**Van der Waals Gas**

Let’s reconsider the Van der Waals gas, and attempt to apply the last file’s stuff to it. The heat capacity and pressure were given by:



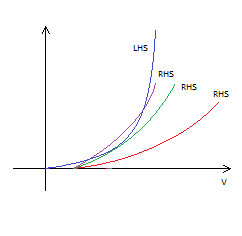
With these two guys, we basically can construct U(T,V) and S(T,V), as discussed under the context of the ideal gas, and that would give us F(T,V), from which we can get everything we need. But alas the pressure equation isn’t an appropriate model at all volumes because it can have a negative compressibility – meaning increasing pressure makes the volume go *up*. We can see this by taking a look at the compressibility.



and so we’ll have problems when this is can go negative. This will happen when,



The LHS and RHS are plotted below, the latter for successively lower T’s (red = hot, purple = not), and V > b.



And can see that when T < Tc (some critical temperature) we can get LHS < RHS for a little while. This will begin to happen when the slopes of the two sides match (the Tc curve is the green guy) at the point of contact. So this means we have:



So requiring the two sides match value and slope requires both following equations:



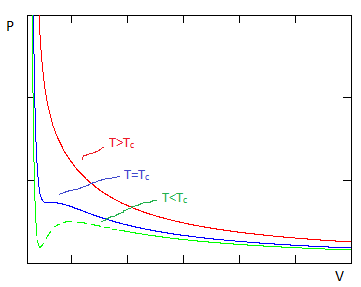
To solve these equations, I guess we can take the ratio of the two sides:



so that’s the volume at which this happens. And the temperature is, filling our result back into the second equation, say,



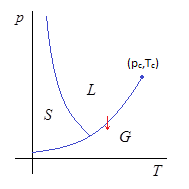
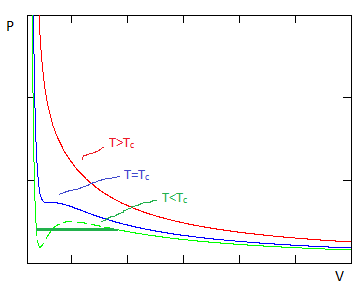
This is called the critical temperature Tc = 8a/27bk (and the volume we found above, Vc = 3bN, is called the critical volume). So when T < Tc, we’ll have problems – namely negative compressibility for some physical volumes. The problem is clear enough when we plot p vs. V. As we drop T lower and lower, a hump begins to appear once we go below Tc, and we get a region where increasing V is associated with increasing pressure (i.e., negative compressibility).



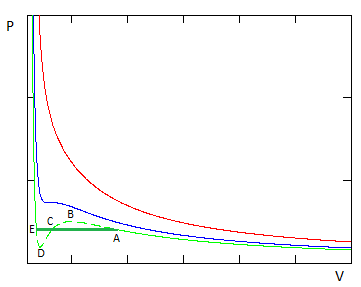
So we have to make a slight fix to the equation. The good news about the VdW equation so far is that the whole negative compressibility region for T < Tc problem physically stems from the gas → liquid phase transition. So it is capturing the transition, just not very well. So what is p vs. V supposed to look like? Well, let’s consider V vs. p. Generally, as we infinitesimally increase p, V infinitesimally decreases. Let’s say we keep dropping T and do the increasing p, decreasing V thing. When we get to the transition point, the 2nd order phase transition point, we should see that an infinitesimal increase in p will result in a finite drop in V, as the substance contracts from a gas state into a liquid state. So the V vs. p curve should vertical for T < Tc. Conversely, p vs. V should go horizontal for T < Tc. We can be less heuristical. Let’s recall the Gibbs-Duhem equation:



And consider the following path (left graph):

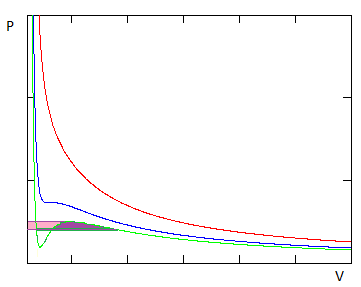
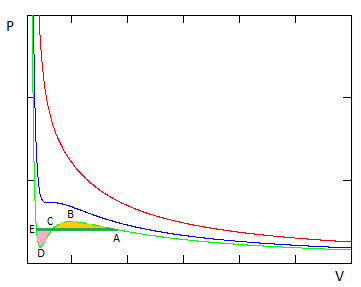
Now if dμ = 0 (as it should during the cross-over as argued above), and dT = 0 (because we’re doing an isothermal expansion), then dp = 0. So we should find that p is constant during the transition. So for instance the green p-V curve should look like what we have on the right, where we’d follow the dark green curve, instead of the dotted one. But next question is, where do we place this line? Well we know that the chemical potential remains the same, as aforementioned, across the transition. So we should place the line at the pressure where μ is the same at the line’s beginning and end point. We have an expression for μ(T,V) but it would be prohibitively difficult to put it in terms of T, p. But we can phrase the answer in a different way.



If we calculate Δμ going from A to E, then we ought to get 0. Now according to the Gibbs-Duhem equation, we have, at constant T:



And so integrating ΔG = N∫dμ (consider that μ can be considered a function of p and V) = ∫Vdp along the dotted line from A to E we should get 0. If you think carefully, you will see that this integral is simply the signed area bounded by the curve and the purple line (left graph). For instance the integral from A → B gives the pink + purple area, while the integral from B → C gives the negative pink area, which together leaves the area under the top curve. Similarly the integral from C to E would give the negative area of the bottom hump. And so Δμ = 0 implies that the magnitudes of the two areas are the same, i.e, the yellow area above the green line equals the pink area below the green line (right graph).

So that is how, geometrically, one could locate the pressure at which to place the horizontal line. And from this we can get the real F(T,V), in principle at least.

**Critical point**

OK, now let’s try to identify the critical point. We already did, but another way…this is when p(V) develops an inflection point, as can sort of see from the p-V graph above. So we have ∂p/∂V = 0 (because the compressibility must be ∞, i.e. must diverge since it’s a ‘susceptibility’), and ∂2p/∂V2 = 0 (because in general p must be steady or decreasing with V and so I don’t see a way for this to be true and p΄ = 0, than for p΄΄ = 0 as well).



where we define υ = V/bN, and



We must solve these two equations. I guess I’ll take the ratio of the equations:



And plugging this back in we get:



Plugging this into Van der Waals equation to get pc we have,



So we have:



Before moving on, we’ll find it useful to write the equation of state in terms of these critical values by defining p = pcp´, T = TcT´, and V = VcV´.



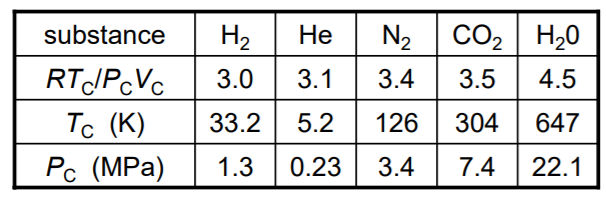
and so,



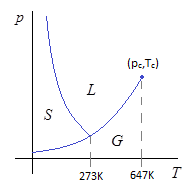
Interestingly, when expressed this way, the equation of state assumes a universal form, a prediction which has been confirmed for many gasses I believe. Will also note that the equation predicts all gasses should have a universal constant (k = Boltzman’s constant 1.38×10-23J/K)



A table of values for some gasses is given below:



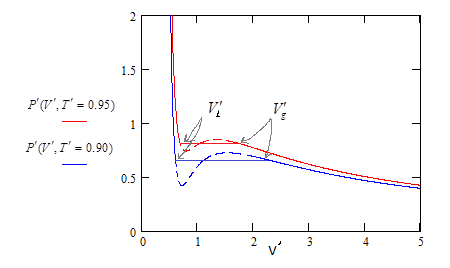
The actual RTc/pcVc values are all higher than the theoretical prediction, but in the ball park. And with Tc and pc values, we can work backwards to estimate the parameters a and b, FWIW. Note the critical point for water is at T = 647K, more than double room temperature.



By contrast the triple point is at roughly 273K.



What about the order parameter, φ = Vg – Vℓ? Below I graphed p´(V´,T´).



What we want is basically the width of the line as a function of T – Tc. To determine the width we need to determine the pressure p0 at which the net area about the p = p0 is 0. And then once we have that pressure p0, we can determine the length of the line by subtracting the max/min roots of the equation V(p´) = p0. So there are three equations to solve for the three unknowns,



working on the last one,



So our three equations are:



So we could technically invert the first two equations and solve for V´, and then plug into the last equation. Going back to the VdW equation,



This is a cubic equation, which has known solutions. So define,



and,



Then the solutions are



Numerically, it appears the n = 1, 0 terms are the left and right solutions, and n = 2 is the middle one we don’t care about. So we have:



Can we simplify? Not really. Let’s just try to solve the three equations close to the critical point. Let’s define T´ = 1-ε, where ε = 1-T´ obviously, and we’ll operate in the region where ε is small. I’m just going to presume that p´ is an analytic function of ε which we can Taylor expand for small ε and write p´ = 1 - p1ε + O(ε2). Then I’ll plug these into our V´ℓ,g equations and expand out to O(ε), and so I’ll have hopefully simpler expressions for V´ℓ,g, accurate to O(ε), close to the critical point, but in terms of the unknown p1. Then I’ll plug these expressions into the equal area equation (last of the three boxed equations), and try to solve for p1. So starting…



and,



Plugging into V’s,



Can see that we’ll have problems if p1 ≠ 4, cause argument of cos-1 will blow up in the small ε limit. So I’ll presume p1 does equal 4. So didn’t even have to plug this into the equal area equation to get p1. So then,



So for our liquid and gas, we have:



nice. Then our order parameter is of course the difference of these two. And can see we will have:



So critical exponent β = ½ here. FWIW, we could probably expand p´0 further out in powers of ε, and plug into the equal-areas equation and solve for more coefficients. I’ll try that in next file.



And we’d like to know how the order parameter varies with respect to its critical value as we lower the pressure, at Tc. But this is easy. At Tc, the equation of state reads:



and near V´ = 1, then, the equation will read:



So clearly V´ - 1 ~ (p´ - 1)1/3, and so δ = 3.



Heat capacity (constant volume) is a constant according to theory,



so α = 0.



And the isothermal compressibility, evaluated at Vc, is given by:



and so we see that γ = 1.

**Summary**

Summarizing, we have:



And might observe that these satisfy the scaling relations we discussed earlier in the Critical Exponents file. For instance,



The modern theory with renormalization groups, etc., gives better predictions, like:



We’ll discuss that in the context of ferromagnets in the Stat Mech folder, and also in the Condensed Matter folder.