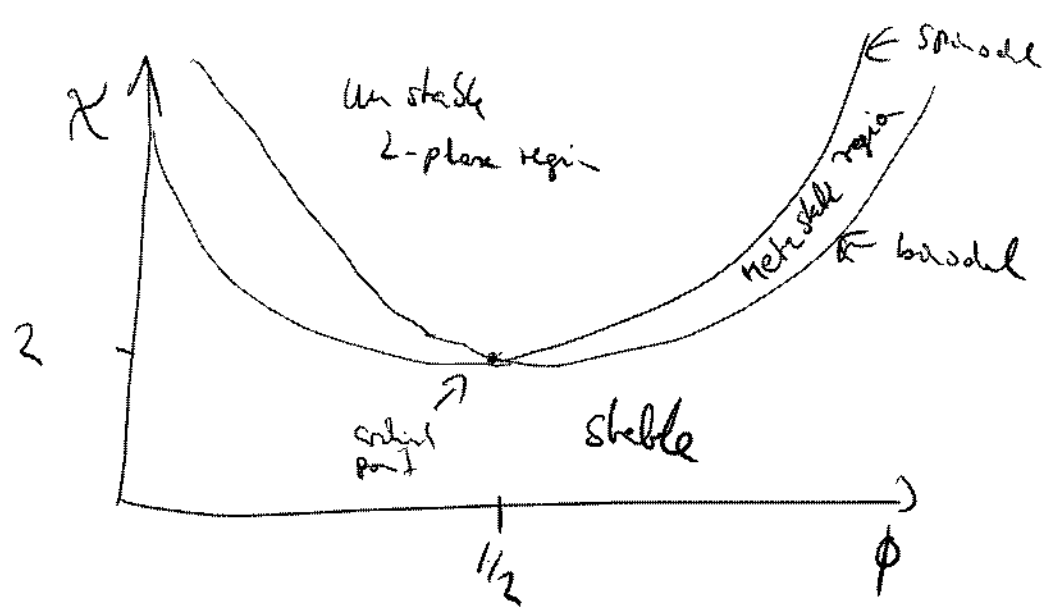
For $\chi < 2$ we have a single minimum at $\phi = 1/2$ while for $\chi \geq 2$ we have two minima and a maximum at $\phi = 1/2$

a mixture with composition ϕ_0 between ϕ_1 and ϕ_2 can lower its free energy by separating into 2 phases, "spinodality gap"

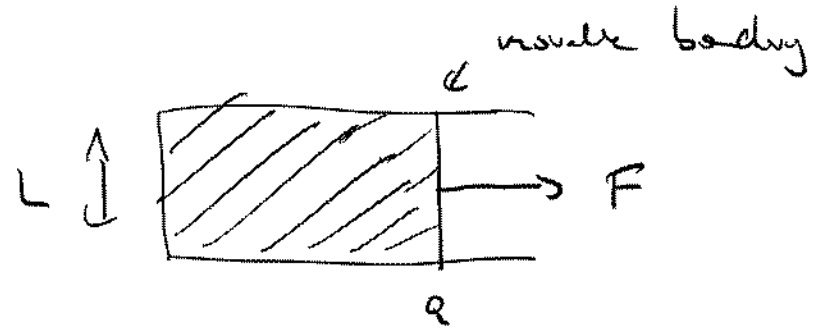
close to the transition

$$\left| \phi_A - \frac{1}{2} \right| \sim (\chi - 2)^{1/2}$$

example of a critical exponent



Interfacial tension



$$\gamma \cdot L = F$$

↑
(Force/length)

Interfacial free energy is due to energetic interactions of A and B molecules at the interface

For the regular solution model one can show:

$$\gamma_{\text{slip}} = \frac{\chi k_B T}{2 v^{2/3}}$$

↑
molecular volume

only true for a slip at face

at T_c $\gamma \rightarrow 0$

Unmixing kinetics:

- ① → between spinodal and binodal: nucleation and growth
- ② → within spinodal region: spinodal decomposition

Nucleation:

$$\Delta\mu = \mu_g - \mu_l$$

for $\Delta\mu > 0$ the bulk liquid has a lower free energy

the surface free energy is positive, and tends to increase the free energy



The surface can be dominant ($\sim R^2$) over the bulk (R^3)

$$\Delta G = G_l - G_g = -\frac{4\pi}{3} R^3 c_l \Delta\mu + 4\pi R^2 \gamma$$

The liquid drop will grow when $\Delta G < 0$, or $G_l < G_g$

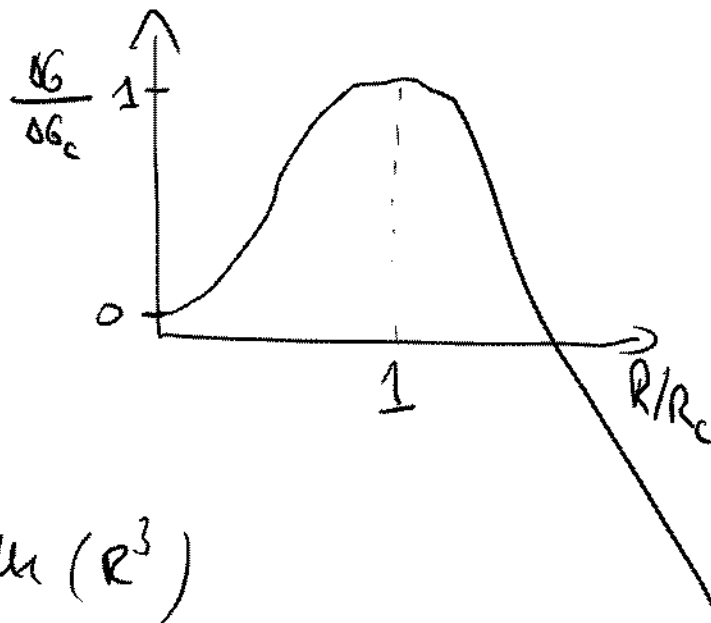
An unstable extremum (max) when

$$\frac{d\Delta G}{dR} = 0 = -4\pi R^2 c_l \Delta\mu + 8\pi R \gamma$$

$$\hookrightarrow R_c = \frac{2\gamma}{c_l \Delta\mu}$$

↑
critical radius for nucleation

$$\begin{aligned} \Delta G_c &= -\frac{4\pi}{3} R_c^3 c_l \Delta\mu + 4\pi R_c^2 \gamma \\ &= \frac{16\pi}{3} \frac{\gamma^3}{c_l^2 (\Delta\mu)^2} \end{aligned}$$



If we assume that the vapor behaves like an ideal gas:

$$\Delta \mu = k_B T \log(p/p_{eq})$$

p : vapor pressure

p_{eq} : eq. vapor pressure ($R \rightarrow \infty$)

For water at 300 K, $\gamma \sim 72 \text{ erg/cm}^2$, $p = 1.1 p_{eq}$

$$\hookrightarrow R_c \sim 10^{-6} \text{ cm} \sim 10^{-8} \text{ m} \sim 10 \text{ nm}$$

The nucleation barrier is normally greatly reduced by the presence of dust particles (seeds). This is called heterogeneous nucleation!