ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Thermodynamik
Serie 10

HS 08
Prof. G. Blatter

Aufgabe 10.1 Raising of the boiling point

Consider the balance between a diluted solution (i.e. salt in water) and the steam of the solvent - we assume the solute not to be volatile, so that it does not go into the gaseous phase. Hence the interface between the two phases acts as a semipermeable wall.

(a) Using the equlibrium condition (as in ex. 9.3), derive the law for the raising of the boiling point. Find the formula for ΔT_{boil} at fixed pressure. (c.f. script 8.2.1, pg. 84)

(b) *Le Chatelier*'s principle states: “When a thermodynamic system is perturbed, it tries to counter-act the imposed change”. Discuss its implications when one disturbs the system by increasing the salt concentration and compare to your findings in (a).

(c) Assuming the amount of salt in ice is also negligible, derive the qualitative change for the melting point. Indicate both changes in a p - T phase diagram.

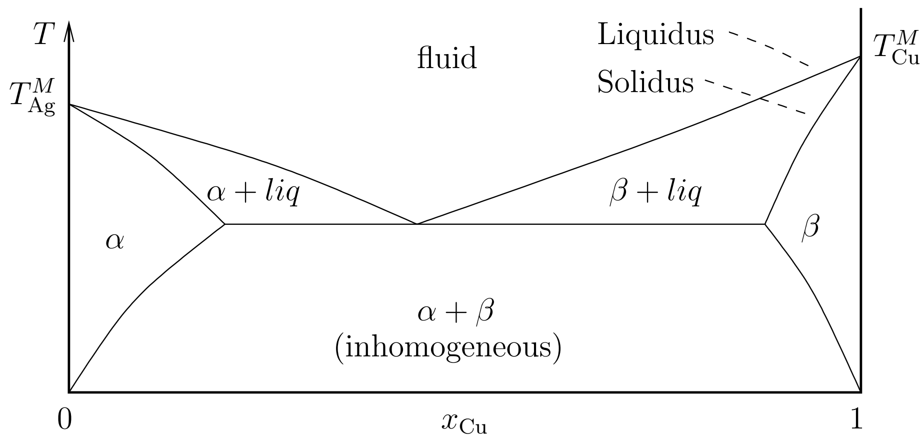
(d) How much salt would one need in order to cook an egg on Mount Everest? (Egg white requires at least $T_{\text{egg}} > 60°C$ to coagulate).

Aufgabe 10.2 Binary phase diagrams

(a) Consider two isotopes (e.g. ^3He and ^4He) which mix homogeneously in arbitrary ratios above a critical temperature T_{mix}. Show that the 3rd principle, $S(T \to 0) \to 0$, prohibits a mixed state in the limit $T \to 0$.

(b) Similarly, an arbitrary alloy of x copper and $(1-x)$ silver does not solidify in a single homogeneous phase. Define two phases, α and β, which coexist and derive the qualitative form of the T - x phase diagram at low temperatures.

(c) Discuss the above aspects for this typical phase diagram of an alloy:



Note: Most alloys have a melting range, where a solid phase coexists with a liquid of both components. The limits of this range are called solidus and liquidus.

Aufgabe 10.3 Landau theory of second-order phase transitions

In most cases, a phase transition is accompanied by a lowering ("breaking") of the symmetry of the system. The high temperature (disordered) phase has a higher symmetry than the (ordered) phase at lower temperature. In Landau theory, this aspect is taken care of by introducing an order parameter which increases (continuously) from zero as the temperature drops below T_c. As a simple example, we consider in this exercise a (Heisenberg) ferromagnet where the order parameter is the magnetization density $\vec{m}$ which becomes finite below the critical temperature.
In Landau theory, we only consider the part of the free energy which is associated with the phase transition and, since the order parameter is small around T_c, expand it in powers of $\vec{m}$. As we want to describe a real system, we require the free energy to be analytic and incorporate the underlying symmetry. In the case of a ferromagnet, the symmetry is O(3) and we find the following expression for the free energy (density):

$$f(m,T) = a(T)m^2 + \frac{b(T)}{2}m^4 \tag{1}$$

where $m = |\vec{m}|$ is the magnetization density.

(a) Above T_c we can create a finite magnetization by applying a (conjugate) magnetic field $\vec{h}$. Show that for $h = |\vec{h}| = 0$ we can find the magnetization by minimizing the free energy $f(m,T)$ with respect to m.
Hint: How can one change to the corresponding new potential?

(b) We expect m to be 0 for $T > T_c$ and finite for $T < T_c$. What conditions should we stipulate for $a(T)$ and $b(T)$ such that this behaviour is fulfilled?

(c) We now set $a(T) = a_0(T - T_c)$, $a_0 > 0$ and $b(T) = b = \text{const} > 0$.

In the vicinity of a second order phase transition, the behaviour of thermodynamic quantities can be described by so-called critical exponents α, β, γ and δ:

$$\begin{array}{llll} m(T) & \propto & (T_c - T)^\beta & (h=0 \text{ and } T < T_c), \\ c_V(T) & \propto & |T - T_c|^{-\alpha} & (h=0), \\ \chi(T) & = & \partial_h m|_{h=0} \ \propto \ |T - T_c|^{-\gamma} & (h=0), \\ m(h) & \propto & h^{1/\delta}(T = T_c). & \end{array} \tag{2}$$

Note: Critical exponents are *universal* in the sense that they only depend on few properties such as the dimension of the system, the dimension (number of components) of the order parameter and the interaction range. Models sharing the same set of critical exponents are said to be in the same *universality class*. Furthermore these critical exponents are linked by a group of scaling relations such as:

$$\begin{array}{lll} \alpha & = & 2 - \gamma - 2\beta\,, \\ \beta & = & \gamma/(\delta - 1)\,. \end{array} \tag{3}$$

For the given model (1), calculate the above quantities (2) to obtain the critical exponents α, β, γ and δ. Verify that they satisfy the scaling relations (3).