Physics 317 – Chowdary
Thermodynamics and Statistical Physics
Fall 2005

Homework #21, due Fri. Oct. 21

Universal van der Waals Phase Diagram

In this assignment, you will (1) determine the critical point values of volume, temperature, and pressure for a van der Waals fluid; (2) derive the reduced equation of state for a van der Waals fluid; (3) derive the reduced Gibbs free energy for this fluid; (4) make plots of the reduced Gibbs free energy vs. reduced pressure and of the reduced pressure vs. reduced volume; (5) determine transition pressures (vapor pressures); and (6) make a universal phase diagram for van der Waals fluids.

(1) Problem 5.48. As you can see from Figure 5.20, the critical point is the unique point on the original van der Waals isotherms (before the Maxwell construction) where both the first and second derivatives of P with respect to V (at fixed T) are zero. Use this fact to show that $V_c = 3Nb$, $P_c = \frac{1}{27}\frac{a}{b^2}$, and $kT_c = \frac{8}{27}\frac{a}{b}$.

(2) Problem 5.51. When plotting graphs and performing numerical calculations, it is convenient to work in terms of **reduced variables**,

$$t \equiv T / T_c \qquad p \equiv P / P_c, \qquad v \equiv V / V_c$$

Rewrite the van der Waals equation $P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$ in terms of these variables, and notice that the constants a and b disappear.

(You should obtain the reduced pressure $p = \frac{P}{P_c} = \frac{8t}{3v - 1} - \frac{3}{v^2}$.)

(3) The Gibbs free energy for the van der Waals fluid is given by eq. (5.56) as $G = -NkT\ln(V - Nb) + \frac{(NkT)(Nb)}{V - Nb} - \frac{2aN^2}{V} + c(T)$, where the integration constant, $c(T)$, can be different for different temperatures, but is unimportant for our purposes (since it's just a constant additive term). Define the reduced Gibbs free energy $g \equiv \frac{G}{NkT_c}$. Divide both sides of eq. (5.56) by NkT_c and rewrite this equation in terms of the reduced variables.

(You should obtain the reduced Gibbs free energy $g = \frac{G}{NkT_c} = -t\ln(3v - 1) + \frac{t}{3v - 1} - \frac{9}{4v} + C(T)$, where "left-over" constant terms are absorbed into $C(T)$. Again, notice that the constants a and b "disappear".)

(4) Make plots of the reduced pressure p vs. the reduced volume v and the reduced Gibbs free energy g vs. the reduced pressure p for the isotherm $t = T/T_c = 0.8$. I produced the plots shown in class (for $t = 0.9$) using a spreadsheet program, though you should produce them however you like. I've shown a small portion of my tabulated results for the $t = 0.9$ case so that you have the option of checking. Note that there's no point in calculating p for $v \le \frac{1}{3}$ (as discussed in class), which is why my table starts at $v = 0.34$. Also note that in my table, v increases by 0.001 in each row. My table extended down as far as necessary to make good plots.

v	**p**	**g**
0.34	334.0484	41.90317
0.341	287.2439	35.92723
0.342	251.2742	31.32113
0.343	222.7763	27.66113
0.344	199.6485	24.68212
0.345	180.5095	22.20971
0.346	164.4144	20.12447
0.347	150.6947	18.34183
0.348	138.8643	16.80024
0.349	128.5611	15.45379
0.35	119.5102	14.26759
0.351	111.4986	13.21459
0.352	104.3591	12.27355
0.353	97.95859	11.4275
0.354	92.18955	10.66276
0.355	86.96443	9.968157
0.356	82.2111	9.334492
0.357	77.86962	8.754103
0.358	73.88979	8.220567

Low v results for $t = 0.9$

Please present clear plots; don't present the spreadsheet results.
Here are some requirements:

(a) For g vs. p, rescale so that you can clearly see the unstable triangle, along with a small region outside the unstable triangle.

(b) For p vs. v, use the same range of p values that you used for the previous plot, and rescale the horizontal axis as necessary.

(c) Make sure your axes are clearly labeled.

(d) Clean up your plots. If you're using Excel, get rid of that stupid grey background. Pick a nice symbol or line or combination.

(e) Be kind to trees. Copy your graphs so that you can print them out on one page. Note that you will also make a plot in part (6), so you may want to wait to print out your plots.

(5) Determine the transition pressure (vapor pressure) p_{v} for $t = 0.8$ to within ± 0.001. Describe your method, and indicate the vapor pressure with a vertical line on your g vs. p plot and a horizontal line on your p vs. v plot.

Determine the vapor pressure for several other values of $t < 1$. It's unnecessary to present either your spreadsheet results or your graphs, but do copy and fill out the following table. I've already provided some entries: we know that at $t = 1 \Rightarrow p_{\mathrm{v}} = 1$ (the critical point), and from class, we saw that $t = 0.9 \Rightarrow p_{\mathrm{v}} = 0.647$.

t	p_{v}
1	1
0.9	0.647
0.8	
Your choice	
Your choice	
Your choice	
. . .	

(6) Make a phase diagram of a van der Waals fluid by plotting p vs. t. Specifically, plot your table from part (5). Label the critical point, the coexistence line, and indicate which region is the liquid phase and which region is the gas phase. Note that since we worked in reduced variables the whole way, this phase diagram is a ***universal*** phase diagram for any van der Waals fluid. Make a clear plot of the phase diagram.