

## HELMHOLTZ FREE ENERGY OF A VAN DER WAALS FLUID

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.54.

For the van der Waals equation of state, we've looked at how the Gibbs free energy predicts a phase transition. We can also analyze a van der Waals fluid using the Helmholtz free energy  $F$ . We begin with the thermodynamic identity

$$(1) \quad dF = -S dT - P dV + \mu dN$$

At constant temperature and number, this reduces to

$$(2) \quad dF = -P dV$$

so we can write this as a derivative:

$$(3) \quad \left( \frac{\partial F}{\partial V} \right)_{T,N} = -P$$

We can use the van der Waals equation of state to eliminate  $P$ :

$$(4) \quad \left( \frac{\partial F}{\partial V} \right)_{T,N} = -P = -\frac{NkT}{V - Nb} + a\frac{N^2}{V^2}$$

Integrating, we get

$$(5) \quad F(V) = -NkT \ln(V - Nb) - \frac{aN^2}{V} + c(T)$$

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:

$$(6) \quad V_c = 3Nb$$

$$(7) \quad T_c = \frac{8}{27} \frac{a}{bk}$$

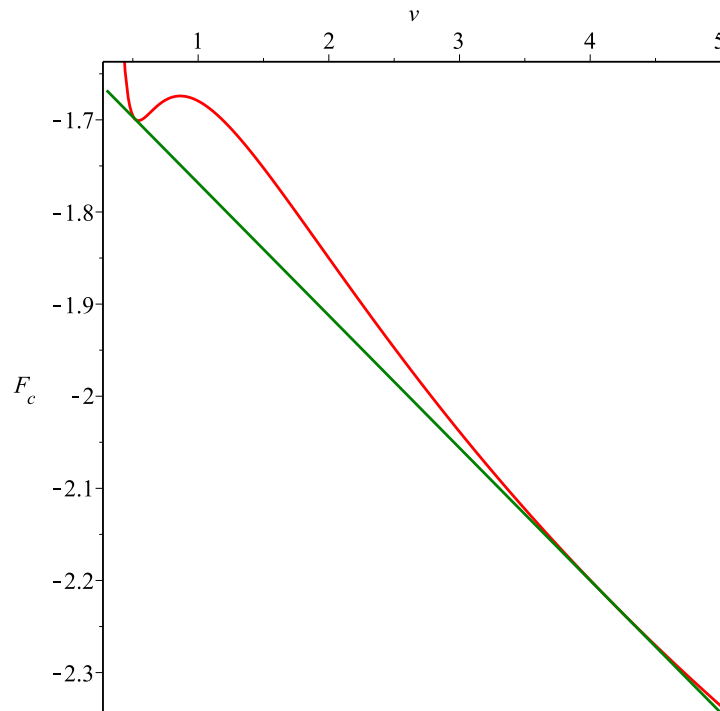
$$(8) \quad P_c = \frac{a}{27b^2}$$

If we divide both sides of 5 by  $NkT_c$  and simplify using the above equations, we get

$$(9) \quad F_c \equiv \frac{F}{NkT_c} = -t \ln(3v - 1) - \frac{9}{8v} + c'(t)$$

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.

A plot looks like this, with the red curve being  $F_c$ :



We saw in the last post that for  $t = 0.8$ , the vapour pressure (the pressure at which the phase transition occurs) is  $p_0 = 0.3834$ . In terms of reduced variables, the van der Waals equation of state is

$$(10) \quad p = \frac{8tv^2 - 9v + 3}{(3v - 1)v^2}$$

For given values of  $p$  and  $t$ , we can solve this equation to get three values for  $v$  (because this is a cubic equation in  $v$ ). Using Maple for this, we find

$$(11) \quad v_1 = 0.5174$$

$$(12) \quad v_2 = 1.2083$$

$$(13) \quad v_3 = 4.1725$$

The smallest volume  $v_1$  corresponds to the liquid state; the largest  $v_3$  to the gas (the other state is unstable). We can locate these volumes on the plot above and join them with a straight line (the green line). The first thing to notice is that this line appears to be the lowest line we can draw that is tangent to the curve in two points, with these two points being  $v_1$  and  $v_3$ . (You can check this is true by calculating  $dF_c/dv$  at these two points; you'll find that the slope of the line is indeed equal to the tangents to the curve at both these points.) Thus it would appear that we can use a plot of  $F_c$  to find the two volumes at which the phase transition occurs by drawing the lowest line that is tangent to the curve in two places. The vapour pressure can then be found by plugging either of these volumes into 10 (and as a check, both volumes should give the same pressure).

[As an aside, the value of  $dF_c/dv$  at  $v_2$  is also the same as at  $v_1$  and  $v_3$ , so the tangent at that point is parallel to the green line but lies on the top side of the red curve. I don't think this is physically significant, though.]

As for a proof that for volumes between  $v_1$  and  $v_3$ , the stable form of the fluid is a mixture of gas and liquid phases (rather than some homogenous state that is neither liquid nor gas), we can observe that if the total volume of the system is constant,  $F$  satisfies the condition

$$(14) \quad \left( \frac{\partial F_\ell}{\partial V} \right)_{T,N} = \left( \frac{\partial F_g}{\partial V} \right)_{T,N}$$

That is, the tangent lines to the curve are the same for the liquid and gas phases. This condition must hold for any mixture of the two phases, so the value of  $F$  for such a mixture must be the straight line between  $v_1$  and  $v_3$ . Since this line is below the red curve, the Helmholtz energy is lower, so the mixture is more stable than the homogeneous state. [I'm not sure this constitutes a rigorous proof, but it seems to make sense.]