Homework Assignment Number Nine Solutions

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 $a(T) = 0.45724\frac{R^2T_c^{\ 2}}{P_c}\alpha(T)$, $b = 0.07780\frac{RT_c}{P_c}$,

$\alpha(T) = \left[1+\kappa\left(1-\sqrt{\frac{T}{T_c}}\right)\right]^2$ where, for the oxygen molecule $\kappa = 0.4069$, $T_c = 154.6$ K, and $P_c = 5.046 \cdot 10^6$ Pa.

Solution:

Using the Newton-Raphson method with numerical derivatives as implemented in the code, nrnd1.m, we input the function,

```
function f = funkeval(x)
V = x;
T = 98; % K
p = 101325; % Pa
R = 8.314; % J/mol/K
Tc = 154.6; % K
pc = 5.046e+6; % Pa
kappa = 0.4069;
alpha = (1 + kappa*(1 - sqrt(T/Tc)))^2;
b = 0.07780*R*Tc/pc;
a = 0.45724*R^2*Tc^2/pc*alpha;
f = R*T/(V-b) - a/(V*(V+b) + b*(V-b)) - p;
```

(a) T = 98.0 K

This temperature is below the critical temperature. We should find three roots.

The ideal gas should give a good estimate of the vapor root

```
T = 98; % K
p = 101325; % Pa
R = 8.314; % J/mol/K
V = R*T/p

V =   0.008041174438687
```

We now run the Newton Raphson with Numerical Derivatives code for 1 unknown (nrnd1) with that initial guess.

```
>>  [x0,err] = nrnd1(0.008)
icount = 1 xold = 8.000000e-03 f = -1.955300e+03 df = -1.211452e+07 xnew = 7.838599e-03  err = 1.000000e+02
icount = 2 xold = 7.838599e-03 f = 3.903320e+01 df = -1.260542e+07 xnew = 7.841695e-03  err = 3.948818e-04
icount = 3 xold = 7.841695e-03 f = 1.871688e-02 df = -1.259572e+07 xnew = 7.841697e-03  err = 1.894962e-07

x0 =   0.007841696626165

err =     1.894961977606645e-07
```

Therefore, the vapor root is 0.00784 moles/m^3.

Next, we find the liquid root, which is a little larger, say 10% larger, than the b parameter. First we calculate b.

```
>> R = 8.314; % J/mol/K
Tc = 154.6; % K
pc = 5.046e+6; % Pa
b = 0.07780*R*Tc/pc

b =    1.981763660721363e-05
```

Then we run nrnd1 with a guess 10% larger than b.

```
>>  [x0,err] = nrnd1(1.1*1.98e-05)

icount = 1 xold = 2.178000e-05 f = 2.292908e+08 df = -1.978558e+14 xnew = 2.293888e-05  err = 1.000000e+02
icount = 2 xold = 2.293888e-05 f = 9.255337e+07 df = -7.027407e+13 xnew = 2.425591e-05  err = 5.429746e-02
icount = 3 xold = 2.425591e-05 f = 3.173420e+07 df = -2.992303e+13 xnew = 2.531644e-05  err = 4.189086e-02
icount = 4 xold = 2.531644e-05 f = 7.798334e+06 df = -1.688450e+13 xnew = 2.577830e-05  err = 1.791675e-02
icount = 5 xold = 2.577830e-05 f = 8.614611e+05 df = -1.340424e+13 xnew = 2.584257e-05  err = 2.486897e-03
icount = 6 xold = 2.584257e-05 f = 1.599850e+04 df = -1.298885e+13 xnew = 2.584380e-05  err = 4.765980e-05
icount = 7 xold = 2.584380e-05 f = 5.309695e+01 df = -1.298103e+13 xnew = 2.584381e-05  err = 1.582719e-07

x0 =    2.584380714366121e-05

err =    1.582718742543172e-07
```

Therefore, the liquid root is 2.58x10^{-5} moles/m^3.

Next we find the intermediate root. This root must be between the liquid and vapor root. We can try 10*b.

```
>>  [x0,err] = nrnd1(10*1.98e-05)

icount = 1 xold = 1.980000e-04 f = 7.086039e+05 df = 9.471210e+09 xnew = 1.231834e-04  err = 1.000000e+02
icount = 2 xold = 1.231834e-04 f = -1.147320e+06 df = 5.361335e+10 xnew = 1.445833e-04  err = 1.480109e-01
icount = 3 xold = 1.445833e-04 f = -2.611509e+05 df = 3.149117e+10 xnew = 1.528761e-04  err = 5.424543e-02
icount = 4 xold = 1.528761e-04 f = -2.408423e+04 df = 2.590168e+10 xnew = 1.538059e-04  err = 6.045494e-03
icount = 5 xold = 1.538059e-04 f = -2.641220e+02 df = 2.534796e+10 xnew = 1.538164e-04  err = 6.774216e-05
icount = 6 xold = 1.538164e-04 f = -9.473805e-02 df = 2.534183e+10 xnew = 1.538164e-04  err = 2.430434e-08

x0 =   1.538163686174564e-04

err =     2.430434345736832e-08
```

Therefore, the intermediate root is 1.54x10^{-4} moles/m^3.

(b) T = 298.0 K

This temperature is above the critical temperature. We should find one root.

First, I change the input function in nrnd1.m. The only change is a change in temperature.

```
function f = funkeval(x)
V = x;
T = 298; % K
p = 101325; % Pa
R = 8.314; % J/mol/K
Tc = 154.6; % K
pc = 5.046e+6; % Pa
kappa = 0.4069;
```

```
alpha = (1 + kappa*(1 - sqrt(T/Tc)))^2;
b = 0.07780*R*Tc/pc;
a = 0.45724*R^2*Tc^2/pc*alpha;
f = R*T/(V-b) - a/(V*(V+b) + b*(V-b)) - p;
```

The ideal gas should give a good estimate of the root.

```
>> T = 298; % K
p = 101325; % Pa
R = 8.314; % J/mol/K
V = R*T/p

V =   0.024451734517641

>> [x0,err] = nrnd1(0.024)
icount = 1 xold = 2.400000e-02 f = 1.808531e+03 df = -4.293565e+06 xnew = 2.442122e-02  err = 1.000000e+02
icount = 2 xold = 2.442122e-02 f = 3.134197e+01 df = -4.146867e+06 xnew = 2.442878e-02  err = 3.093887e-04
icount = 3 xold = 2.442878e-02 f = 1.281518e-02 df = -4.144303e+06 xnew = 2.442878e-02  err = 1.265819e-07

x0 =   0.024428780172505

err =     1.265818784914305e-07
```

Therefore, the root is 0.0244 moles/m^3.

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.

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

$$= -RT\left[\ln\left(V_{liq}-b\right) - \frac{b}{V_{liq}-b} + \frac{2a}{V_{liq}RT}\right] + RT\left[\ln\left(V_{vap}-b\right) - \frac{b}{V_{vap}-b} + \frac{2a}{V_{vap}RT}\right]$$

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

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

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=3.184×10^{-5} m^3/mol. The gas constant is R=8.314 J/mol/K. Also report the liquid and vapor molar volumes.

Solution:

First we modify the input function in nrnd1.m

```
function f = funkeval(x)
p = x;
T = 77; % K
R = 8.314; % J/mol/K
a = 0.1381;
b = 3.184e-5;
Vvec = roots([p,-(p*b+R*T),a,-a*b]);
Vvap = max(Vvec);
Vliq = min(Vvec);
muliq = R*T*(log(Vliq-b) - b/(Vliq-b) + 2*a/(Vliq*R*T));
muvap = R*T*(log(Vvap-b) - b/(Vvap-b) + 2*a/(Vvap*R*T));
f = muliq - muvap;
```

Next we guess that the vapor pressure is 10 atm (1013250 Pa).

```
>> [x0,err] = nrnd1(1013250)
icount = 1 xold = 1.013250e+06 f = 1.031053e+03 df = 2.737563e-04 xnew = -2.158245e+06  err = 1.000000e+02
...
icount = 100 xold = 1.808793e+07 f = 3.215774e+03 df = -6.053046e-05 xnew = 1.808841e+07  err = 1.650221e+00
icount = 101 xold = 1.808841e+07 f = 3.215771e+03 df = -6.052910e-05 xnew = 1.808742e+07  err = 1.650262e+00
Sorry.  You did not converge in 100 iterations.
The final value of x was 1.808742e+07

x0 =      1.808741850893457e+07 - 2.641805411122832e+07i

err =   1.650261686195342
```

Well, 10 atm was a bad guess and did not converge. Let’s try a new guess of 1 atm (101325 Pa).

```
>> [x0,err] = nrnd1(101325)
icount = 1 xold = 1.013250e+05 f = -1.836244e+02 df = 6.089856e-03 xnew = 1.314775e+05  err = 1.000000e+02
icount = 2 xold = 1.314775e+05 f = -2.376403e+01 df = 4.639125e-03 xnew = 1.366000e+05  err = 3.750018e-02
icount = 3 xold = 1.366000e+05 f = -4.744139e-01 df = 4.456224e-03 xnew = 1.367065e+05  err = 7.787557e-04
icount = 4 xold = 1.367065e+05 f = -1.946510e-04 df = 4.452568e-03 xnew = 1.367065e+05  err = 3.197840e-07

x0 =     1.367065379805641e+05

err = 3.197840381851619e-07
```

Well, 1 atm was a good guess and converged. The vapor pressure of vdW Argon at 77 K is 1.367×10^5 Pa.

The corresponding liquid and vapor molar volumes are

```
>> p = x0

p =     1.367065379805641e+05

>> T = 77; % K
R = 8.314; % J/mol/K
a = 0.1381;
b = 3.184e-5;
Vvec = roots([p,-(p*b+R*T),a,-a*b]);
Vvap = max(Vvec)
Vliq = min(Vvec)

Vvap =   0.004491379329435

Vliq =     3.881286647807421e-05
```

Therefore, the vapor root is 0.00449 moles/m^3 and the liquid root is 3.88x10-5 moles/m^3.