ChemE 240, Homework 4
Assigned: February 8, 2007
Due: February 15, 2007

Topics: Equilibrium and stability criteria, Clausius-Clapeyron equation, the VDW equation of state, the Maxwell construction method.

1) Derive the stability criterion for:
\[
\left( \frac{\partial \gamma}{\partial \sigma} \right)_{T,P,n}
\]
where \( \gamma \) is the surface tension and \( \sigma \) is the surface area.

2) Consider two phases of a 1-component system. Let’s call them \( \alpha \) and \( \beta \). They have the following Helmholtz free energies, where \( n, \varepsilon, \) and \( \nu_o \) are positive constants.

\[
A_\alpha = \frac{n \varepsilon}{2} b(T) \left( \frac{\nu_o}{\nu_\alpha} \right) \quad A_\beta = \frac{n \varepsilon}{3} c(T) \left( \frac{\nu_o}{\nu_\beta} \right)^2
\]

At coexistence, the following is true for the molar volumes of each phase:

\[
\nu_\alpha = \frac{9}{16} \left( \frac{c}{b} \right) \nu_o \quad \nu_\beta = \frac{3}{4} \left( \frac{c}{b} \right) \nu_o
\]

Now, let’s make a specific choice for \( b(T) \) and \( c(T) \), where \( \theta \) is also positive.

\[
b(T) = 2 - \left( \frac{T}{\theta} \right)^2 \quad c(T) = 2 - \left( \frac{T}{\theta} \right)^3
\]

a) Calculate the latent heat, \( \Delta H_{\alpha \beta} = T(S_\beta - S_\alpha) \) for the transition from phase \( \alpha \) to phase \( \beta \). Express your result in terms of the ratio \( b/c \) and other system properties.

b) Sketch the curve along which phases \( \alpha \) and \( \beta \) coexist in the plane of pressure and temperature. Focus on the behavior near \( T = \theta \). Also, note that \( b/c \approx 1 \) for \( T \) near \( \theta \). Describe the phase transition(s) that would occur as temperature is increased at constant pressure.

3) Consider the van der Waals equation of state:

\[
(p + \frac{a}{\nu^2})(\nu - b) = RT
\]

where \( \nu \) is the molar volume of the gas and \( a \) and \( b \) are constants that depend on the nature of the gas.
a) Explain how you would find the values of the pressure, temperature and molar volume at the critical point (P\(_c\), T\(_c\) and V\(_c\) respectively) in terms of the constants \(a\) and \(b\). You don’t need to do the math, just show me your method.

b) Using the Maxwell Construction method discussed in class determine the molar volumes of the equilibrium phases of oxygen at \(T = T_c/1.05\) and \(T = T_c/1.15\). If possible construct the binodal curve for oxygen on a P-v phase diagram. Note that for oxygen \(a = 1.378 \text{ atm-L}^2\text{ mol}^{-2}\) and \(b = 0.03183 \text{ L mol}^{-1}\). Also, for oxygen \(P_c=50.37\ \text{atm},\ T_c=156.3\ \text{K, and } v_c=0.0955\ \text{L/mol}\

4) Do the experiment described in Exercise 2.18 in Chandler and then write out the Gibbs adsorption isotherm for that system and describe mathematically what is occurring. Show how an experimental observation can be used to demonstrate what is occurring at the interface.

5) The first programming assignment involves exploring random number generators and arrays using Matlab. By the end of this assignment you should be able to plot variables and write short M-files. Here’s the assignment:

a) Generate a sequence of N random numbers uniformly distributed on the interval (0,1).

b) Calculate their mean and standard deviation. How do these change as N is varied? Written comments are fine here (I don’t need to see your code).

c) Compute the following function, starting at \(m=0\), where the brackets indicate average quantities: \(g(m) = \langle x_n x_{n+m} \rangle\). What do you expect this result to be? Is it possible to calculate the result by hand? How do the simulated results compare? Make a plot of \(g(m)\) and comment on it. Print out your code and a plot of \(g(m)\) to give to me.