A Normal and anomalous phase behaviour

1) The three-dimensional (P,V,T) phase diagram of water is sketched in Fig. 1.

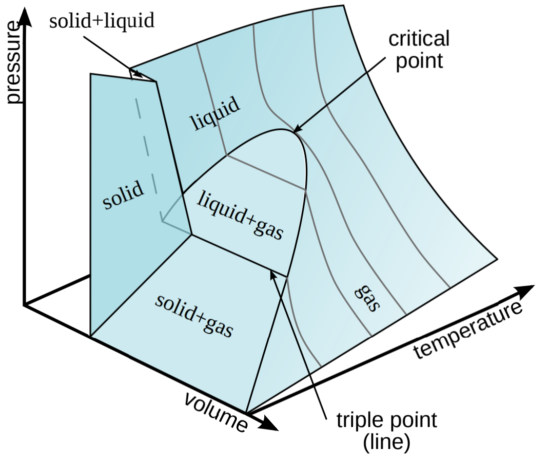


Figure 1: 3D representation of water phase behaviour in a pressure-volume-temperature diagram

2) For water, the specific volume of the solid is larger than that of the liquid, which results in a negative slope for the coexistence line in the (P,T) diagram. For a normal substance, this inequality is reversed, which results in the diagram given in Fig. 2

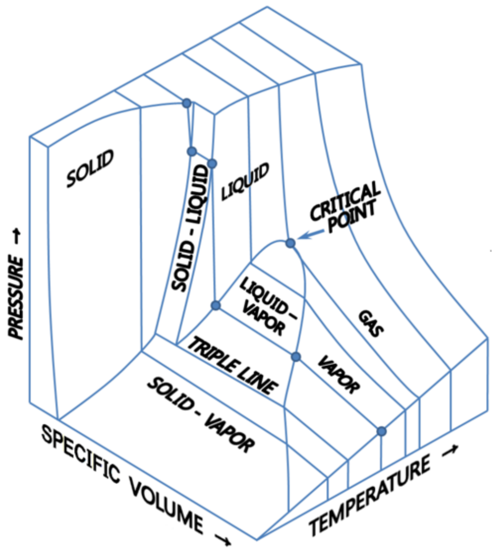


Figure 2: Case of a normal substance. Note the difference now concerning the solid-liquid coexistence region. There is a temperature window for which at a given T, the three phases may be found, depending on the pressure. The distinction between vapor and gas is not important.

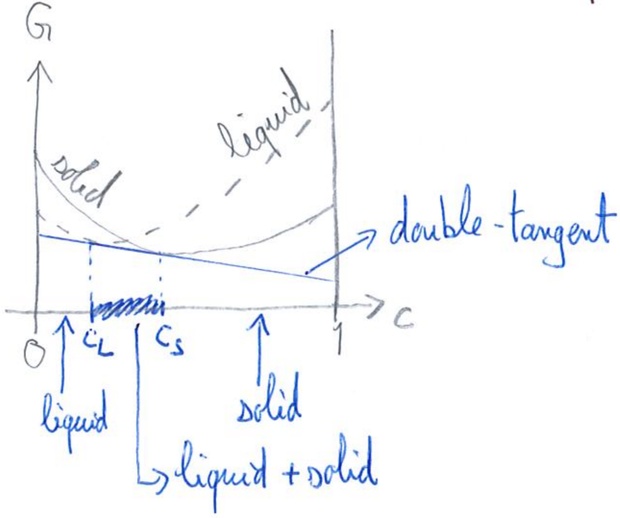
③ Free energy scenarii and binary phase diagrams

1°) For a binary mixture (2 species), the variance is $v = 2 + 2 - \varphi = 4 - \varphi$ where φ is the number of phases in coexistence. Thus,

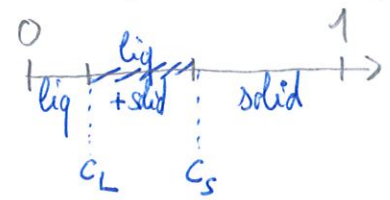
$\varphi = 1 \Rightarrow v = 3$: when T and P are given, there is still room for an extra degree of freedom $\to$ c, the molar fraction

$\varphi = 2 \Rightarrow v = 2$: when T and P are fixed, all intensive variables are specified, and c cannot be chosen freely.

2°)



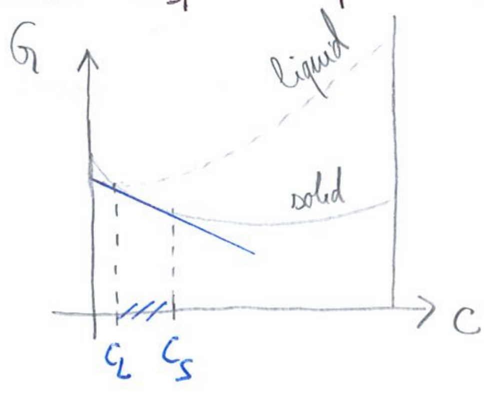
We invoke the double-tangent construction to find a region of liquid-solid phase coexistence marked as the hatched region. At this particular temperature, the phase diagram is:



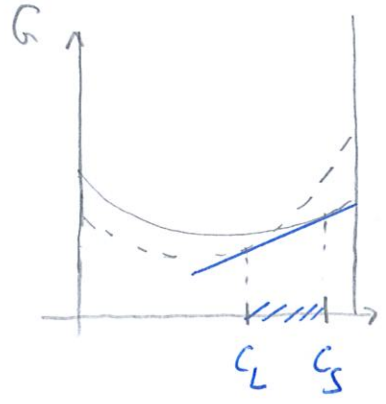
3°) For $c_L \leqslant c \leqslant c_S$, two phases coexist: the variance is 2. Here, P and T are fixed, meaning that one cannot freely chose the concentration. The system demixes in a combination of liquid at concentration c_L and solid at concentration c_S.

4°) We have to repeat the double-tangent argument at various T, from low where the solid is stable, to high where the liquid is stable.

Consider 2 special temperatures, a bit above, and a bit below T_0:

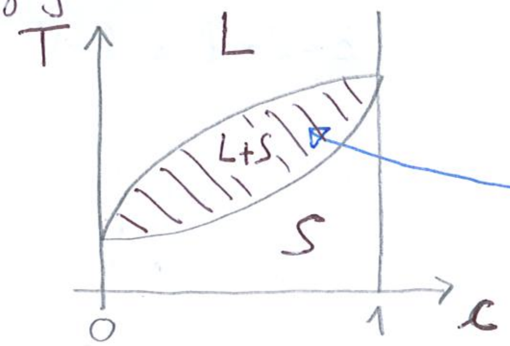


$T \underset{\approx}{<} T_0$



$T \underset{\approx}{>} T_0$

Summarizing results in a (T, c) diagram, we get

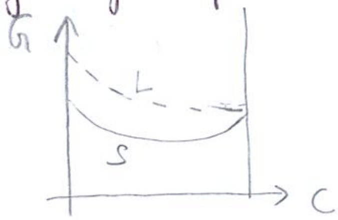


$L \equiv$ liquid

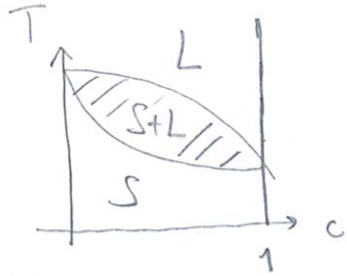
$S \equiv$ solid

//// for phase coexistence

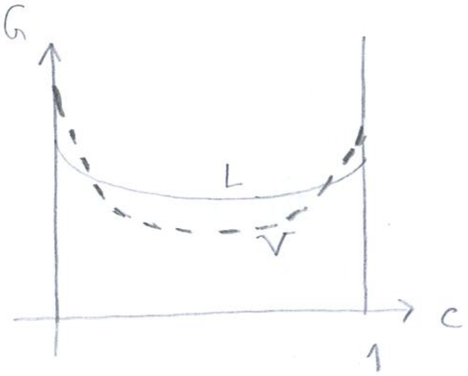
5°) Slight changes in the free energy profiles may have profound consequences on the phase behaviour. We still assume that the solid branch (resp liquid in case ⓐ) is fixed and that the liquid branch (resp. vapor in case ⓐ) is T dependent, and merely shifts up/down. For instance, with



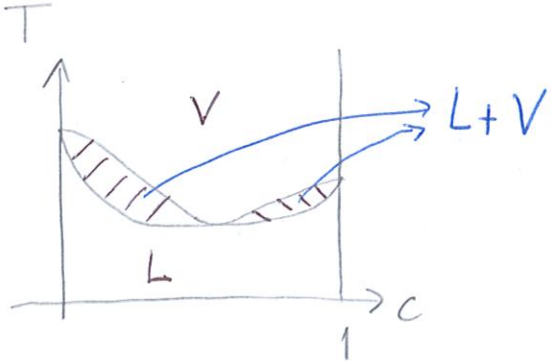
we would have gotten



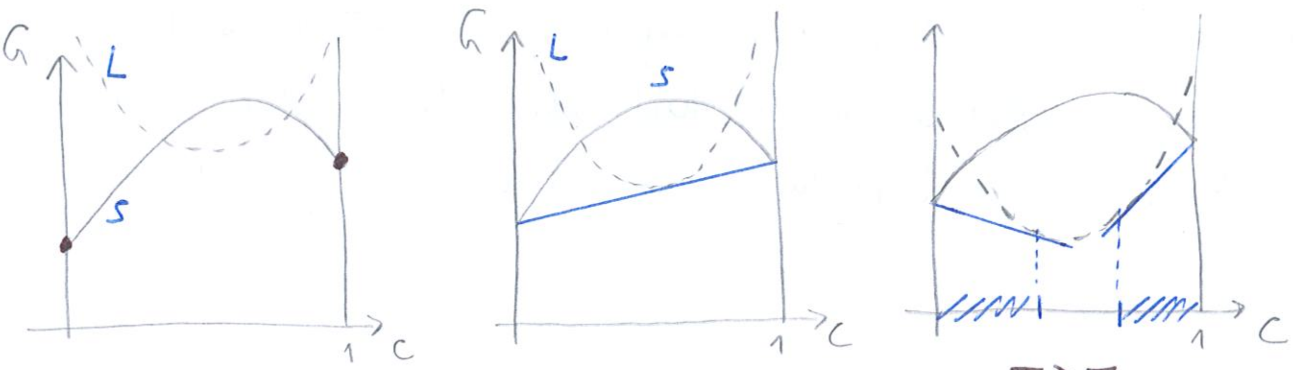
Then:



yields



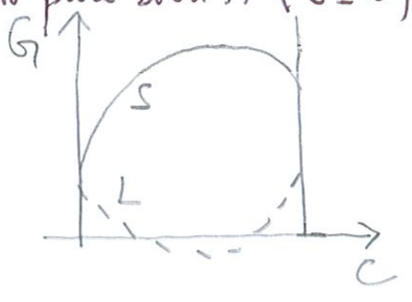
and



$T < T_E$ $\qquad$ $T = T_E$ $\qquad$ $T > T_E$

For $T < T_E$, the system demixes into pure solid A $(c = 0)$ and pure solid B $(c = 1)$.

For T high enough, we get the liquid as the stable phase



C Mean-field approximation for the Potts model

1) The coordination number is $z = 6$.

2) The way to approach this is the same as for the Ising model on the regular square lattice, where we use the trick $S_i \to S_i - m + m$ and we rewrite the Hamiltonian in terms of $(S_i - m)$, subsequently ignoring factors in $(S_i - m)(S_j - m)$. We get:

$$H_{\rm MF} = -J \sum_{\langle ij \rangle} \left(2(S_i - m) + m^2 \right) - B \sum_i S_i \tag{1}$$

We rewrite it as:

$$H_{\rm MF} = -Jzm \sum_i S_i + \frac{JNz}{2} m^2 - B \sum_i S_i \tag{2}$$

3) The partition function can be computed:

$$Z_{\rm MF} = e^{-\beta JNz \frac{m^2}{2}} \left(1 + 2\cosh(\beta(Jzm + B)) \right)^N , \tag{3}$$

from which the free energy follows

$$F = N \frac{Jzm^2}{2} - k_B T N \log \left[1 + 2\cosh(\beta(Jzm + B)) \right] . \tag{4}$$

4) The magnetization is obtained by using:

$$m = \frac{1}{\beta N} \frac{\partial \log Z_{\rm MF}}{\partial B} \tag{5}$$

which gives:

$$m = \frac{2\sinh(\beta(Jzm + B))}{1 + 2\cosh(\beta(Jzm + B))} . \tag{6}$$

If the factor 1 were absent, we would recover the usual Ising model.

5) At $B = 0$, m obeys

$$m = \frac{2\sinh(\beta(Jzm))}{1 + 2\cosh(\beta(Jzm))} , \tag{7}$$

and we note that the value $m = 0$ is always a solution of the self-consistent equation. Given the shape of the function of m on the right-hand side (linear at the origin, and saturating at large $|m|$), we get the critical temperature when the slope at the origin is unity

$$1 = \frac{2\beta_c Jz}{3} \qquad \Longrightarrow \qquad \beta_c = \frac{3}{2Jz} \quad ; \quad k_B T_c = \frac{2}{3} Jz \tag{8}$$

6) The free energy is, for $B = 0$,

$$f = \frac{Jm^2}{2} - \frac{k_B T}{z} \log \left[1 + 2\cosh(\beta Jzm) \right] \tag{9}$$

Using $T = T_c(1 + t)$ and $zJ = 3k_B T_c/2$, we have

$$f = \frac{Jm^2}{2} - \frac{2}{3} J(1 + t) \log \left[1 + 2\cosh \left(\frac{3m}{2(1 + t)} \right) \right] . \tag{10}$$

Using $\log(1+2\cosh(ax)) \sim \log(3) + \frac{a^2}{3}x^2 - \frac{a^4}{36}x^4$, we get:

$$f = \frac{Jm^2}{2} - \frac{2}{3}J(1+t)\log 3 - \frac{J}{2}\frac{m^2}{1+t} + J\frac{3\,m^4}{32(1+t)^2} \tag{11}$$

$$= -\frac{2}{3}J(1+t)\log 3 + \frac{J}{2}\,m^2\,\frac{t}{1+t} + J\frac{3\,m^4}{32(1+t)^2}. \tag{12}$$

The first term (with the $\log 3$) is immaterial, since it does not depend on m. The second tells us that the free energy changes convexity at $t = 0$, which is a restatement of the fact that $t = 0$ defines the critical temperature. For consistency, we truncate the expansion to leading order in t:

$$f = -\frac{2}{3}J(1+t)\log 3 + \frac{J}{2}\,m^2\,t + J\frac{3\,m^4}{32}. \tag{13}$$

Taking the derivative wrt m yields the equation obeyed by the spontaneous magnetization

$$0 = J\,m\,t + J\frac{3\,m^3}{8}. \tag{14}$$

The non-vanishing root is

$$m = \pm\sqrt{-8t/3} \tag{15}$$

This yields $\beta = 1/2$.

7) Following Curie-Weiss treatment, we start by studying independent spins in a field B, for which the probabilities to find a given spin in state $S = -1$, 0 or 1 are

$$p(S) = \frac{e^{\beta BS}}{e^{\beta B} + 1 + e^{-\beta B}}\,, \tag{16}$$

from which we get the magnetization per spin:

$$m = \sum_{S=-1,0,1} S\,p(S) = \frac{2\sinh(\beta B)}{1+2\cosh(\beta B)}. \tag{17}$$

The second step is to average the local field felt at a given lattice site i, thereby neglecting site to site fluctuations, as $B + zJm$, exactly as on the square lattice for Ising model. The third step is to replace B in Eq. (17) by $B + zJm$, and we recover the self-consistent relation for m.