Statistical physics I

Spring 2012

Problem set 1

Please return the solved problems in the metal box ("Statistinen fysiikka I") located at the 2nd floor A-wing lobby by **16 o'clock Wednesday 25th of January**. The problems will be given back and discussed (in Finnish!) during the exercise session on Friday 27th of January at 12:15 in D112.

Let's recapitulate some thermodynamics.

1. Consider a closed system in a bath. The total entropy S_{tot} is a sum of the bath's (S_0) and system's (S) entropies ($S_{\text{tot}} = S_0 + S$). The second law of thermodynamics says that all the spontaneous processes tend to evolve towards the thermodynamical equilibrium, the state of maximum entropy. In other words, for these processes it holds: $dS_{\text{tot}} \geq 0$.

   a) Assume that the bath's temperature is $T_0 \neq 0$ K. Derive an expression for the differential of a general thermodynamical potential, $d\varphi$, which reaches its *minimum* in thermodynamical equilibrium.

   b) Assume such a coupling between the bath and the system that the system's entropy, volume and particle number stay constant. Find φ. What if the system is in heat and pressure bath?

   c) Thermodynamical potentials are also called free energies. Explain why.

2. The Maxwell relations are useful tools in thermodynamics. With the help of common thermodynamical potentials derive the following relations:

$$\left(\frac{\partial p}{\partial N_i}\right)_{S,V,N_{j\neq i}} = -\left(\frac{\partial \mu_i}{\partial V}\right)_{S,N_i}, \qquad \left(\frac{\partial V}{\partial N_i}\right)_{S,p,N_{j\neq i}} = \left(\frac{\partial \mu_i}{\partial p}\right)_{S,N_i},$$

$$\left(\frac{\partial p}{\partial N_i}\right)_{T,V,N_{j\neq i}} = -\left(\frac{\partial \mu_i}{\partial V}\right)_{T,N_i}, \qquad \left(\frac{\partial p}{\partial \mu_i}\right)_{T,V} = \left(\frac{\partial N_i}{\partial V}\right)_{T,\mu_i}.$$

3. The thermal expansion coefficient α, compressibility κ, isobaric$_p$ and isochoric$_V$ heat capacity are defined as follows:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \qquad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T,$$

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p, \qquad C_V = T\left(\frac{\partial S}{\partial T}\right)_V.$$

a) Show that

$$\left(\frac{\partial \alpha}{\partial p}\right)_T = -\left(\frac{\partial \kappa}{\partial T}\right)_p.$$

b) Show that

$$\frac{\alpha}{\kappa} = \left(\frac{\partial p}{\partial T}\right)_V.$$

c) Further, show that

$$C_p - C_V = \frac{TV\alpha^2}{\kappa}.$$

4. The Joule-Thomson coefficient

$$\alpha_{\mathrm{JT}} \equiv \left(\frac{\partial T}{\partial p}\right)_H$$

tells how far the gas is from its ideal state (here H is enthalpy). Show that

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{T\left(\frac{\partial V}{\partial T}\right)_p - V}{C_p},$$

here C_p is the isobaric heat capacity. For the real-world gases the Joule-Thomson coefficient is negative in high temperatures and positive in lower temperatures. Find α_{JT} for gases obeying *the Dieterici's equation of state*

$$pe^{aN/VT}(V - bN) = NT$$

and further find the inversion temperature T_{inv}, where $\alpha_{\mathrm{JT}}(T_{\mathrm{inv}}) = 0$ (keep the particle number N constant and leave the heat capacity as C_p). What is α_{JT} for ideal gas?