**Van der Waals Gas**

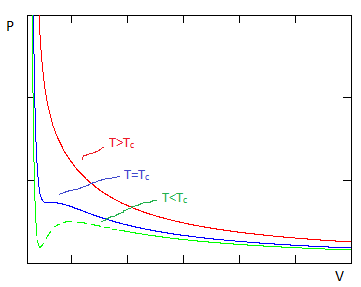
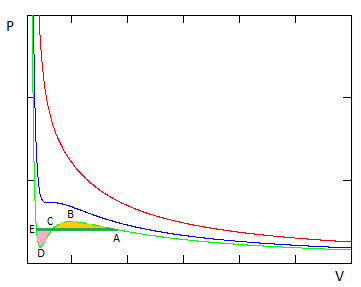
I’d like to work out the free energy and such *below* the critical point. And from this I’d like to get the p(T) coexistence curve and latent heat, and some other things. To do this, need to get the *actual* equation of state below the critical point.

**Equation of State Below (but near) the Critical Point**

To do that, we need to go out to 4th order in the order parameter? That would be order ε2. In the last file, I worked everything out to order ε. So I guess I’ll keep going. So just to recapitulate…we have:



But as we drop T lower and lower, a hump begins to appear in the equation of state 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 we worked out the answer in previous file – the Maxwell construction, shown on the right. We replace the curvy part with a flat line at the pressure p0 which bisects the areas above and below that value. So that is how, geometrically, one could locate the pressure at which to place the horizontal line.

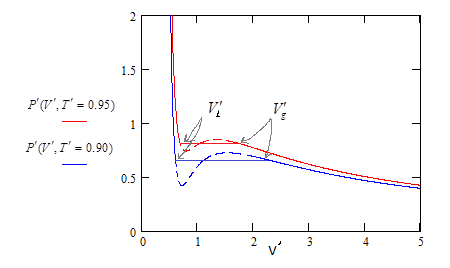
To facilitate calculating where this pressure p0 is, we worked out the critical temperature, pressure, and volume, where the phase transition begins. We found,



and we put the VdW equation in terms of the reduced (primed) variables defined via: p = pcp´, T = TcT´, and V = VcV´. We found,



So the Maxwell construction tells us to replace the curvy part with a flat line at pressure p´0 which bisects the area.



To work this out we have three equations. The first two determine the roots where p´0 intersects the equation of state, and the last says that p´0 is such as to separate equal areas above and below.



Filling in the VdW equation into the last guy, and doing the integral, our three equations come to:



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



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:



So now we 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 – p2ε2. Then I’ll plug these into our V´ℓ,g equations and expand out to O(ε2), and so I’ll have hopefully simpler expressions for V´ℓ,g, accurate to O(ε2), close to the critical point, but in terms of the unknown p1, p2 Then I’ll plug these expressions into the equal area equation (last of the three boxed equations), and try to solve for p1, p2 So starting…using Mathcad for help on the Taylor series expansion,



and,



Plugging into V’s,



Should’ve done this from the beginning, but obviously p1 needs to be 4, like last time. So,



which is,



Now I need to expand this in powers of ε, out to 2nd order. Expanding the inverse cos function,



And so last, sort of,



Well that’s interestingly symmetric. V´ℓ(√ε) = V´g(-√ε), apparently. I’m going to call these:



for short. Well then we’d plug this into the equal areas equation…



and using Mathcad again, for the Taylor expansion of those two other terms,



Picking out the orders,



The first equation is satisfied. The second …



is automatically satisfied too. This is weird. Maybe I can’t presume to expand p in a power series in ε, past O(ε)?

**Constructing the Free Energy below (but near) the Critical Point**

Oh well. So if I just stick with what I’ve got, then,



where, θ(x) = 1 if x > 0, and 0 otherwise. And,



and p0 is the value of the Van der Waals p(T,V) function at Vℓ and Vg (recall both give same value), and Vℓ,g are where p0 intersects the Van der Waals p(T,V) function. Of course we have, to first order in T-Tc, that,



There is a problem with this equation of state though. In the VdW file, we derived a relationship between CV and p, for any substance. Namely,



and we don’t have that here, for our new p(T,V), since the boundaries regions are T-dependent. I guess this means I should ignore that T-dependence when taking derivatives? Might also note that in order for this identity to hold, we’d have to *have* the p0(T) is linear in T. That would kind of make looking for O(ε2) contributions to p0(T), like we did above, pointless, unless we postulate a different CV. Hmmm….So looking at F(T,V). We know,



So let’s integrate p w/r V. I guess I’ll integrate from Vc.



where g(T) is an arbitrary integration constant (w/r to V). Now,



So that means, integrating from Tc I guess,



So we can say,



So, adding an arbitrary constant,



Like we did with VdW gas in a previous file, we can also say, where \_ means dividing by N.



and to first order,



I guess I’ll put that in there,



Integrating, I guess with respect to Tc and Vc,



and,



Now let’s look at the entropy. We found in the VdW file, maybe the ideal gas file before that, the relationship,



So plugging stuff in,



Guess I’ll use ∂p0(T)/∂T = 4pc/Tc. So then,



Then integrating,



and,



So,



Let’s go back to F and put it in terms of critical values. First I think I’ll define F´ = F/kTc. Then,



and recalling T/Tc = T´.



Then using V´ = V/Vc,



We’ll commit to p0(T) = pc(1-4ε) = pc(1-4(1-T/Tc) = pc(4T´-3),



Now have to evaluate some constants,



So now,



I’ll divide everything through by N, so now we’re looking at F´.



Make note that F´is linear in V´ between Vℓ and Vg. Here’s what p´ and F´ look like at T´ = 0.87, for instance. The dotted lines between Vℓ(T´) and Vg(T´) are what the uncorrected p´ and F´ look like between these points. The solid lines are what the we get from the Maxwell construction, i.e., our p´ above, and the F´ in the box above.

Chart, line chart

Description automatically generated

Can tell that since the solid line in the Maxwell constructed p´ curve connects points of equal pressure, the solid line in the Maxwell constructed F´plot connects points of equal slope, since p = -∂F/∂V. So for this temperature, say, if the substance is at any volume V < Vℓ, it will be a liquid. And if it’s at volume V > Vg, it’ll be a gas. If we start our substance out at Vℓ and add heat, keeping pressure constant, then its volume will expand along the straight part of the p(V) curve. Basically some of the liquid will boil off into vapor. And while the liquid part will lose volume therefore, the vapor part will gain volume, more than is lost to the liquid part, and so the volume overall will increase. As we continue adding heat, keeping pressure constant, along the straight line p(V) curve, the ever decreasing liquid part will keep its density constant, so that if Nℓ\*, Vℓ\* are the number of particles and volume of the remaining liquid part, then its density Nℓ\*/Vℓ\* will always be equal to the density it started out with Nℓ/Vℓ. In similar fashion, the ever increasing vapor part will always have the density the substance will acquire when it has fully converted to a gas, i.e., if we say Ng\*, Vg\* are the number of particles and volume of the vapor part, then its density Ng\*/Vg\* will always be equal to the density it will eventually have once the transformation is over Ng/Vg. We can figure out what Nℓ\* and Ng\* are at any given V along the straight p(V) curve. Our equations are the ones aforementioned, along conservation of overall volume and overall particle number:



Let’s start with the last one:



So now we can solve for Vℓ\*.



and follows that for the gas part,



Follows that the particle numbers are:

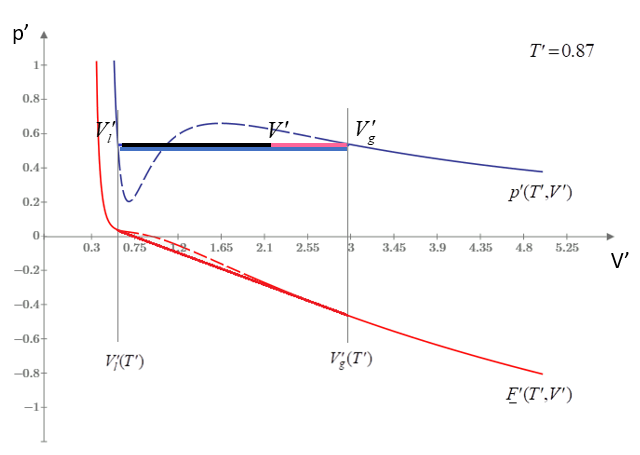


So altogether,



This is called the Lever Rule(s). Basically, making reference to the diagram below:





Would like to make sure that the free energy of our substance is the same, whether we regard it as a single ‘thing’ at volume V, or a composite liquid+gas at volumes Vℓ\* and Vg\*. So want to check,



Plugging in our expressions for Nℓ\*, and Ng\*, we have:



Now since this portion of the free energy curve is a straight line, we can also write it as:



and can see these two expressions for F(V) are the same, as they’re both linear in V, and both match at V = Vℓ, and V = Vg. So that’s good, and these two points of view are equivalent. I’ve seen people say that when we’re at volume V, the system decides to lower its free energy by partitioning into a liquid at volume Vℓ\* and gas at volume Vg\*. But can see that’s not the case. It *does* partition itself, but not to ‘lower’ its free energy below what it has at volume V, rather, partitioning is just how it manifests the free energy it has at volume V.

**p(T) coexistence curve and latent heat**

It would be interesting to solve for the p(T) curve, near the critical point, that separates the liquid and gas regions. And we’d also like to solve for the latent heat if possible. Well, the p(T) curve would simply be the value of the aforementioned p that evenly splits the areas, at each value of T. This is, to our approximation at least,



The latent heat is just L = TΔS. Perhaps it would be easiest to evaluate ΔS by calculating, directly from the equation of state. From free energy, and equality of cross-partials, we have:



Well, we have S, so might as well just use it.



So across the boundary, at temperature T, we have:



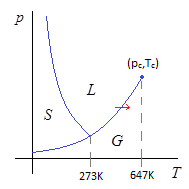
So we have Lv = TΔS is equal to:



As it should, this goes to zero as T → Tc, which is kind of the hallmark of a 2nd order phase transition. FWIW, we could try to estimate this value at room temperature. For water, Tc = 647K, and so,



which is off by a factor of 4, roughly. Well, the Van der Waals equation is only good near the critical point, so we shouldn’t expect it to work well at such low temperatures, as we’re (i.e., room temperature) practically at the triple point.



**Treating phases as different substances?**

Often the coexistence region is treated as equilibrium between two different substances – a gas phase and a liquid phase. These regions are separate because gravity will usually pull the liquid below the gas. Suppose that we have a substance coexisting in two different phases. Then we’d have something like:



and also have



so we see that in either description, we have only 3 d.o.f., as we should. Now let’s suppose that I consider two substances in equilibrium. One is just a gas of species A and the other a bonded state gas where the two species bond together with a bond strength φ, which is negative. I’d like to see if there is a temperature where only one or the other will exist, etc. So I could write:



And then we need to maximize w/r to NB and UB. First I’ll do UB.



Or maybe I’ll consider the phase at temperature T and volume V instead. Then F = U – TS should be additive so,



And now must minimize w/r to NB.



Still quite complicated to solve. But if did, then solve for NB in terms of N and plug back in to get F(T,V,N) as we should. But graphing it yields expected results. So far as I can tell, there is not much of a phase transition per se΄. The # of particles in the bound state varies fairly continuously as adjust T or φ. Not sure how V affects it. But whatever.