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The van der Waals Equation as a Cubic

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The van der Waals (from his thesis of 1873) equation is a cubic in the molar volume. Since this is the first equation of state studied in chemistry and physics more complicated than the ideal gas equation, it is noteworthy that the solution of this cubic is rarely if ever addressed.

When (lowering the temperature) the two imaginary roots coalesce with the real root of the van der Waals equation we have the critical point. At Kelvin temperatures below T_c , the equation has three real roots; we explore obtaining those roots to aid in the Maxwell construction required to obtain the vapor pressure.

I. INTRODUCTION

It is well known that the van der Waals equation is a cubic equation in v whose solution is rarely addressed [1, 10, 11]. There no longer exists a reason for this lack of familiarity, as computer assisted calculus programs have made it simpler than ever to manipulate the complicated expressions that constitute the traditional cubic polynomial solutions (*vide supra*). Rather than trusting a computer calculus program, however, this paper introduces the complete solution to the cubic using elementary algebra.

In an age in which algebra inclusion [4] in high school curricula is being questioned, it seems reasonable to argue that the two years of calculus learning prior to studying physical chemistry is worth the effort. Therefore, avoiding the phrase "integration by parts" in Winn's paper [11] and avoiding the cubic solution which employs only algebra (not counting DeMoivre's theorem) seems bad pedagogy. Instead, we should emphasize the usefulness of what we've forced students to learn, validating the prerequisite structure that differentiates STEM education from other fields.

Since this solution is rather long-winded, this paper has been written in sufficient detail that it should be able to be read without resorting to paper and pencil.

II. PRELIMINARIES

Consider that the Maxwell construction [6] (*vide infra*) requires that one has the three roots (if $T < T_c$) of the cubic van der Waals equation so that one can integrate ($p_{vdW} - p_{trial}$) dv from the first (smallest) to the second, and from the second to the third (largest) root (or *vice versa*). Setting the sum of these two integrals equal to zero gives an equation whose only remaining variable is the pressure (p_{trial}); that solution pressure is the predicted vapor pressure.

The reduced van der Waals equations $p_r(v_r, T_r)$ in the reduced variable scheme, i.e., $T_r = \frac{T}{T_c}$, $p_r = \frac{p}{p_c}$ and $v_r = \frac{v}{v_c}$, where the subscript c refers to the critical temperature, pressure and/or molar volume and r , similarly, refers to the appropriate reduced variables, is

$$p_r(v_r, T_r) = \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2} \quad (1)$$

We will derive the solution to the cubic, and then use that solution in the Maxwell construction searching for the vapor pressure.

III. THE GENERAL CUBIC EQUATION [7]

The general cubic equation is

$$x^3 + a_1x^2 + a_2x + a_3 = 0 \quad (2)$$

which Cardan transformed using

$$x = y - \frac{a_1}{3}$$

i.e.,

$$\left(y - \frac{a_1}{3}\right)^3 + a_1\left(a_1y - \frac{a_1}{3}\right)^2 + a_2\left(y - \frac{a_1}{3}\right) + a_3 = 0$$

which expands to

$$y^3 + \left(a_2 - \frac{a_1^2}{3}\right)y = -\frac{2}{27}a_1^3 + \frac{a_1a_2}{3} - a_3 \quad (3)$$

which we write in the form:

$$z^3 + \eta z + q = 0 \quad (4)$$

This (Equation 4) is called a "reduced" cubic form (the mathematicians and chemists use the term "reduced" differently). We will solve the "reduced" equation for $z \rightarrow y$ and then take the solutions and convert them back to x at the end of the computation.

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IV. THE VAN DER WAALS EQUATION AS A CUBIC

The van der Waals gas equation can be expanded to

$$v_r^3 - \left(\frac{8T_r}{p_r} + 1\right) \frac{v_r^2}{3} + \frac{9v_r}{3p_r} - \frac{1}{p_r} = 0$$

which is of the form

$$v_r^3 + a_1 v_r^2 + a_2 v_r + a_3 = 0 \quad (5)$$

In terms of the original cubic equation (Equation 2), we have

$$a_1 = -\frac{\frac{8T_r}{p_r} + 1}{3} \quad (6)$$

$$a_2 = \frac{3}{p_r} \quad (7)$$

and finally

$$a_3 = -\frac{1}{p_r} \quad (8)$$

In terms of the reduced cubic Equation 4, we have

$$\eta = a_2 - \frac{a_1^2}{3} \quad (9)$$

and

$$q = -\left(\frac{2}{27}a_1^3 - \frac{a_1 a_2}{3} + a_3\right) \quad (10)$$

Consider the known equation

$$4\cos^3\vartheta - 3\cos\vartheta - \cos 3\vartheta = 0 \quad (11)$$

(DeMoivre's theorem gave us Equation 11) and the aforementioned prototype "reduced" cubic:

$$z^3 + \eta z = q \quad (12)$$

where η and q are constants (see Equation 4). Their commonality suggests a procedure, e.g., defining

$$z = u \cos\vartheta$$

where u is to be chosen to force the two forms into conformance. To carry out this agenda, we cube our expression for z and substitute the result into our reduced cubic, i.e.,

$$u^3 \cos^3\vartheta + \eta u \cos\vartheta - q = 0$$

and divide both sides by u^3 . Multiplying by 4, we obtain

$$4\cos^3\vartheta + \frac{4\eta}{u^2} \cos\vartheta - \frac{4q}{u^3} = 0$$

which suggests writing

$$\frac{4\eta}{u^2} = -3$$

so that

$$u = \sqrt{\frac{4\eta}{-3}}$$

becomes the choice we have to make. Then,

$$4\cos^3\vartheta + \frac{4\eta}{u^2} \cos\vartheta - \frac{4q}{\sqrt{\frac{4\eta}{-3}}^3} = 0$$

which is a mimic of the equation we are trying to solve.

$$4\cos^3\vartheta - 3\cos\vartheta + \frac{3q}{\eta \sqrt{\frac{4\eta}{-3}}} = 0$$

so, we obtain

$$\cos 3\vartheta = -\frac{3q}{\eta \sqrt{\frac{4\eta}{-3}}}$$

or

$$\cos 3\vartheta = -\frac{3q}{2\eta \sqrt{\frac{\eta}{-3}}} = -\frac{3q}{2\eta} \sqrt{\frac{-3}{\eta}}$$

which leads us to values of ϑ for which this equation will be true.

We have

$$\vartheta = \frac{1}{3} \cos^{-1} \left[-\frac{3q}{2\eta} \sqrt{\frac{-3}{\eta}} \right]$$

which means, back-substituting

$$u \cos\vartheta = \sqrt{\frac{4\eta}{-3}} \cos \left[\frac{1}{3} \cos^{-1} \left(-\frac{3q}{2\eta} \sqrt{\frac{-3}{\eta}} \right) \right]$$

or, in terms of the reduced cubic equation we have

$$z = y = \sqrt{\frac{4\eta}{-3}} \cos \left[\frac{1}{3} \cos^{-1} \left(-\frac{3q}{2\eta} \sqrt{\frac{-3}{\eta}} \right) \right] \equiv z_1$$

Dividing this $z - z_1$ into the original reduced cubic would yield a quadratic which then itself would be soluble, i.e.,

$$\frac{z^3 + \eta z - q}{(z - z_1)} = \frac{z^3 + \eta z - q}{z - \sqrt{\frac{4\eta}{-3}} \cos \left[\frac{1}{3} \cos^{-1} \left(-\frac{3q}{2\eta} \sqrt{\frac{-3}{\eta}} \right) \right]}$$

Synthetic division yields

$$z^2 + z_1 z + (\eta + z_1^2) - \frac{((\eta + z_1^2) z_1 - q)}{z - z_1}$$

where the numerator of the residual is zero!

The other two roots of

$$z^2 + z_1 z + (\eta + z_1^2) = 0$$

are

$$z_2 = \frac{-z_1 + \sqrt{z_1^2 - 4(\eta + z_1^2)}}{2}$$

and

$$z_3 = \frac{-z_1 - \sqrt{z_1^2 - 4(\eta + z_1^2)}}{2}$$

which lead to the second and third roots of the “reduced” cubic.

1. back substituting

We thus have for the original cubic we started this discussion with: $x^3 + a_1 x^2 + a_2 x + a_3 = 0$, Equation 2, (with v_r rather than x):

$$v_{r\ell} = \sqrt{\frac{4\eta}{-3}} \cos \left[\frac{1}{3} \cos^{-1} \left(\frac{3q}{4\eta} \sqrt{\frac{-3}{\eta}} \right) \right] - \frac{a_1}{3}$$

(corresponding to the z_1 root of the “reduced” cubic) where we have employed Equation 5 and its similar form Equation 2 to return from the reduced form to the ultimately desired v form of the cubic van der Waals equation we are trying to solve.

We had $\eta = a_2 - \frac{a_1^2}{3}$ (Equation 9) and $q = -\frac{2}{27}a_1^3 + \frac{a_1 a_2}{3} - a_3$ (Equation 10). It is clear that substituting these into our equation for v would lead to a fearful mess. And then the substitutions which was Equation 6, Equation 7 and finally Equation 8 make evaluation possible. Unfortunately, the resultant equation is enormous.

A similar discussion for each of the other two roots leads to explicit solutions for all three roots.

V. THE MAXWELL CONSTRUCTION [6]

To achieve the Maxwell construction (see Figure 1) one needs to integrate $p_r dv_r$ from the lowest root to the central root, and from the central root to the largest root, and set these two integrals equal to each other (except for the sign, i. e., using the absolute magnitude of the integrals) thereby obtaining an equation for p_{trial} (to be called p_r^{vp} after solution) which we declare to be the vapor pressure for this particular isotherm. Alternatively, one could write $\int (p_{vdW} - p_{trial}) dv = 0$ with the rule that $p_{trial} \rightarrow p_r^{vp}$ when the equation is true.

The integral itself is trivial, i.e.,

$$\int_{v_g}^{v_\ell} p_r dv_r = \int_{v_g}^{v_\ell} \left(\frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2} \right) dv_r - \frac{8T_r}{3} \ln \left(\frac{(3v_{r\ell} - 1)}{(3v_{r_g} - 1)} \right) + \frac{3}{v_{r\ell}} - \frac{3}{v_{r_g}} \quad (13)$$

This must be set equal to the equivalent path integral from “ g ” to “ ℓ ” using the trial vapor pressure, i.e.,

$$\int_g^\ell p_{trial} dv = p_r^{vp} (v_\ell - v_g) \quad (14)$$

so the equation whose solution yields the vapor pressure is

$$\frac{8T_r}{3} \ln \left(\frac{(3v_{r\ell} - 1)}{(3v_{r_g} - 1)} \right) + \frac{3}{v_{r\ell}} - \frac{3}{v_{r_g}} = p_r^{vp} (v_{r\ell} - v_{r_g}) \quad (15)$$

This equation depends on a trial pressure which itself is adjusted until the equality holds ($p_{trial} = p_r^{vp}$). However, as noted by Lekner[5] [8], this can be written as

$$\frac{8T_r}{3} \ln \left(\frac{(3v_{r\ell} - 1)}{(3v_{r_g} - 1)} \right) + \frac{3}{v_{r\ell}} - \frac{3}{v_{r_g}} = p_{trial} (v_{r\ell} - v_{r_g}) = \left(\frac{8T_r}{3v_{r\ell} - 1} - \frac{3}{v_{r\ell}^2} \right) (v_{r\ell} - v_{r_g}) \quad (16)$$

or

$$\frac{8T_r}{3} \ln \left(\frac{(3v_{r\ell} - 1)}{(3v_{r_g} - 1)} \right) + \frac{3}{v_{r\ell}} - \frac{3}{v_{r_g}} = \left(\frac{8T_r}{3v_{r_g} - 1} - \frac{3}{v_{r_g}^2} \right) (v_{r\ell} - v_{r_g}) \quad (17)$$

since the trial pressure is the same at “ ℓ ” and “ g ”, or

$$\frac{8T_r}{3} \ln \left(\frac{(3v_{r\ell} - 1)}{(3v_{r_g} - 1)} \right) + \frac{3}{v_{r\ell}} - \frac{3}{v_{r_g}} = \left(\frac{8T_r}{3v_{r\ell} - 1} - \frac{3}{v_{r\ell}^2} \right) v_{r\ell} - \left(\frac{8T_r}{3v_{r_g} - 1} + \frac{3}{v_{r_g}^2} \right) v_{r_g} \quad (18)$$

or “vice versa”. This last equation becomes

$$\frac{8T_r}{3} \ln \left(\frac{(3v_{r\ell} - 1)}{(3v_{r_g} - 1)} \right) + \frac{3}{v_{r\ell}} - \frac{3}{v_{r_g}} = \left(\frac{8T_r v_{r\ell}}{3v_{r\ell} - 1} - \frac{3}{v_{r\ell}} \right) - \left(\frac{8T_r v_{r_g}}{3v_{r_g} - 1} + \frac{3}{v_{r_g}} \right) \quad (19)$$

which becomes, segregating variables,

$$\frac{8T_r}{3} \ln(3v_{r_\ell} - 1) - \left(\frac{8T_r v_{r_\ell}}{3v_{r_\ell} - 1} - \frac{6}{v_{r_\ell}} \right) = \frac{8T_r}{3} \ln(3v_{r_g} - 1) - \left(\frac{8T_r v_{r_g}}{3v_{r_g} - 1} \right) + \frac{6}{v_{r_g}} \quad (20)$$

which is à la Sage,

```
var ('Tr , vr , vg , vl , pvp , pvp ')
assume (vg >0)
assume (vl > vg )
assume ((3* vl -1) >0)
assume ((3* vg -1) >0)
p ( vr , Tr ) = 8* Tr / (3* vr -1) -3/ vr ^2
EQN1 ( Tr ,g , l ) = integrate ( p ( vr , Tr ) ,vr ,vg , vl )
print (" EQN1 = ", EQN1 )
eqn2 (g ,l , Tr ) = EQN1 ( Tr ,vg , vl ) - ( p (vl , Tr ) *l - p (vg , Tr ) * vg )
print (" eqn2 = ", eqn2 , " and the latex :")
eqn3(vp,vl,Tr) = eqn2 (vg ,vl , Tr ) . expand ()
print(eqn3(vp,vl,Tr))
latex ( eqn3 )
```

$$(vp, vl, Tr) \mapsto -\frac{8}{3} Tr \log(3vg - 1) + \frac{8}{3} Tr \log(3vl - 1) + \frac{8 Tr vg}{3vg - 1} - \frac{8 Tr vl}{3vl - 1} - \frac{6}{vg} + \frac{6}{vl}$$

We are looking for the best form for “solving” this equation, so we re-write it as

$$\frac{8T_r}{3} \ln \left(\frac{3v_{r_\ell} - 1}{3v_{r_g} - 1} \right) - \frac{8T_r v_{r_\ell}}{3v_{r_\ell} - 1} + \frac{6}{v_{r_\ell}} + \frac{8T_r v_{r_g}}{3v_{r_g} - 1} + \frac{6}{v_{r_g}} = 0 \quad (21)$$

or

$$\frac{8T_r}{3} \ln \left(\frac{3v_{r_\ell} - 1}{3v_{r_g} - 1} \right) - 8T_r \left(\frac{v_{r_\ell}}{3v_{r_\ell} - 1} + \frac{v_{r_g}}{3v_{r_g} - 1} \right) + \frac{6}{v_{r_\ell}} + \frac{6}{v_{r_g}} = 0 \quad (22)$$

This is a transcendental equation [9].

VI. SOLVING THE MAXWELL CONSTRUCTION GENERATED EQUATION

To proceed one fixes T_r , chooses a trial pressure, obtains the two relevant reduced volumes, one for liquid, one for gas, evaluates the left hand side of Equation 22, compares it to zero; adjusting the trial pressure until the equation yields zero results in the final trial pressure being declared the vapor pressure at that temperature.

Having proved insoluble using the tools (Maxima, Sage) available to the author, the computations were carried out using a spreadsheet (https://docs.google.com/spreadsheets/d/1fmfaj1sYURADmGw05hma8_ujFtzE5bgDZMZ2iH5XAH8/pubhtml). Some more details concerning goal seeking for the solution can be found at [2] A few of the values obtained numerically for the vapor pressures (p_r^{vp} in reduced terms) are displayed in Table 1. Figure 2 is a plot of this vapor pressure data.

On any given isotherm, the pressure (if $T_r < 1$) at which gas and liquid exist in equilibrium (p_r^{vp}) intersects

Datum	T_r	p_r^{vp}
1	1	1
2	0.9	0.67517
3	0.8	0.49533
4	0.7	0.34429
5	0.6	0.21505

TABLE I. The relation between the vapor pressure and the temperature of the van der Waals fluid as obtained using a spreadsheet to obtain the data presented here.

the isotherm itself at two points.. The locus of these volumes represent a ruled surface in the 3-D $p_r - v_r - T_r$ space; this surface can be projected onto the $p_r - v_r$ plane, giving rise to Figure 3, which is the familiar coexistence locus (absent tie-lines).

It would have been nice had we obtained an analytic solution of the vapor pressure as a function of temperature, i.e., $p_r^{vp}(T_r)$ which would have allowed us to take the derivative of this function with respect to temperature, and, knowing the Δv_r for a given temperature (from two of the roots of the cubic, i.e., not the central root), ob-

tained the heat of vaporization. Sadly, this did not come about.

The use of computer assisted calculus programs alluded to above for manipulation of the equations considered in this paper reveals some inherent problems which the reader is forewarned about. Specifically, the solution of Equation 13 fails using Maxima and SageMath (or at

least doesn't help me in understanding the produced solution). It is not known what Mathematica and Maple (or others) do with this equation. Further, for several values of the pressure and temperature, the aforementioned programs reported imaginary values of the reduced volumes, at temperatures below the critical temperature. The reported vapor pressures reported here had to be obtained by explicit computation using a spreadsheet.

VII. FIGURES

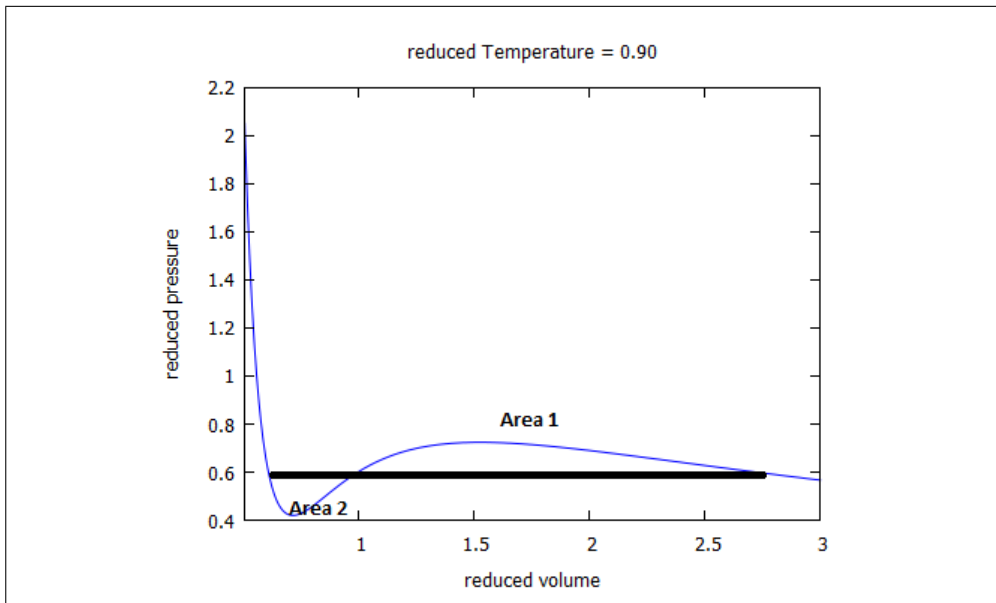


FIG. 1. The Maxwell construction needed to determine the vapor pressure. Here, we choose a working (trial) pressure, integrate $(p_{vdW} - p_{trial})dv$ from the smallest to the intermediate intersection (Area 2), and from the intermediate to the largest intersection (Area 1), and compare the two areas. Adjusting the pressure until the areas are equal but opposite in sign fixes that resultant trial pressure as the vapor pressure. Technically, this is $\int (p_{vdW} - p_{trial}) dv \rightarrow 0$ not to be confused with the circular integral $\oint p_r dv_r$ which would be a net work. This happens to be zero for a different reason in this case, when one uses the van der Waals path going and the constant pressure path when returning, but work is not a state property and this integral generally is not zero.

VIII. REFERENCES

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- [4] Andrew Hacker. The math myth. 2015. <http://themathmyth.net/>.
- [5] John Lekner. Parametric solution of the van der waals liquid-vapor coexistence curve. *Am. J. Phys.*, 50:161, 1982.
- [6] J. C. Maxwell. On the dynamical evidence of the molecular constitution of bodies. *Nature*, 11:357, 1875.
- [7] Paul J. Nahin. *An Imaginary Tale The Story of $\sqrt{-1}$* . Princeton University Press, Princeton, NJ, 1998.
- [8] When this manuscript was originally written (with an error in it[3]) I had not stumbled upon Lekner's paper. In reading his paper I discovered my own error, and revised the manuscript so that it had its current form which you are now reading. Some 400 people have downloaded the original (incorrect) paper, and I apologize copiously to them for my error. Since this paper was also submitted to both *J. Chem. Ed.* and *Am. J. Phys.*, and rejected without refereeing, I believe that had it been allowed proper refereeing the error would have been discovered.
- [9] At this point, I need to confess that this equation is not the one I used in the original paper on this topic. In reading Lekner's [5] paper, I started to doubt what I had written, and in going back, discovered a calculus error (*mea culpa*), and rushed to re-write the paper without the error. In the process, I found myself unable to reproduce Lekner's result, specifically eliminating T_r from the equivalent equation. If, indeed, I've made a different mistake this time, I would appreciate it if you would tell me!
- [10] G. Soave. Direct calculation of pure-compound vapour pressures through cubic equations of state. *Fluid Phase Equilibria*, 31:203, 1986.

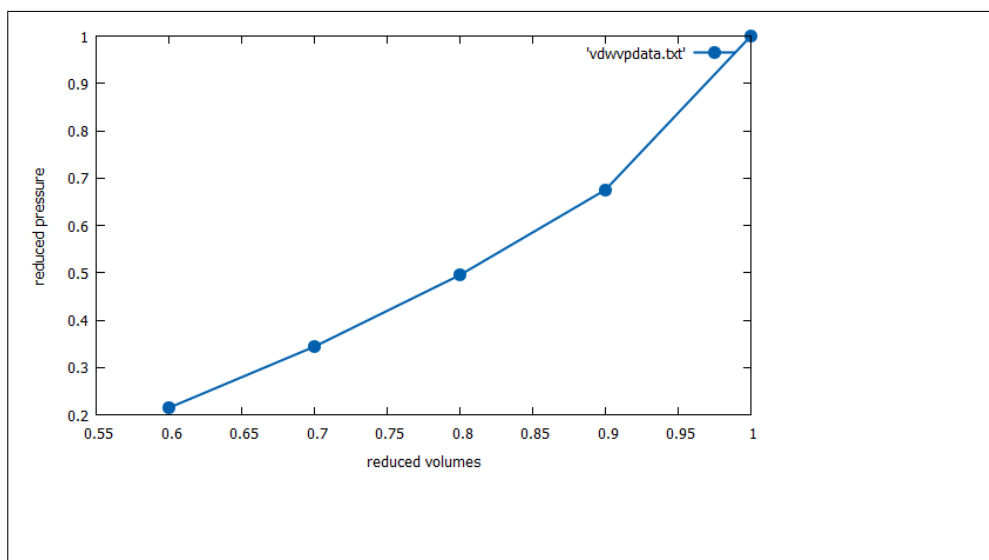


FIG. 2. A plot of the data in Table 1 showing the typical vapor pressure versus temperature behavior. Of course, the van der Waals gas knows nothing about solids.

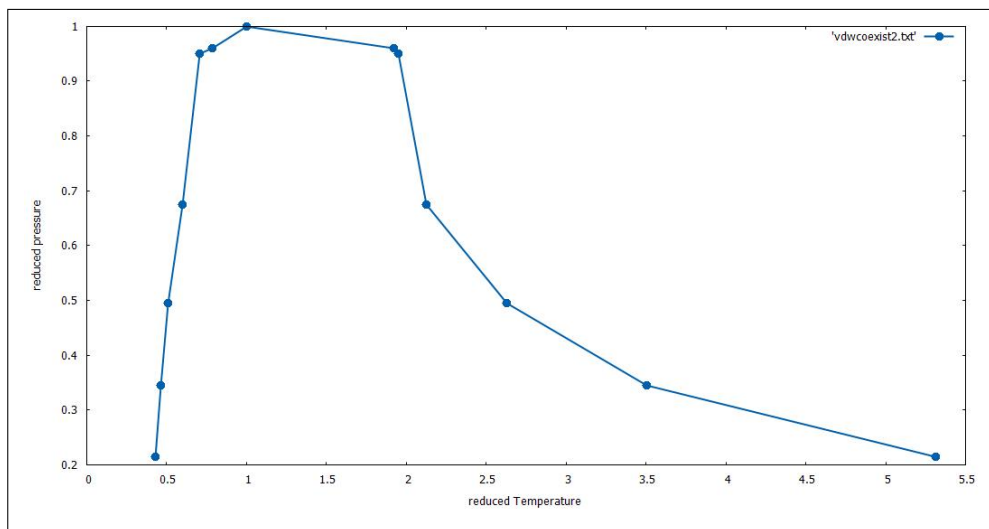


FIG. 3. The locus of gas and vapor molar volumes when the two coexist projected onto the $p_r - v_r$ plane. The tie lines are not shown, but two data points at the same vapor pressure are “connected” i.e., they represent the volumes, pressure (and temperature) of the coexisting liquid and gaseous phases.

[11] John S. Winn. The fugacity of a van der waals gas.

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