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# The van der Waals Fluid's liquid vapor coexistence locus

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The liquid vapor coexistence locus is plotted from the analytical solution to the Maxwell construction for the van der Waals fluid.

## I. INTRODUCTORY REVIEW

The Nobel Prize for 1910 was awarded to Johannes Diderik van der Waals

”for his work on the equation of state for gases and liquids”.

These days, the van der Waals equation of state plays a minor role in the study of gases (of the non ideal variety) during the first few weeks of a typical physical chemistry course. Part of its current appeal is as an exercise vehicle illustrating practice that the ideal gas example templates. As an example, the reversible isothermal work of an ideal gas under compression or expansion would be

$$\int_A^B p dv \rightarrow - \int_A^B \frac{RT}{v} dv \rightarrow -RT \ln \frac{v_B}{v_A}$$

while the same question phrased for a van der Waals fluid would yield

$$\int_A^B p dv \rightarrow - \int_A^B \left( \frac{RT}{v-b} + \frac{a}{v^2} \right) dv$$

an exercise in elementary calculus. In the same spirit, the vdW fluid can be used instead of the ideal gas fluid to illustrate fugacity [1] via integration of

$$\left( \frac{\partial G}{\partial p} \right)_T = v$$

which reminds students of integration by parts.

Chemical potential, partial molar quantities, etc., all can be obtained explicitly for vdW fluids, as exercises.

Phase changes can also be explored using vdW fluids, where no such behavior is exhibited by the ideal gas. This does, however, require the Maxwell construction, which although conceptually simple, is analytically quite demanding. The Maxwell construction requires employing the cubic nature of the vdW equation of state.

Although the cubic nature of the vdW fluid's equation of state has been known since 1910, its use in solving the Maxwell [2] construction for the discontinuities that a real gas suffers as two phases develop from one phase on an isotherm whose temperature lies below the critical temperature, has never been seen in a textbook as American students do not learn how to solve cubics.

The first paper in this series[3] addressed this question. The second paper addressed the question why the Maxwell construction works[4].

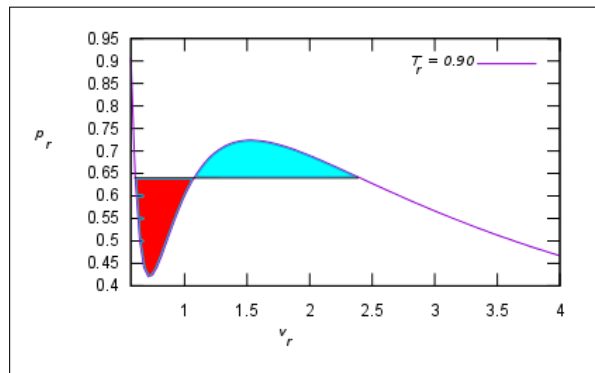


FIG. 1. The Maxwell construction. An isotherm, with  $T < T_c$  or  $T_r < 1$ .  $p_{test}$  is adjusted until the two colored areas are equal. In the case shown,  $p_{test}$  is too high (the aqua area (positive) is smaller than the red (negative) one) so the two areas are not equal (and their sum is therefore not zero). When  $p_{test}$  is properly chosen (the sum of the two areas is zero),  $p_{test} \rightarrow p^{vp}$ , the vapor pressure at this particular temperature.

## II. INTRODUCTION

In a paper by Lekner [5] a method for analytically solving the Maxwell construction for the van der Waals fluid<sup>1</sup> was discussed whose equations were solved using Sage/CoCalc [6].

The final figure of this paper was drawn in Sage/CoCalc, and is primitive. This submission presents an improved figure which, if replicated on a computer can be rotated and inspected so that the liquid  $\rightleftharpoons$  gas phase transition can be better understood.

### A. Lekner's approach

The Maxwell construction requires us to force  $\int p_r dv_r - \int p_r^{vp} dv_r \rightarrow 0$  Figure 1 shows the traditional graphic representation of this integral. We then have  $\int \left( \frac{8T_r}{3v_r-1} - \frac{3}{v_r^2} \right) dv_r - \int p_r^{vp} dv_r$  from the smallest root to

<sup>1</sup> The reduced van der Waals equation is written as

$$p_r = \frac{8T_r}{3v_r-1} - \frac{3}{v_r^2}$$

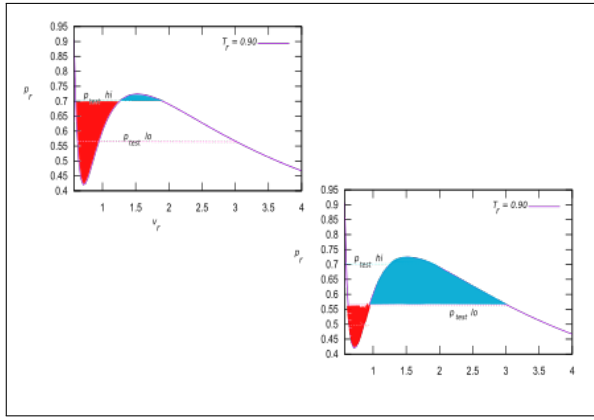


FIG. 2. The Maxwell Construction. Two test pressures are shown, one too high, the other too low. Neither therefore qualifies as  $p^{vp}$ .

the center root, and from the center root to the largest root, so that the sum of these two integrals is zero (since one part is negative and the other part positive).

As shown in the earlier cited paper, we have upon integration

$$\frac{8}{3}T\ell n\left(\frac{3v_g-1}{3v_\ell-1}\right) + \frac{3}{v_g} - \frac{3}{v_\ell} - p^{vp}v_g + p^{vp}v_\ell = 0 \quad (1)$$

(We have removed the reminder that these are reduced variables) to emphasize the *gas* and *liquid* ends of the isotherm's intersection with the constant vapor pressure.

### B. Removing $T$ and $p^{vp}$ from these expressions

Equation 1 can be rewritten as

$$\frac{8}{3}T\ell n\left(\frac{3v_g-1}{3v_\ell-1}\right) + \frac{3}{v_g} - \frac{3}{v_\ell} - \left(\frac{8T}{3v_g-1} - \frac{3}{v_g^2}\right)v_g + \left(\frac{8T}{3v_\ell-1} - \frac{3}{v_\ell^2}\right)v_\ell = 0 \quad (2)$$

which is specific to the Maxwell construction where we have removed  $p^{vp}$  from Equation 1.

Next, we need to remove  $T$ . We had

$$T = \frac{\frac{3}{v_g^2} - \frac{3}{v_\ell^2}}{\left(\frac{8}{3v_g-1} - \frac{8}{3v_\ell-1}\right)} \quad (3)$$

All that needs doing now is to solve Equation 2 with  $T$  removed (using Equation 3), for  $v_g$  and  $v_\ell$ , a non trivial business.

### C. A trick

As noted previously, the term  $3v_\ell - 1$  and  $3v_g - 1$  are defined as

$$v_g(\delta) = \frac{f(\delta)e^\delta + 1}{3}$$

and

$$v_\ell(\delta) = \frac{f(\delta)e^{-\delta} + 1}{3}$$

The Sage code displayed earlier obtains  $f(\delta)$  as

$$f(\delta) = -\frac{4\delta e^{(2\delta)} - e^{(4\delta)} + 1}{2(\delta e^{(3\delta)} + \delta e^\delta - e^{(3\delta)} + e^\delta)} \quad (4)$$

From this, the formulas of  $v_g$  and  $v_\ell$  follow immediately.

The equation obtained for the Temperature as a function of  $\delta$  is:

$$\begin{aligned}
N(\delta) &= -\frac{27}{4} \left( \frac{(4\delta e^{(2\delta)} - e^{(4\delta)} + 1) \left( \frac{(4\delta e^{(2\delta)} - e^{(4\delta)} + 1)e^{(-\delta)}}{\delta e^{(3\delta)} + \delta e^\delta - e^{(3\delta)} + e^\delta} - 2 \right)^2 e^\delta}{\delta e^{(3\delta)} + \delta e^\delta - e^{(3\delta)} + e^\delta} + \right. \\
&\left. \left( \left( \frac{(4\delta e^{(2\delta)} - e^{(4\delta)} + 1)e^\delta}{\delta e^{(3\delta)} + \delta e^\delta - e^{(3\delta)} + e^\delta} - 2 \right)^2 + \frac{4(4\delta e^{(2\delta)} - e^{(4\delta)} + 1)e^\delta}{\delta e^{(3\delta)} + \delta e^\delta - e^{(3\delta)} + e^\delta} - 4 \right) \left( \frac{(4\delta e^{(2\delta)} - e^{(4\delta)} + 1)e^{(-\delta)}}{\delta e^{(3\delta)} + \delta e^\delta - e^{(3\delta)} + e^\delta} - 2 \right) + \right. \\
&\left. 2 \left( \frac{(4\delta e^{(2\delta)} - e^{(4\delta)} + 1)e^\delta}{\delta e^{(3\delta)} + \delta e^\delta - e^{(3\delta)} + e^\delta} - 2 \right)^2 + \frac{4(4\delta e^{(2\delta)} - e^{(4\delta)} + 1)e^\delta}{\delta e^{(3\delta)} + \delta e^\delta - e^{(3\delta)} + e^\delta} - 8 \right) \quad (5) \\
D(\delta) &= \left( \frac{(4\delta e^{(2\delta)} - e^{(4\delta)} + 1)e^{(-\delta)}}{\delta e^{(3\delta)} + \delta e^\delta - e^{(3\delta)} + e^\delta} - 2 \right)^2 \left( \frac{(4\delta e^{(2\delta)} - e^{(4\delta)} + 1)e^\delta}{\delta e^{(3\delta)} + \delta e^\delta - e^{(3\delta)} + e^\delta} - 2 \right)^2 \quad (6)
\end{aligned}$$

and  $T(\delta) = \frac{N(\delta)}{D(\delta)}$ .

Since the pressure is always governed by the vdW equation, it's value can be easily obtained from the aforementioned equations for volume (either) and Temperature.

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The resultant pseudo 3D plot of  $v_g(\delta)$  and  $v_\ell(\delta)$  loci plots are shown here as a function of  $\delta$ . The other two dimensions are the reduced pressure and reduced Temperature, all parameterized by the same  $\delta$ .

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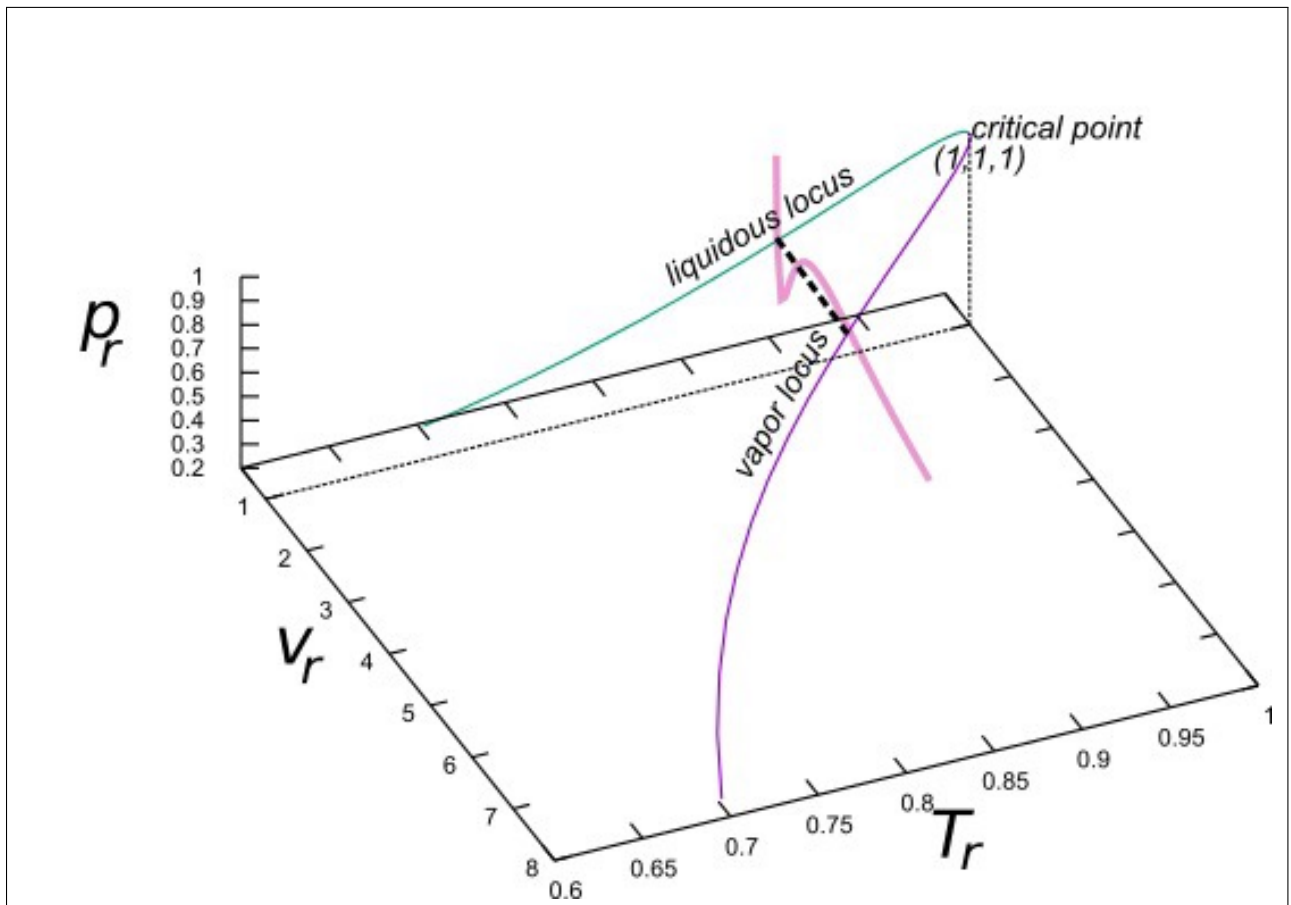


FIG. 3.  $v_g$  and  $v_\ell$  as separate locii with  $T_r$  and  $p_r$ . Data taken from tables shown herein. The third curve is an isotherm of the vdW fluid at  $T_r = 0.90$ .

The table of values which are plotted here are taken from the SageMath coding which is reproduced here in the following three tables.

The first line of data, (1,1,1), has been added manually to the first two tables. This is the critical point. The third curve is a standard vdW isotherm at  $T_r = 0.9$ . Notice that the intersections of the vdW isotherm and the two loci are shown in bold in the tables.

### III. DISCUSSION

Figure 3 is drawn with real data. Therefore, the perfect intersection of the isotherm with the two appropriate loci shows that the Maxwell construction has correctly broken the isotherm at the right points.

### IV. ACKNOWLEDGEMENTS

At the end of the prior submission, I wrote that it would be my last submission. I lied. Mea Culpa. Again, I want to thank my wife for putting up with my obvious obsession with this material.

Between gnuplot and inkscape, I could not resist the temptation of improving the last plot in that prior submission. Even this submission, which is much clearer than the earlier 3D plot, lacks something. Most likely this is the last!

| $T_r$          | $v_r^g$       | $p_r$          |
|----------------|---------------|----------------|
| 1              | 1             | 1              |
| 0.99889        | 1.0709        | 0.99557        |
| 0.99558        | 1.1509        | 0.98240        |
| 0.99011        | 1.2414        | 0.96090        |
| 0.98256        | 1.3439        | 0.93169        |
| 0.97303        | 1.4603        | 0.89560        |
| 0.96166        | 1.5927        | 0.85365        |
| 0.94859        | 1.7434        | 0.80692        |
| 0.93399        | 1.9153        | 0.75658        |
| 0.91802        | 2.1119        | 0.70380        |
| <b>0.90088</b> | <b>2.3368</b> | <b>0.64970</b> |
| 0.88275        | 2.5948        | 0.59534        |
| 0.86380        | 2.8912        | 0.54165        |
| 0.84423        | 3.2323        | 0.48944        |
| 0.82419        | 3.6254        | 0.43937        |
| 0.80385        | 4.0794        | 0.39196        |
| 0.78335        | 4.6044        | 0.34759        |
| 0.76284        | 5.2126        | 0.30650        |
| 0.74241        | 5.9182        | 0.26884        |
| 0.72219        | 6.7381        | 0.23461        |
| 0.70226        | 7.6923        | 0.20378        |

TABLE I. Gaseous locus

| $T_r$          | $v_r^l$        | $p_r$          |
|----------------|----------------|----------------|
| 1              | 1              | 1              |
| 0.99889        | 0.93716        | 0.99557        |
| 0.99558        | 0.88134        | 0.98240        |
| 0.99011        | 0.83168        | 0.96090        |
| 0.98256        | 0.78743        | 0.93169        |
| 0.97303        | 0.74794        | 0.89560        |
| 0.96166        | 0.71264        | 0.85365        |
| 0.94859        | 0.68105        | 0.80692        |
| 0.93399        | 0.65274        | 0.75658        |
| 0.91802        | 0.62732        | 0.70380        |
| <b>0.90088</b> | <b>0.60448</b> | <b>0.64970</b> |
| 0.88275        | 0.58391        | 0.59534        |
| 0.86380        | 0.56538        | 0.54165        |
| 0.84423        | 0.54865        | 0.48944        |
| 0.82419        | 0.53353        | 0.43937        |
| 0.80385        | 0.51984        | 0.39196        |
| 0.78335        | 0.50743        | 0.34759        |
| 0.76284        | 0.49617        | 0.30650        |
| 0.74241        | 0.48593        | 0.26884        |
| 0.72219        | 0.47661        | 0.23461        |
| 0.70226        | 0.46812        | 0.20378        |

TABLE II. Liquid locus

| $T_r$      | $v_r$          | $p_r$          |
|------------|----------------|----------------|
| 0.9        | 0.40000        | 17.250         |
| 0.9        | 0.50000        | 2.4000         |
| <b>0.9</b> | <b>0.60000</b> | <b>0.66667</b> |
| 0.9        | 0.70000        | 0.42301        |
| 0.9        | 0.80000        | 0.45536        |
| 0.9        | 0.90000        | 0.53159        |
| 0.9        | 1.0000         | 0.60000        |
| 0.9        | 1.1000         | 0.65110        |
| 0.9        | 1.2000         | 0.68590        |
| 0.9        | 1.3000         | 0.70761        |
| 0.9        | 1.4000         | 0.71939        |
| 0.9        | 1.5000         | 0.72381        |
| 0.9        | 1.6000         | 0.72286        |
| 0.9        | 1.7000         | 0.71804        |
| 0.9        | 1.8000         | 0.71044        |
| 0.9        | 1.9000         | 0.70089        |
| 0.9        | 2.0000         | 0.69000        |
| 0.9        | 2.1000         | 0.67822        |
| 0.9        | 2.2000         | 0.66588        |
| 0.9        | 2.3000         | 0.65323        |
| 0.9        | 2.4000         | 0.64046        |
| 0.9        | 2.5000         | 0.62769        |
| 0.9        | 2.6000         | 0.61504        |
| <b>0.9</b> | <b>2.7000</b>  | <b>0.60256</b> |
| 0.9        | 2.8000         | 0.59032        |
| 0.9        | 2.9000         | 0.57835        |
| 0.9        | 3.0000         | 0.56667        |
| 0.9        | 3.1000         | 0.55529        |
| 0.9        | 3.2000         | 0.52309        |
| 0.9        | 3.5000         | 0.51300        |
| 0.9        | 3.6000         | 0.50321        |
| 0.9        | 3.7000         | 0.49373        |
| 0.9        | 3.8000         | 0.48455        |
| 0.9        | 3.9000         | 0.47566        |
| 0.9        | 4.0000         | 0.46705        |
| 0.9        | 4.1000         | 0.45870        |
| 0.9        | 4.2000         | 0.45062        |
| 0.9        | 4.3000         | 0.44279        |

TABLE III. Pure van der Waals isotherm at  $T_r = 0.90$

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