Homework Assignment Number Nine

Problem 1.
Consider the Peng-Robinson Equation of state as given below. The critical temperature and pressure of oxygen are also given below. Each root of this equation is a molar volume. Find all of the roots of the Peng-Robinson equation for oxygen at the temperatures given below and for a pressure of 1.0 atmosphere.

(a) T = 98.0 K
(b) T = 298.0 K

(For those of you who have not had thermodynamics, there can only be one phase above the critical temperature.)

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)}$$

where, $R = 8.314$ J/mol/K, and $a(T) = 0.45724\frac{R^2{T_c}^2}{P_c}\alpha(T)$, $b = 0.07780\frac{RT_c}{P_c}$, $\alpha(T) = \left[1+\kappa\left(1-\sqrt{\frac{T}{T_c}}\right)\right]^2$ where, for the oxygen molecule $\kappa = 0.4069$, $T_c = 154.6$ K, and $P_c = 5.046 \cdot 10^6$ Pa.

Problem 2.
Consider the van der Waals equation of state. Vapor-liquid equilibrium at a given temperature, T, occurs at a specific pressure, the vapor pressure, p_{vap}. Therefore, we can consider the vapor pressure our unknown. However, you can't calculate the vapor pressure without knowing the molar volumes of the vapor, V_{vap}, and liquid, V_{liq}, phases. Therefore, we have three unknowns: p_{vap}, V_{vap} and V_{liq}. Solving a system of three equations and three unknowns is much harder than solving a system of equations with one equation and one unknown. Therefore, a useful trick in this problem is to recognize that the van der Waal's equation of state is a cubic equation of state and the roots of a cubic equation of state are easily obtained using the Matlab "roots" function. Therefore, we can pose the solution of the vapor-liquid equilibrium problem of the van der Waals fluid as a single equation with a single equation, in which we guess the vapor pressure, use the roots command to solve for the V_{vap} and V_{liq}. and substitute them into the equation stating that the chemical potentials are equal.

For your reference, the pressure of the van der Waal's equation of state is

$$p = \frac{RT}{V-b} - \frac{a}{V^2}$$

This is a cubic equation of state and can also be written as

$$pV^3 - (pb+RT)V^2 + aV - ab = 0$$

The chemical potential for a van der Waals gas is

$$\mu = -RT\left[ln\left(\frac{V-b}{\Lambda^3}\right) - \frac{b}{V-b} + \frac{2a}{VRT}\right]$$

This expression for the chemical potential of a van der Waals gas introduces a new constant, the thermal de Broglie wavelength, Λ, but we don't need it because it drops out when we equate chemical potentials.

$$\begin{aligned}\mu_{liq} - \mu_{vap} &= -RT\left[ln\left(\frac{V_{liq}-b}{\Lambda^3}\right) - \frac{b}{V_{liq}-b} + \frac{2a}{V_{liq}RT}\right] \\ &\quad + RT\left[ln\left(\frac{V_{vap}-b}{\Lambda^3}\right) - \frac{b}{V_{vap}-b} + \frac{2a}{V_{vap}RT}\right] \\ &= -RT\left[ln\left(V_{liq}-b\right) - \frac{b}{V_{liq}-b} + \frac{2a}{V_{liq}RT}\right] + RT\left[ln\left(V_{vap}-b\right) - \frac{b}{V_{vap}-b} + \frac{2a}{V_{vap}RT}\right]\end{aligned}$$

So, in order to solve this problem as a single nonlinear algebraic equation with a single variable, p_{vap}, we have an equation,

$$f(p_{vap}) = \mu_{liq} - \mu_{vap} = 0$$

where we solve for the molar volumes each iteration.

Find the vapor pressure of Argon at T=77 K. The van der Waals constants for argon are a=0.1381 m^6/mol^2 and b=3.184x10^{-5} m^3/mol. The gas constant is R=8.314 J/mol/K. Also report the liquid and vapor molar volumes.