VAN DER WAALS FLUID AT THE CRITICAL POINT

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 5.55.

We can use the van der Waals equation of state to investigate the behaviour of a fluid near the critical point (the point where the distinction between the liquid and gas phases disappears). In the problem statement in Schroeder's book, he recommends that we use reduced variables, but all parts of the problem use ordinary variables, so we'll use reduced variables and then translate the results back into ordinary variables at the end.

We start with the van der Waals equation in reduced variables

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

where $v \equiv V/V_c$, $t \equiv T/T_c$ and $p \equiv P/P_c$, with:

$$V_c = 3Nb \tag{2}$$

$$T_c = \frac{8}{27}\frac{a}{bk} \tag{3}$$

$$P_c = \frac{a}{27b^2} \tag{4}$$

Near the critical point all of p, v and t are close to 1, so we can rewrite 1 in terms of the deviation of these quantities from their values at the critical point. Using

$$A \equiv v - 1 = \frac{1}{V_c}(V - V_c) \tag{5}$$

we have

$$p = \frac{8t(A+1)^2 - 9(A+1) + 3}{(3(A+1) - 1)(A+1)^2} \tag{6}$$

Near the critical point $A \approx 0$ so we can expand this equation in a Taylor series about $A = 0$ to get (I used Maple, but you can grind through the derivatives by hand if you like):

1

$$p = 4t - 3 + 6\left(1 - t\right)A + 9\left(t - 1\right)A^2 + \left(12 - \frac{27}{2}t\right)A^3 + \mathcal{O}\left(A^4\right) \quad (7)$$

Near the critical point $t \approx 1$ and $A \approx 0$ so the term in A^2 will be much smaller than the other terms. [OK, the term in A is also the product of two near-zero terms, but for small A, $A^2 \ll A$ so we'll discard the A^2 term and keep the A term.] Our approximation for the pressure near the critical point is then

$$\begin{align} p\left(v\right) &= 4t - 3 + 6\left(1 - t\right)\left(v - 1\right) + \left(12 - \frac{27}{2}t\right)\left(v - 1\right)^3 & (8) \\ P\left(V\right) &= P_c p & (9) \\ &= P_c\left[4t - 3 + 6\left(1 - t\right)\left(v - 1\right) + \left(12 - \frac{27}{2}t\right)\left(v - 1\right)^3\right] & (10) \end{align}$$

For $t = 0.95$, a plot of p looks like this:
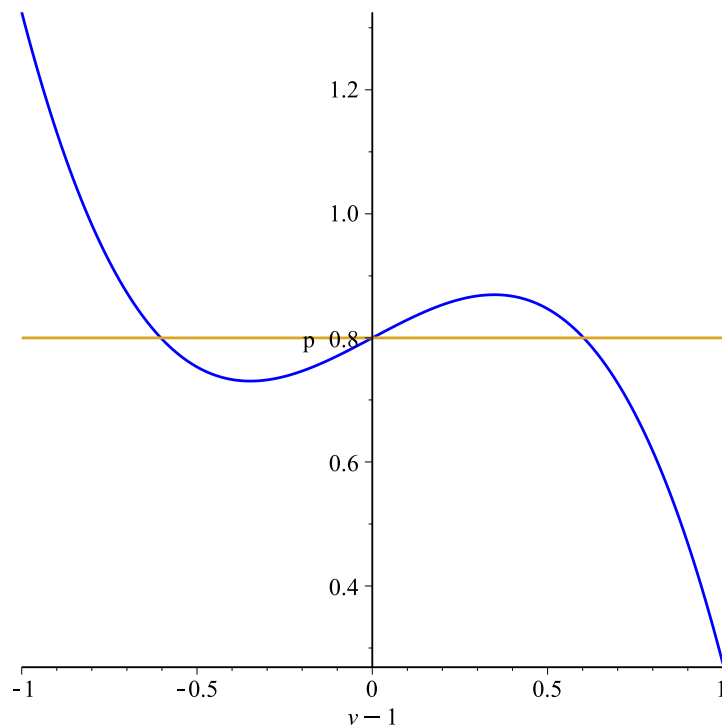
Because 8 is antisymmetric about the the vertical axis, if we draw a horizontal line passing through the point $p\left(v - 1 = 0\right)$ (the yellow line above), the areas between this line and the curve on either side of the axis are equal, so we have effectively performed a Maxwell construction. This shows that

the pressure at which the blue curve crosses the vertical axis is the vapour pressure for the given temperature. From 8 with $v = 1$, we have

$$p_v = 4t - 3 \tag{11}$$

Comparing this to our earlier results, for $t = 0.95$ our approximation gives $p_v = 0.8$ (the earlier result was $p_v = 0.8119$), while for $t = 0.8$, we get $p_v = 0.2$ compared to the earlier result of $p_v = 0.3834$. As we'd expect, as t gets farther from 1, the approximation deteriorates, but for $t = 0.95$, it's not too bad.

Using this approximation, the slope of the phase boundary is approximately

$$\frac{dp_v}{dt} = 4 \tag{12}$$

$$\frac{dP}{dT} = \frac{P_c}{T_c}\frac{dp_v}{dt} = \frac{4k}{8b} = \frac{k}{2b} \tag{13}$$

We can also use our approximation to get an estimate of the difference in volumes between the gas and liquid phases. As we can see from the above plot, there are three values of $v - 1$ that give the same pressure. The largest volume is v_g, the volume of the gas phase, while the smallest volume is v_l, the volume of the liquid. When $p = p_v$, 8 reduces to

$$6(1-t)(v-1) + \left(12 - \frac{27}{2}t\right)(v-1)^3 = 0 \tag{14}$$

which has 3 roots: $v = 1$ and

$$v - 1 = \pm\sqrt{\frac{12(1-t)}{27t - 24}} \tag{15}$$

The operand of the square root is positive for $\frac{24}{27} \approx 0.889 < t < 1$, so the approximation should be reasonably valid in this region. The difference $v_g - v_l$ is therefore

$$v_g - v_l = 2\sqrt{\frac{12(1-t)}{27t - 24}} \tag{16}$$

We can expand this in a series (I used Maple, but again you're welcome to do the binomial expansion by hand):

$$v_g - v_l \approx 4\sqrt{1-t} + \mathcal{O}\left((1-t)^{3/2}\right) \tag{17}$$

Converting back to ordinary variables, we have

$$V_g - V_l \approx \frac{4V_c}{\sqrt{T_c}} \sqrt{T_c - T} \tag{18}$$

That is, $V_g - V_l \propto (T_c - T)^{1/2}$. As Schroeder notes in the problem, the experimental value of the critical exponent β in $V_g - V_l \propto (T_c - T)^{\beta}$ is closer to $\frac{1}{3}$.
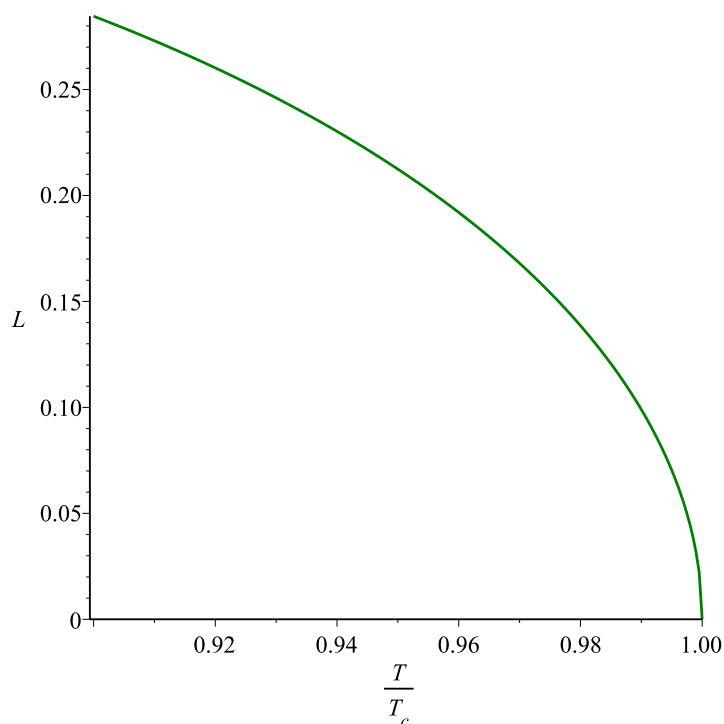
From this and 13, we can use the Clausius-Clapeyron equation to get an estimate of the latent heat of vapourization:

$$
\begin{aligned}
L &= T\Delta V \frac{dP}{dT} \tag{19} \\
&= T\frac{4V_c}{\sqrt{T_c}} \sqrt{T_c - T} \frac{k}{2b} \tag{20} \\
&= \frac{2kV_c}{b\sqrt{T_c}} T \sqrt{T_c - T} \tag{21}
\end{aligned}
$$

The shape of the curve as a function of temperature is determined by the $T\sqrt{T_c - T}$ factor, and looks like this:

The latent heat decreases to zero at the critical temperature, where there is no difference between the liquid and gas phases, so no transformation takes place.

Another critical exponent called δ is defined by the relation between pressure and volume near the critical point:

$$(P - P_c) \propto (V - V_c)^\delta \tag{22}$$

The value of δ in our approximation is $\delta = 3$ since we're saving terms up to the cubic term in the Taylor expansion 8. If we saved higher order terms, we'd get a higher value for δ, and as Schroeder points out, experimental values are around 4 or 5.

There is one final critical exponent known as γ which is defined by the behaviour of the isothermal compressibility

$$\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{23}$$

The derivative is the reciprocal of the slope of the pv curve in the plot above. As the temperature approaches the critical temperature, $t \to 1$ and the pv plot looks like this:
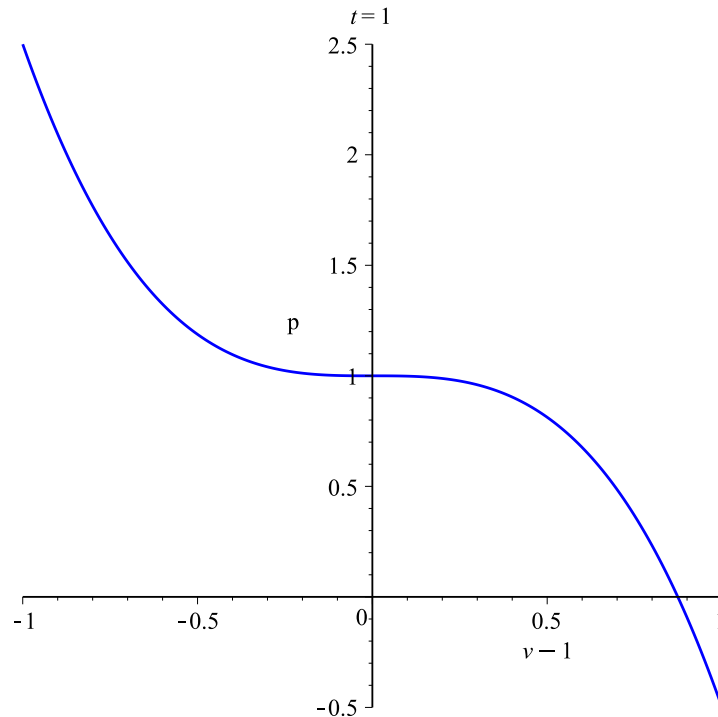
There is now only one phase possible and it occurs when $v - 1 = 0$. At this point, the curve has an inflection point and its slope is zero, so $\partial V/\partial P \to \infty$. For temperatures higher than T_c, the curve looks like this:
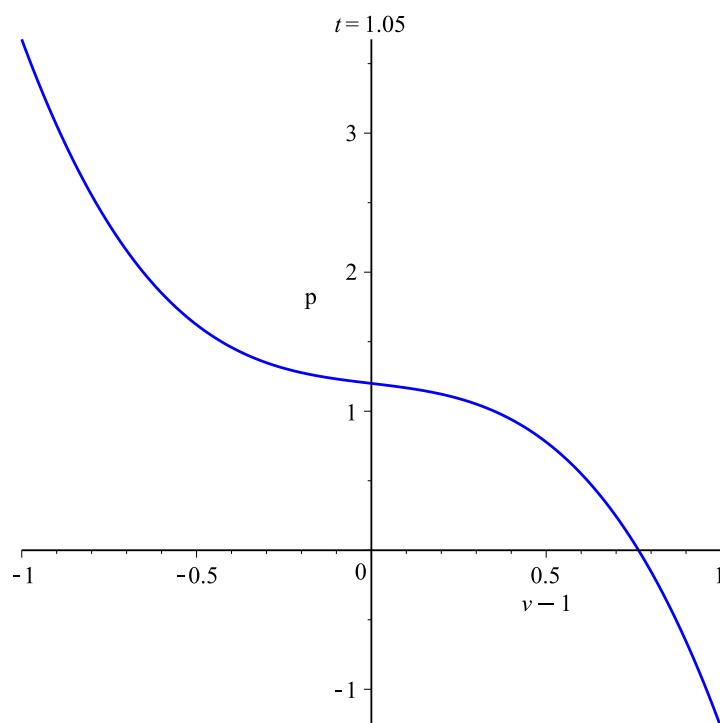
The slope is now non-zero at $v - 1 = 0$ so $\partial V / \partial P$ is again finite.

We'd like an estimate of how rapidly the derivative $\partial V / \partial P$ goes to infinity, that is, we'd like to find γ in the proportion

$$\left(\frac{\partial V}{\partial P}\right)_T \propto (T_c - T)^{-\gamma} \tag{24}$$

As the shape of the pv curve is qualitatively different on each side of $t = 1$ (for $t < 1$, there are two distinct phases and three possible volumes at the vapour pressure; for $t \geq 1$, there is only one phase and corresponding volume), we need to look at the two cases separately.

Using our approximation 8, we have

$$\frac{\partial p}{\partial v} = 6\left(1 - t\right) + (v - 1)^2 \left(36 - \frac{81}{2}t\right) \tag{25}$$

For $t > 1$, there is only one value of v that corresponds to a physical state of the fluid, and that is $v = 1$, so in this case

$$\left(\frac{\partial V}{\partial P}\right)_T \propto (T_c - T)^{-1} \tag{26}$$

For $t < 1$, however, two physical phases exist, and they correspond to the smallest and largest values of v. It can be seen from the top plot above that

the slopes at these two points are equal (since the curve is antisymmetric). We can rewrite 25 as (this is just a Taylor expansion about $t = 1$):

$$\frac{\partial p}{\partial v} = -\frac{9}{2}(v-1)^2 + \left(6 + \frac{81}{2}(v-1)^2\right)(1-t) \tag{27}$$

As we approach the critical temperature from below, the volumes of the two phases both approach $v = 1$, so again we see that

$$\frac{\partial p}{\partial v} \to 6(1-t) \tag{28}$$

Thus we have, for $t \to 1$ from below

$$\left(\frac{\partial V}{\partial P}\right)_T \propto (T_c - T)^{-1} \tag{29}$$

The value of γ is thus $\gamma = 1$ on both sides of the critical temperature.