Sheet 08: Phase transitions

Discussion: Thursday 13.07.23

Exercise 1 Dieterici gas

Besides the van der Waals gas, there are other real gases, such as the Dieterici gas, which is described by the following equation of state: $P = \frac{k_B T}{v-b} \exp\left(-\frac{a}{v k_B T}\right)$, where a and b are positive constants. Determine the critical values v_c, T_c and P_c!

Exercise 2 Ehrenfest equation

In the lecture you have derived the Clausius-Clapeyron equation for first order phase transition. In the case of second-order phase transition, no heat flows (i.e., the entropy is continuous), and the volume remains constant. Derive the counterpart for this, the Ehrenfest equations (in terms of specific quantities) for the response functions:

$$\Delta c_P = T \frac{\mathrm{d}P}{\mathrm{d}T} \Delta \left(\left.\frac{\partial v}{\partial T}\right|_P \right), \tag{1}$$

$$\Delta \left(\left.\frac{\partial v}{\partial T}\right|_P \right) = -\frac{\mathrm{d}P}{\mathrm{d}T} \Delta \left(\left.\frac{\partial v}{\partial P}\right|_T \right) \tag{2}$$

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{1}{v\,T} \frac{\Delta c_P}{\Delta \alpha} = \frac{\Delta \alpha}{\Delta \chi}, \tag{3}$$

where $\alpha = \frac{1}{v} \left.\frac{\partial v}{\partial T}\right|_P$, $\chi = -\frac{1}{v} \left.\frac{\partial v}{\partial P}\right|_T$ and $\Delta X = X_2 - X_1$ for any quantity X in the two phases.

Exercise 3 Triple points

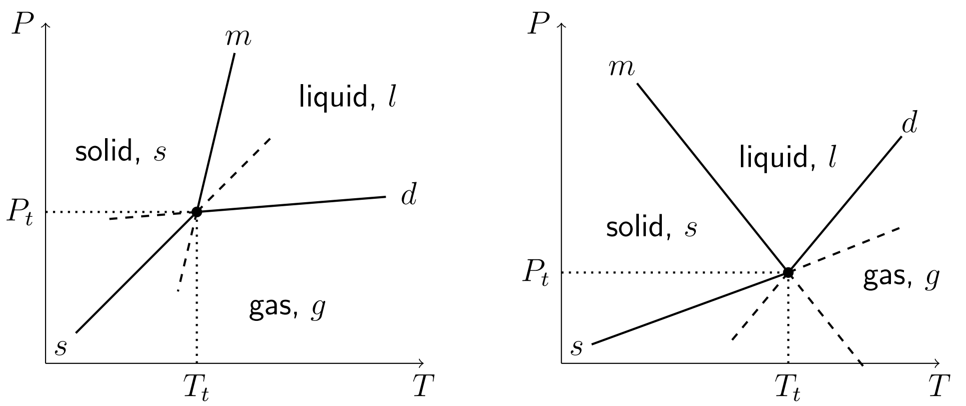
At the triple point $t = (P_t, T_t)$ in the (P, T) diagram of a one-component fluid, the sublimation curve with slope $(\mathrm{d}P_s/\,\mathrm{d}T)_t \equiv \dot{P}_s$, the melting curve (slope $\dot{P}_m$) and the vapor pressure curve (slope $\dot{P}_d$) meet.

(a) Derive the Clausius-Clapeyron equation.

(b) Find a relationship between $\dot{P}_s$, $\dot{P}_m$ and $\dot{P}_d$ as a function of molar volumes.

For the entropies per mole let $s_s < s_l < s_g$. For the volumes per mole let $v_g \gg v_s, v_l$ hold.

(c) Are the two outlined for all compatible with these assumptions? Explain your answer.



(a) Phase diagram **A** (b) Phase diagram **B**

Figure 1: Solid lines symbolize phase transition. Dashed and dotted lines are for illustrative purposes only.