

PHY306: Homework#8 Solutions, Spring 10

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1 Problem 2.37(5pts)

The number of B molecules is xN . When the partition is removed, these molecules expand to fill a volume that is greater by a factor of $1/x$, so their entropy increases by

$$\Delta S_B = (xN)k \ln \frac{1}{x} = -Nkx \ln x$$

According to the Sackur-Tetrode equation. Similarly, the number of A molecules is $(1-x)N$ and these expand in volume by a factor of $1/(1-x)$, so

$$\Delta S_A = [(1-x)N]k \ln \frac{1}{1-x} = -Nk(1-x) \ln(1-x)$$

The total entropy increase upon mixing is simply the sum,

$$\Delta S_{mixing} = \Delta S_A + \Delta S_B = -Nk[x \ln x + (1-x) \ln(1-x)].$$

When $x=1/2$, this expression reduces to

$$\Delta S_{mixing} = -Nk \left[\frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2} \right] = -Nk \ln \frac{1}{2} = Nk \ln 2.$$

Since this N is the total number of molecules, which is called $2N$ in equation 2.54, the results are in agreement.

2 Problem 2.38(5pts)

In the unmixed state, this system could have quite a bit of entropy due to molecular energies and (for fluids) configurations. When we allow the system to mix, assuming that the mixture is ideal, the only change is that molecules of different types can now switch places with each other at random (with no inherent tendency to prefer like or unlike neighbors). Therefore, to compute the mixing entropy, we can ignore the initial entropy and pretend that the molecules are initially frozen in place. Upon mixing, molecules randomly switch places with each other but still occupy the same collection of N fixed sites. The increase in multiplicity due to mixing, therefore, is the number of ways of assuming the two species of molecules to the N sites, that is, the number of ways of choosing N_A of the sites to be occupied by molecules of type A:

$$\Omega_{mixing} = \binom{N}{N_A}.$$

The entropy of mixing is then k times the natural log of this expression:

$$\Delta S_{mixing} = k \ln \binom{N}{N_A} = k \ln \left(\frac{N!}{N_A! N_B!} \right).$$

Assuming that both N_A and N_B are large, we can approximate the factorials using Stirling's approximation:

$$\Delta S_{mixing} \approx k [N \ln N - N - N_A \ln N_A + N_A - N_B \ln N_B + N_B] = k [N \ln N - N_A \ln N_A - N_B \ln N_B].$$

Now substitute $N_A = (1-x)N$ and $N_B = xN$:

$$\Delta S_{mixing} = k [N \ln N - (1-x)N \ln [(1-x)N] - xN \ln [xN]] = Nk [\ln N - (1-x) \ln(1-x) - (1-x) \ln N - x \ln x - x \ln N].$$

The $\ln N$ terms now cancel, leaving us with the expression:

$$\Delta S_{mixing} = -Nk [x \ln x + (1-x) \ln(1-x)].$$

3 Problem 5.48(5pts)

From the van der Waals equation (5.52) we can differentiate to obtain

$$\frac{\partial P}{\partial V} = -\frac{NkT}{(V-Nb)^2} + \frac{2aN^2}{V^3}; \frac{\partial^2 P}{\partial V^2} = \frac{2NkT}{(V-Nb)^3} - \frac{6aN^2}{V^4}$$

At the critical point, both of these expressions should equal zero, so

$$\frac{NkT_c}{(V-Nb)^2} = \frac{2aN^2}{V_c^3}; \text{ and } \frac{2NkT_c}{(V-Nb)^3} = \frac{6aN^2}{V_c^4} \quad (1)$$

Dividing the first of these equations by the second gives,

$$\frac{1}{2}(V_c - Nb) = \frac{1}{3}V_c, \text{ or } V_c = 3Nb.$$

To obtain the critical temperature, plug this result into the first equation in (1):

$$\frac{NkT_c}{(3Nb - Nb)^2} = \frac{2aN^2}{(3Nb)^3} \Rightarrow \frac{NkT_c}{4N^2b^2} = \frac{2aN^2}{27N^3b^3} \Rightarrow kT_c = \frac{8}{27} \frac{a}{b}.$$

Finally, to obtain the critical pressure, plug both these results back into the van der Waals equation itself:

$$P_c = \frac{NkT_c}{V_c - Nb} - \frac{aN^2}{V_c^2} = \frac{8Na/27b}{2Nb} - \frac{aN^2}{9N^2b^2} = \left(\frac{4}{27} - \frac{1}{9}\right) \frac{a}{b^2} = \frac{1}{27} \frac{a}{b^2}$$

4 Problem 5.53(5pts)

Here is the *Mathematica* code that I used to plot $p(v)$ and G/NkT_c vs. p and the plots:(see Fig. 1 below):

From either plot, we can see that the transition pressure is at approximately $p=0.38$.

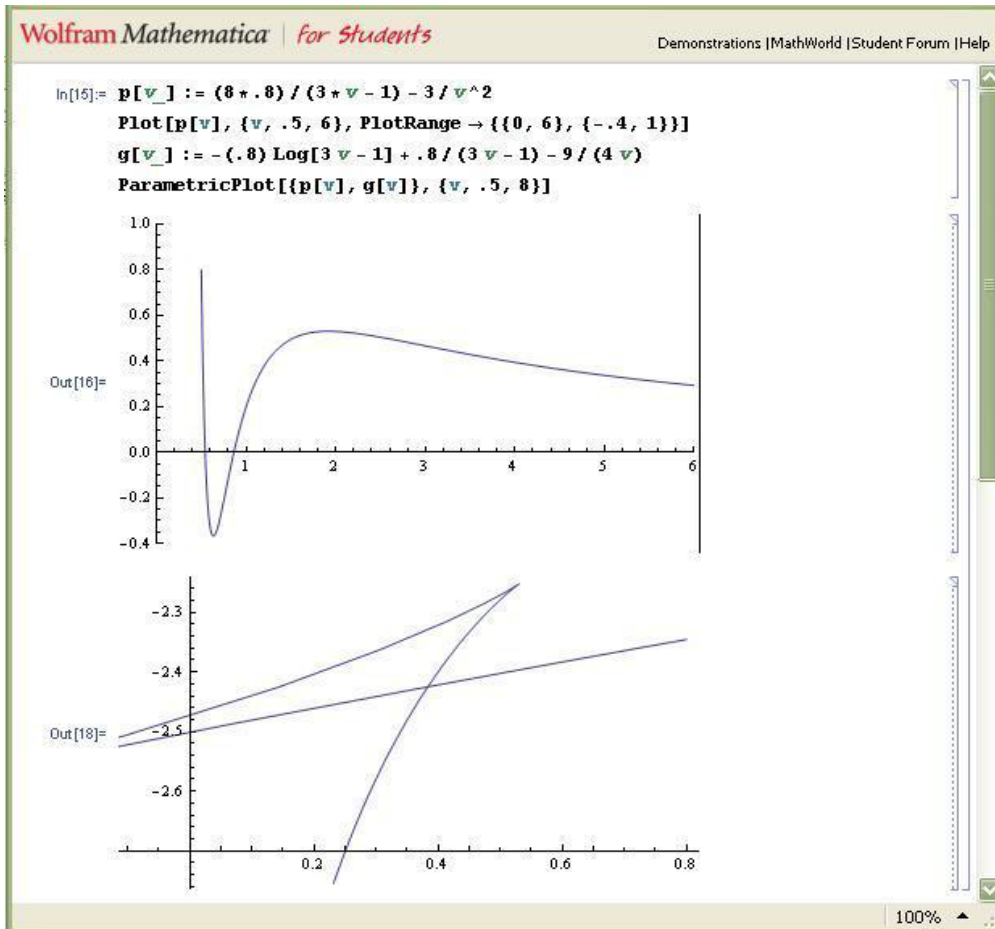


Figure 1: plot for p vs. v and G/nkT vs. p

5 Problem 5.54(5+5pts)

Since $F=G-PV$ for any system, we can start with equation 5.56 for the Gibbs free energy, then subtract off PV , using the van der Waals equation to express P in terms of V :

$$\begin{aligned}
 F &= -NkT \ln(V - Nb) + \frac{(NkT)(Nb)}{V - Nb} - \frac{2aN^2}{V} - PV + c(T) \\
 &= -NkT \ln(V - Nb) + \frac{(NkT)(Nb)}{V - Nb} - \frac{2aN^2}{V} - \frac{NkTV}{V - Nb} + \frac{aN^2}{V} + c(T) \\
 &= -NkT \ln(V - Nb) - NkT - \frac{aN^2}{V} + c(T) \\
 &= -NkT \ln(V - Nb) - \frac{aN^2}{V} + c(T)
 \end{aligned}$$

where in the last step I have absorbed the term $-N k T$ into constant $C(T)$. Now divide by $N k T_c$ and put the expression in terms of the dimensionless variables $v=V/V_c$ and $t=T/T_c$, where $V_c=3Nb$ and $kT_c=8a/27b$:

$$\begin{aligned} \frac{F}{NkT_c} &= -\ln(vV_c - Nb) - \frac{aN^2}{NkT_c v V_c} + C(T) \\ &= -\ln(3v - 1) - \ln(Nb) - \frac{aN^2}{Nv \cdot 3Nb} \frac{27b}{8a} + C(T) \\ &= -\ln(3v - 1) - \frac{9}{8v} + f(t) \end{aligned}$$

where again I have absorbed terms that don't depend on v into final constant term. To plot this function (without the constant term), I used the *Mathematica* command (see Fig. 2 below)

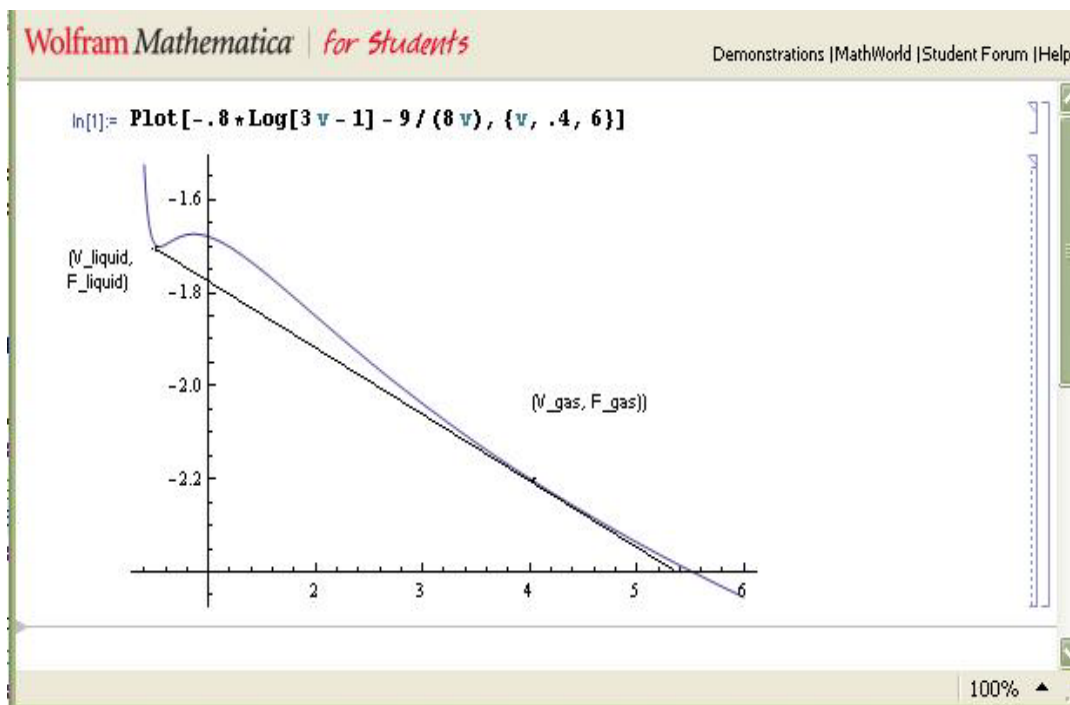


Figure 2: F/NkT vs. v

now suppose the system consists of a combination of two different states represented by the dots: it is part liquid and part gas. Let x be the fraction (by mass) of liquid, so the fraction of gas is $1-x$. The total volume of the system is then

$$V = xV_l + (1 - x)V_g = V_g - x(V_g - V_l)$$

and the total free energy is

$$F = xF_l + (1 - x)F_g = F_g - x(F_g - F_l).$$

Combining these two equations to eliminate x , we obtain

$$F = F_g - \frac{(V_g - V)}{(V_g - V_l)}(F_g - F_l).$$

This equation for $F(V)$ describes a straight line in Fig. 2, going through the points (V_l, F_l) , and (V_g, F_g) . Notice that this straight line lies below the original curve representing the free energy of a homogeneous state of uniform density. Since a system at constant T and V tends to minimize its free energy, the stable states at volumes between V_l and V_g are those represented by the dashed line, not the solid curve. Notice also that at the points where the line meets the curve at each end, it is tangent to the curve, indicating that this is the lowest possible straight line that can be drawn between any two points on the curve, lying entirely below it. In fact, had we not known the transition volumes V_l and V_g , we could have found them by drawing the lowest possible such straight line and then looking at where it meets the curve at a tangent. This process is just another way of doing the so-called Maxwell construction.