

Should be written on a separate paper.

Electronic calculators, cell phones, and documents of all kinds are not allowed. Concise but explicative answers are expected throughout ; no bonus for verbosity. Write as neatly as possible and always specify clearly which question you are answering. No questions will be answered during the exam, for the sake of quietness and equity: if you detect what you believe to be an error or an inconsistency, explain so in your answer, and move on; you are also judged on your ability to understand the questions raised.

A Normal and anomalous phase behaviour

- 1) The three-dimensional (P,V,T) phase diagram of water is sketched in Fig. 1. Specify the meaning of the arrows ¹. Indicate the regions corresponding to the following: gas, liquid, solid, liquid+gas, solid+gas,

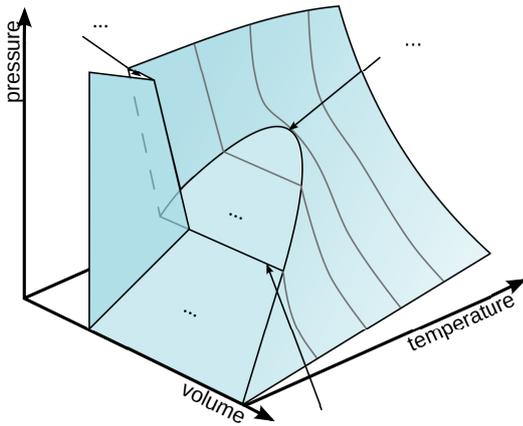


Figure 1: 3D representation of water phase behaviour in a pressure-volume-temperature diagram

- 2) In which respect is water's phase behavior anomalous? For a normal substance exhibiting solid, liquid and vapor phases, how does the (P,V,T) diagram change? Sketch the corresponding three dimensional diagram.

B Free energy scenarii and binary phase diagrams

We are interested in a binary mixture, which can exist under different phases: liquid or solid (unless otherwise stated), under full or partial miscibility. The pressure is fixed throughout.

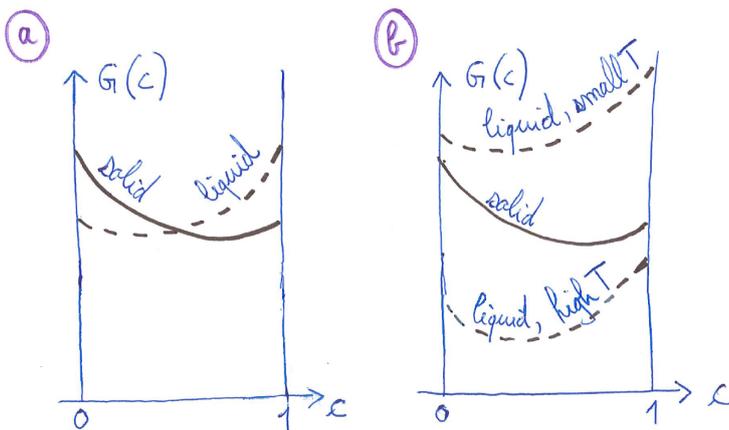


Figure 2: **a)** Solid and liquid branches of the free energy G , as a function of c , at temperature T_0 . The solid branch is shown by the continuous curve, and the dashed line is for the liquid. **b)** While the solid branch is assumed T -independent, the liquid branch depends on T and translated along the y -coordinate axis, from top to bottom, as T increases.

- 1) What do we learn from the Gibbs phase rule, which provides the so-called variance of the mixture?
- 2) At a temperature T_0 , Fig. 2a) shows the Gibbs free energy profile G as a function of c , the molar fraction of species B. Discuss the miscibility scenario, when c is increased from 0 (corresponding to pure A) to 1 (pure B).

¹ write on the figure and do not forget to hand it over at the end of the exam, after having written your name or composition number on it

- 3) Check the compatibility of this scenario with Gibbs phase rule.
- 4) We assume that as temperature T increases, the liquid branch in Fig. 2a) is shifted continuously further and further down; conversely, it is shifted upwards when T decreases, see Fig. 2-b). In addition and for the sake of simplicity, the solid branch is assumed to be fixed (T -independent). Sketch and discuss the resulting phase diagram in the T versus c variables.
- 5) Invoking arguments of the same type as above, propose candidate free energy profiles that would lead to the phase behaviour in Fig. 3: a) with a so-called azeotropic point AZ, and b) with a so-called eutectic point E. In case b), what happens when the liquid is cooled down from a high temperature, when the composition c is that of the eutectic point, c_E ? What happens if $c \neq c_E$?

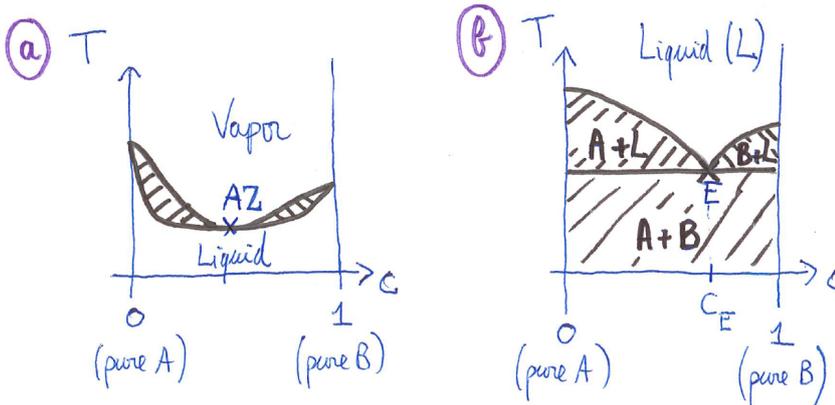
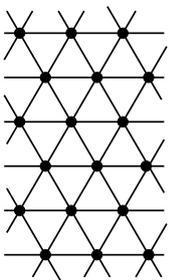


Figure 3: **a)** Phase diagram with an azeotropic point marked as AZ. The hatched region corresponds to partial immiscibility, while the regions indicated as Liquid and Vapor are for full miscibility. **b)** Phase diagram with a eutectic point marked as E. The hatched region is for partial or full immiscibility (solid A + L, solid B + L, solid A + solid B at the bottom).

C Mean-field approximation for the Potts model



We consider a variant of Ising model, the so-called Potts model, where each of the N spins can take three values: $S_i = -1, 0$ or 1 , rather than two at Ising level. The corresponding Hamiltonian reads

$$H = -J \sum_{\langle i,j \rangle} S_i S_j - B \sum_i S_i, \quad (1)$$

where the summation in the interaction term runs over nearest neighbors, on a triangular two-dimensional lattice (see the figure). Periodic boundary conditions are enforced (not important).

- 1) What is here the coordination number z (number of nearest neighbors of a given site)?
- 2) Write the mean-field Hamiltonian by using the same approach as followed in the tutorials for treating the Ising model on a regular square/cubic lattice. *Hint*: consider the mean magnetization per spin $m = \langle S_i \rangle$; rewrite each spin as a fluctuation from m ; then make the proper truncation.
- 3) Compute the free energy within this approximation.
- 4) Find the self-consistent equation for the average magnetization m .
- 5) What is the critical temperature at $B = 0$?
- 6) At $B = 0$, expand the free energy $f = F/(zN)$ with respect to $t = T/T_c - 1$ and m . Find the exponent β such that $m \sim (-t)^\beta$. *Hint*: you may need the following Taylor expansion as $x \rightarrow 0$:

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

- 7) **Bonus.** Obtain the self-consistent magnetization m from a Curie-Weiss argument (molecular field).