

## VAN DER WAALS EQUATION OF STATE: MAXWELL CONSTRUCTION

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problems 5.52 - 5.53.

To get a better feel for the van der Waals equation of state, we can look at how the Gibbs free energy varies with the volume and pressure. Schroeder derives an expression for  $G$  in his equation 5.56, which I will just quote:

$$(1) \quad G = -NkT \ln(V - Nb) + \frac{(NkT)(Nb)}{V - Nb} - \frac{2aN^2}{V} + c(T)$$

where  $c(T)$  is a function of temperature only, and can be ignored in what follows since we'll be specifying a particular temperature in each example, so  $c(T)$  is effectively a constant in each case.

This equation is easier to work with if we rewrite it in terms of the reduced variables, defined earlier as  $v \equiv V/V_c$ ,  $t \equiv T/T_c$  and  $p \equiv P/P_c$ , with:

$$(2) \quad V_c = 3Nb$$

$$(3) \quad T_c = \frac{8}{27} \frac{a}{bk}$$

$$(4) \quad P_c = \frac{a}{27b^2}$$

If we divide both sides of 1 by  $NkT_c$  and simplify using the above equations, we get

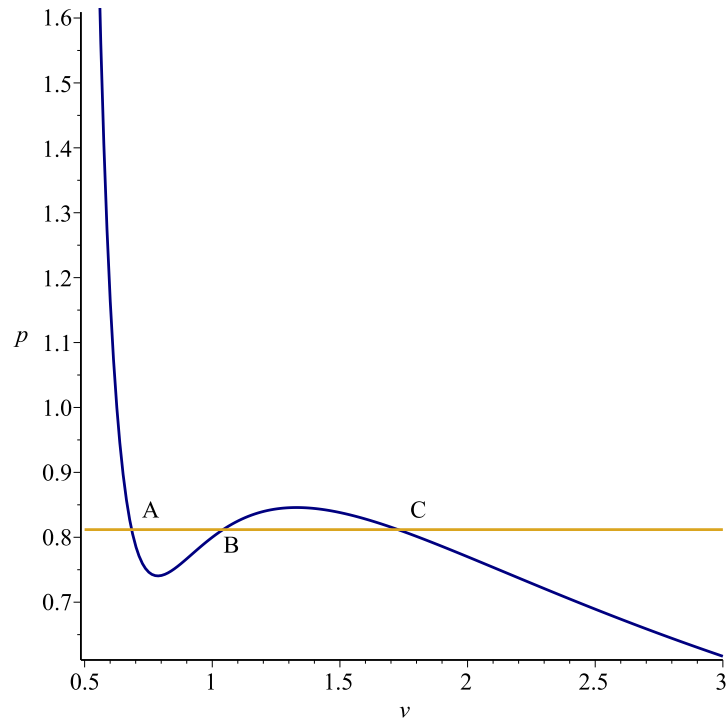
$$(5) \quad G_c \equiv \frac{G}{NkT_c} = -t \ln(3v - 1) + \frac{t}{3v - 1} - \frac{9}{4v} + c'(t)$$

where  $c'(t) = c(T)/NkT_c - t \ln(Nb)$  is another function that depends only on temperature, so can be ignored in what follows.

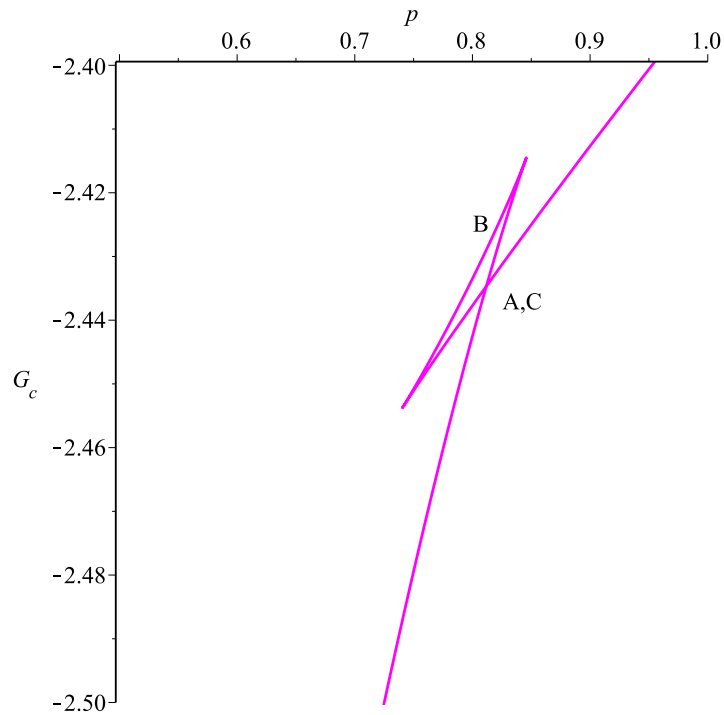
To plot  $G_c$  as a function of reduced pressure, we can use the equation derived in the last post:

$$(6) \quad p = \frac{8tv^2 - 9v + 3}{(3v - 1)v^2}$$

We can specify a temperature  $t$  and then vary  $v$ , using it to calculate  $p$  and the corresponding  $G_c$  from the last two equations, and thus generate a plot of  $G_c$  versus  $p$ . For  $t = 0.95$  the isotherm looks like this:



If we plot the Gibbs energy, we get:



As we reduce the volume, we move from right to left on the  $pv$  plot, and the corresponding path on the Gibbs plot is the line coming up from the bottom. At point  $C$ , we can continue to decrease  $v$ , which causes  $G$  to carry on along the same path above point  $C$ , until it reaches a sharp corner, at which point it decreases until it reaches point  $B$ , which is directly above (that is, it has the same pressure) as point  $C$ . However, note that  $B$  does *not* have the minimum Gibbs energy for that pressure, since point  $C$  is below it. Thus  $B$  is unstable and does not correspond to a physical state of the substance. Back on the  $pv$  plot, as we decrease  $v$  below point  $B$ , the Gibbs path decreases until it reaches the lower sharp corner. This corner corresponds to the minimum between  $A$  and  $B$  on the  $pv$  plot. Again, note that this isn't the minimum Gibbs energy for that pressure, so this is also unstable. In fact the whole section of the  $pv$  plot where the pressure decreases with decreasing volume (between the minimum between  $A$  and  $B$  and the maximum between  $B$  and  $C$ ) lies on a Gibbs path that is not the minimum energy, so this whole range of volumes is unstable and is not found in the real world.

As we continue to decrease  $v$  from the minimum point down to point  $A$ , the Gibbs energy returns from the lower sharp corner until it reaches point  $A$ , where the Gibbs energy is equal to the value it had at point  $C$ . Thus points  $A$  and  $C$  have the same Gibbs energy at the same pressure, but point

$A$  has a much lower volume than point  $C$ , so it corresponds to a condensed state (a liquid) while  $C$  corresponds to a gas.

In fact, this phase transformation occurs for only one pressure, as we can see from the following argument. At constant temperature, the thermodynamic identity states that

$$(7) \quad \left( \frac{\partial G}{\partial P} \right)_T = V$$

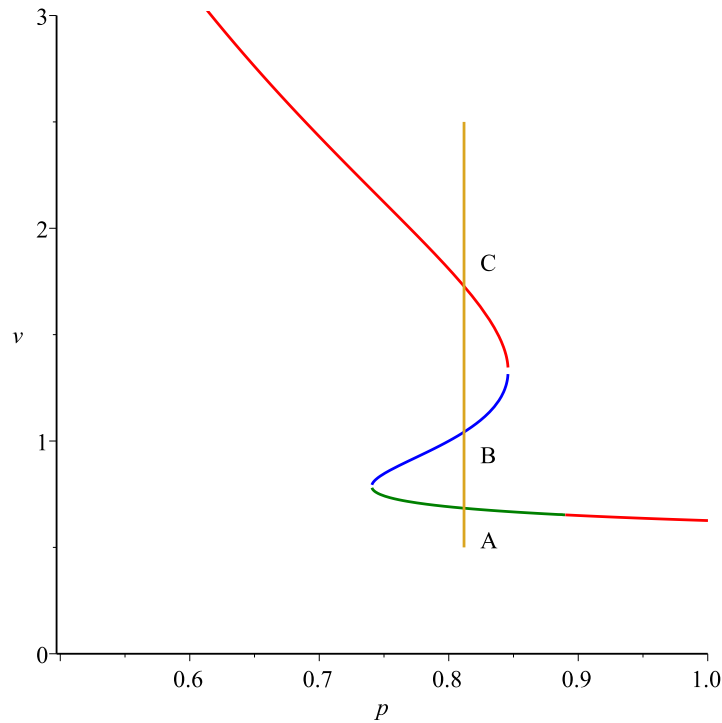
As we go around the triangular loop in the Gibbs plot above, the overall change in  $G$  is zero, so if we integrate it around the loop, we must get zero:

$$(8) \quad 0 = \oint dG = \oint \left( \frac{\partial G}{\partial P} \right)_T dP = \oint V dP$$

If we divide this equation by  $V_c P_c$  it changes nothing, since both these quantities depend only on  $T$ , which is held constant. Thus

$$(9) \quad \oint v dp = 0$$

To do this integral directly requires inverting 6 to get  $v$  as a function of  $p$ . However, this requires solving a cubic equation in  $v$ , which gives 3 different roots. Just for completeness, I did actually do this using Maple, and if we plot the result we get, for  $t = 0.95$ :



The red, blue and green curves represent contributions from each of the three roots. As we go round the triangular loop above, we go from point  $A$  to  $B$  to  $C$ . Requiring this integral to be zero is equivalent (as Schroeder shows) to the area bounded by the vertical line and curve between  $B$  and  $C$  being equal to the area bounded by the vertical line and curve between  $A$  and  $B$ . This is known as the *Maxwell construction* (yes, it's the same Maxwell that devised Maxwell's equations in electrodynamics).

The problem is then to find the value  $p_0$  of  $p$  that makes these two areas equal. Doing this requires moving the yellow line in the plot left or right until the areas are equal. Solving the problem analytically is a bit trickier, of course, since we're dealing with a cubic equation.

It's a lot easier to solve if we revert to the traditional  $p$  $v$  plot above. The area bounded by the vertical line and curve between  $B$  and  $C$  is then given by

$$(10) \quad A_{BC} = \int_{v_B}^{v_C} p \, dv - p_0 (v_C - v_B)$$

That is, it's the area under the  $p$  curve between  $v_B$  and  $v_C$  minus the area of the rectangle under the horizontal line between the same two volumes. By the same reasoning, the area in the  $vp$  plot bounded by the vertical line and curve between  $A$  and  $B$  is

$$(11) \quad A_{AB} = p_0 (v_B - v_A) - \int_{v_A}^{v_B} p \, dv$$

Surprisingly, the integral turns out to be fairly simple, using Maple:

$$(12) \quad \int p \, dv = \int \frac{8tv^2 - 9v + 3}{(3v-1)v^2} dv$$

$$(13) \quad = \frac{3}{v} + \frac{8}{3}t \ln(3v-1)$$

The problem now becomes:

- (1) Specify the temperature.
- (2) Choose a starting value for the pressure  $p_0$ . This can be estimated from the  $p$  $v$  plot by judging by eye what value of  $p_0$  makes the two areas roughly equal.
- (3) Solve 6 to find the 3 volumes  $v_A$ ,  $v_B$  and  $v_C$  for this value of  $p_0$ . This requires solving a cubic equation in  $v$ .
- (4) Calculate the two areas using 10 and 11.
- (5) Adjust  $p_0$  and repeat from step 3 until we get convergence.

I did this using a Maple procedure, with the best result (for  $t = 0.95$ ):

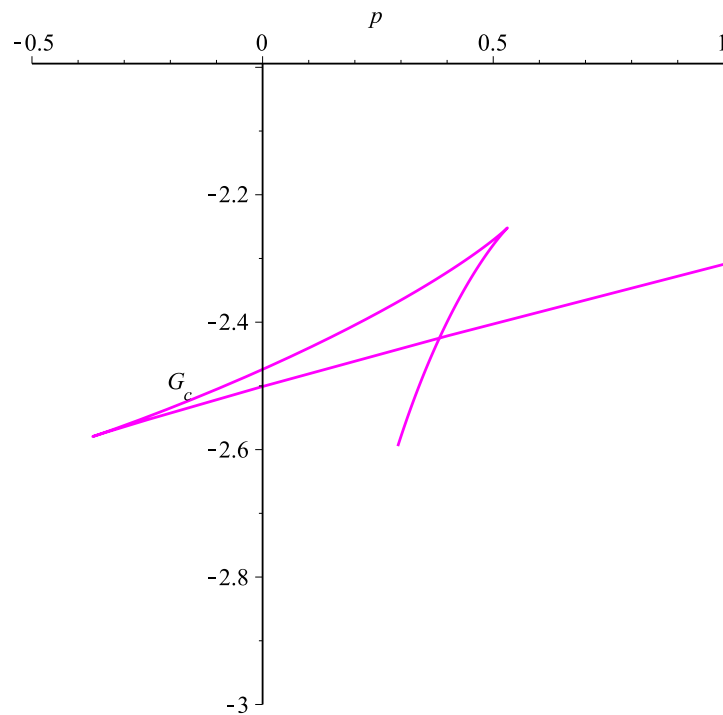
$$(14) \quad p_0 = 0.8119$$

As a check, we can compare this with the Gibbs energy plot above and note that the point  $A, C$  does indeed occur at this pressure.

We can repeat the procedure for  $t = 0.8$  and get the result:

$$(15) \quad p_0 = 0.3834$$

The Gibbs plot for this case is:



Again, we can see that the crossover between the two phases occurs at around  $p_0 = 0.3834$  so it looks like all is well.

#### PINGBACKS

Pingback: Helmholtz free energy of a van der Waals fluid

Pingback: Van der Waals fluid at the critical point