

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:

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

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:

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

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

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

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

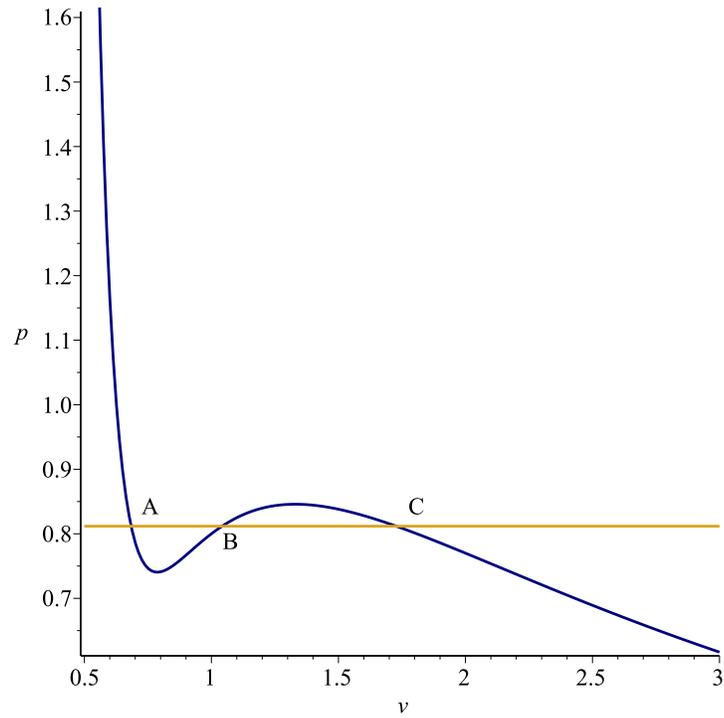
$$G_c \equiv \frac{G}{NkT_c} = -t \ln(3v - 1) + \frac{t}{3v - 1} - \frac{9}{4v} + c'(t) \quad (5)$$

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.

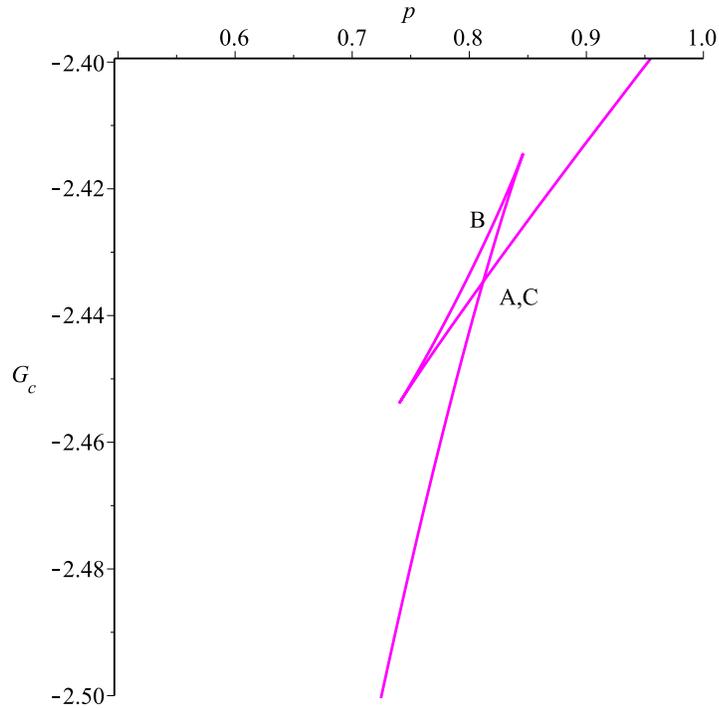
To plot G_c as a function of reduced pressure, we can use the equation derived in the last post:

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

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

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

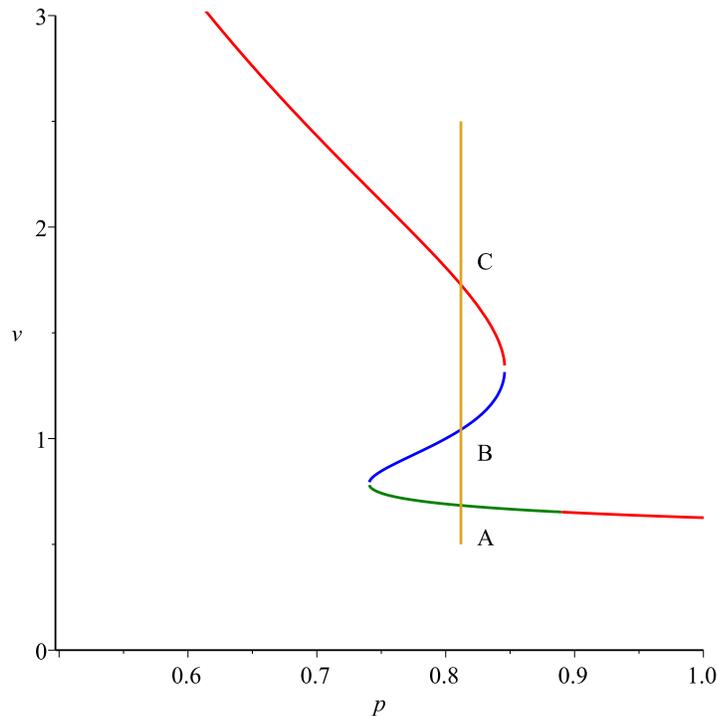
As we go around the triangular loop in the Gibbs plot above, the overall change in G is zero, so if we integrate it around the loop, we must get zero:

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

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

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

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 pv plot above. The area bounded by the vertical line and curve between B and C is then given by

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

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

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

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

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

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

The problem now becomes:

- (1) Specify the temperature.
- (2) Choose a starting value for the pressure p_0 . This can be estimated from the pv 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 $t = 0.95$):

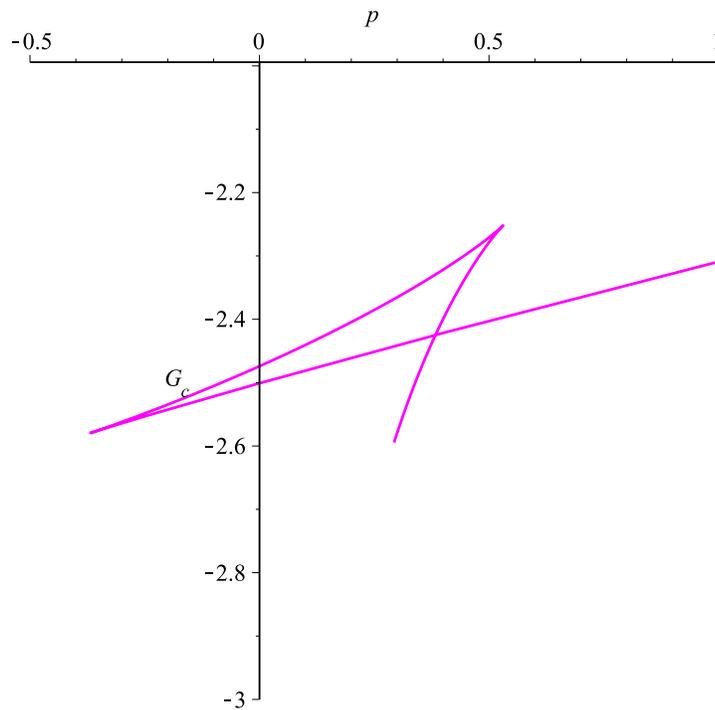
$$p_0 = 0.8119 \quad (14)$$

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:

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

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

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