Advanced Statistical Physics, SS 2017
Sheet 9

Problem 1: **(5 points)**

Consider a system of n independent quantum mechanical harmonic oscillators of frequency ω. Recall that the energy of oscillator i will be $E_i = (m_i + \frac{1}{2})h\omega$, where h is Planck's constant, and m_i is the quantum number of the oscillator. Recall that the $m_i \geq 0$ must be integers. A microstate of the system is given by specifying all the m_i.

a) Show that the total energy of the system is

$$E = \frac{1}{2}nh\omega + Mh\omega, \tag{1}$$

where $M = m_1 + m_2 + \cdots m_n$.

b) Show that the number W_M of microstates that correspond to fixed values of n and M are

$$W_M = \frac{(M+n-1)!}{M!(n-1)!}. \tag{2}$$

c) Freely apply Boltzmann's postulate to obtain the entropy $S = k_B \log W_M$.

d) Calculate the temperature as a function of n and M, and graph the energy as a function of T.

e) Calculate the pressure and chemical potential, if these quantities are well defined.

Problem 2: **(4 points)**

Recall that the Gibbs free energy of a two component system is given by

$$G = \mu_1 N_1 + \mu_2 N_2. \tag{3}$$

Define the molar ratios $n_i := N_i/N$ where $N = N_1 + N_2$. Consider the Gibbs free energy per mole $g := G/N$ as a function of $n_1 \in (0,1)$ where (p, T, N) is fixed.

Assume that g is continuously differentiable on $(0,1)$. Further, assume that there exist $0 < n_1^{\mathrm{a}} < n_1^{\mathrm{b}} < 1$ such that the points $(n_1^{\mathrm{a}}, g(n_1^{\mathrm{a}}))$ and $(n_1^{\mathrm{b}}, g(n_1^{\mathrm{b}}))$ of the graph of g have a common tangent τ. Especially, g is not convex. (For simplicity you may assume that there is precisely one such pair of molar ratios.)

a) Show, that the formula $\dfrac{\partial g}{\partial n_1} = \mu_1 - \mu_2$ holds.

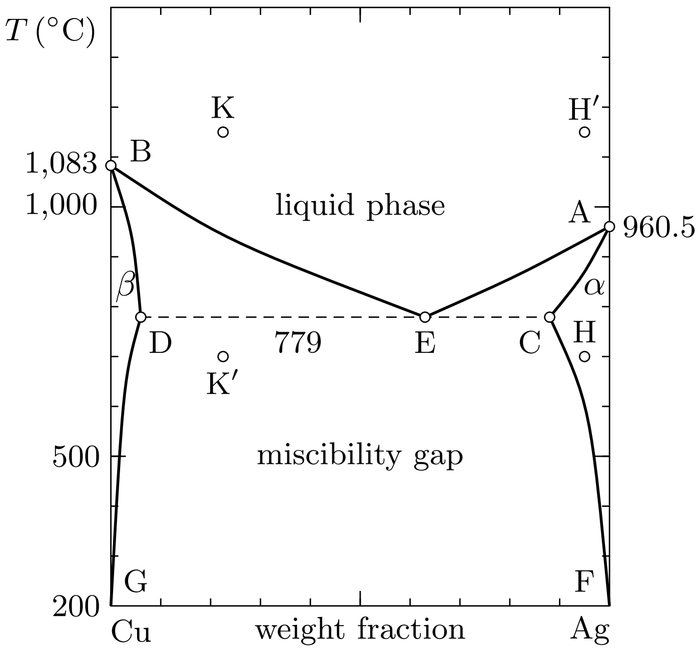
b) Give three different expressions for the slope of the tangent τ, and from this, derive $\mu_1(n_1^{\mathrm{a}}) = \mu_1(n_1^{\mathrm{b}})$ and $\mu_2(n_2^{\mathrm{a}}) = \mu_2(n_2^{\mathrm{b}})$.

c) Explain, why the system separates into two phases when $n_1^{\mathrm{a}} < n_1 < n_1^{\mathrm{b}}$ and describe the states of these phases.

d) Calculate the ratios of the phases and the Gibbs free energy of the resulting system explicitly for molar ratios $n_1 \in [n_1^{\mathrm{a}}, n_2^{\mathrm{b}}]$.

Problem 3: **(4 points)**

The following figure shows the phase diagram for the Cu-Ag system.



In the range of values given, this system has precisely three different phases. One liquid phase and two different solid solution phases. The β-solid solution phase is in the area BDG to the left and the α-solid solution phase is in the area ACF to the right. The point E in the diagram is the eutectic point at which the liquid and both solid solution phases coexist.

a) Describe the behaviour of the system, when it is quasistatically cooled down from state K to state K'.

b) Do the same, for quasistatic heating from state H to state H'

c) Estimate the ratios of possibly coexisting phases at $T = 900$ °C and 775 °C for the processes in (a) and (b).

d) Do the ratios of α- and β-solid solution phases at the triple point depend on the ratios of solid and liquid phases?

Deliver your hand-written solutions at the beginning of the lecture on Friday, June 23rd.