

## Assignment 3

**3.1** A spherical liquid drop floats in equilibrium with its saturated vapor. The drop has radius  $r$  and surface tension  $\sigma$ , assumed constant.

(a) Find the pressure difference between the liquid inside the drop and the saturated vapor. Assume that the thickness of the surface region is negligible.

(b) Show that the saturated vapor pressure of the droplet is given by

$$P_r = P_\infty \exp\left(\frac{2v_\ell\sigma}{rk_B T}\right)$$

where  $P_\infty$  is the vapor pressure of the bulk liquid and  $v_\ell$  is the specific volume (volume per molecule) of the liquid.

(c) For a given vapor pressure  $P_r$ , are droplets with radius  $r' < r$  stable?

**3.2** A pot of soup boils at 103°C at the bottom of a hill and boils at 98°C at the top. If the hill is 1000 ft high, what is the latent heat of vaporization of the soup?

**3.3** The Dieterici equation of state,

$$P \exp\left(\frac{Na}{Vk_B T}\right)(V - b) = Nk_B T$$

is another way to describe an interacting gas in terms of two constants,  $a$  and  $b$ . Find the critical temperature, pressure, and volume for a Dieterici gas. Express the equation of state in terms of the reduced variables  $\bar{T} = T/T_c$ ,  $\bar{P} = P/P_c$  and  $\bar{v} = v/v_c$ , and show that in these variables, all Dieterici gases are equivalent.

**3.4** As discussed in class, a binary solution of two species  $A$  and  $B$  has a Gibbs free energy per particle of

$$g = x_A \mu_A^0 + x_B \mu_B^0 + k_B T x_A \log x_A + k_B T x_B \log x_B + \lambda x_A x_B$$

where  $x_i = N_i/(N_A + N_B)$  are the fractions of each species, and  $\lambda > 0$  characterizes a repulsive interaction between them.

(a) Express  $g$  in terms of  $t = T/T_c$  and  $\Delta = (\mu_A^0 - \mu_B^0)/(k_B T_c)$ , where the critical temperature is  $T_c = \lambda/(2k_B)$ . Plot  $g(x_A)$  for the case  $t = 0.8$  and  $\Delta = 0.05$ . Since  $T < T_c$ , the solution will separate into two phases: use your graph to estimate the fraction of species  $A$  in each phase.

(b) Denote the fraction of species  $A$  in each phase as  $x_I$  and  $x_{II}$ , and the chemical potential of each phase as  $\mu_I$  and  $\mu_{II}$ . We know that  $\mu_I = \mu_{II}$  in equilibrium. Show further that

$$g(x_I) - x_I \mu_I = g(x_{II}) - x_{II} \mu_{II},$$

(Recall that  $\mu(x) = \partial g / \partial x$ .) This provides two equations that specify the two unknowns  $x_I$  and  $x_{II}$ .

(c) Show that the solutions  $x_I$  and  $x_{II}$  are independent of  $\Delta$ , and use this to argue that  $x_{II} = 1 - x_I$ . That is to say, the fraction of  $A$  molecules in phase I is equal to the fraction of  $B$  molecules in phase II, regardless of the total number of  $A$  and  $B$  molecules in the system.

(d) Using the result of (c), show that the solutions  $x_I$  and  $x_{II}$  must each satisfy

$$\frac{t}{2} \log\left(\frac{x}{1-x}\right) = 2x - 1.$$

Solve this equation graphically or numerically for the conditions of part (a). You should obtain the same answers you got there, but considerably better precision should be possible.