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Plotting the van der Waals Fluid in pseudo-3D and the Maxwell Construction*

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The van der Waals (from his thesis of 1873) equation is a cubic in the molar volume. Plotting the equation in pseudo 3 dimensions is quite simple to do, but including tie lines is quite difficult. Employing the solutions to the cubic van der Waals equation, the tie lines are readily available and can be easily incorporated into the aforementioned 3D plots.

I. INTRODUCTION

A. Intro 1

After studying the ideal gas, one usually is introduced to non-ideal behavior by means of the van der Waals gas, whose traditional molar form is $(p + a/v^2)(v - b) = RT$. Two competing effects are accounted for in this equation of state, the attraction between molecules (a) and the finite volume of molecules (b), although these associations are not explicitly derivable from first principles. Since this equation of state is continuous with continuous derivatives when viewed as $p(v, T)$, it clearly can not show or even imitate the behavior of a real fluid below the critical temperature without some *ad hoc* adjustments.

But it does display an interesting behavior with temperature; it has a critical temperature above which the pressure monotonically decreases with volume at fixed temperature. Below the critical temperature, the isotherms show pathological behavior which is clearly non-physical. When plotted, isotherms at temperatures below the critical temperature show a local minimum and a local maximum; this behavior of the extrema in the vicinity of the critical temperature is usually used to obtain the relationship between the two constants, a and b , and the critical constants, v_c , p_c and T_c . The derivation is a standard one found in all textbooks of physical chemistry which cover gases, liquids and solids.

Further, the van der Waals equation can be recast into a form in which the molecular constants (a and b) are suppressed via a reduced form in which pressure, volume and temperature are replaced by reduced variables related to the original ones by the critical values of the same variables. This leads to the concept of a universal equation of state, i.e., one which would apply to all substances. This turns out to be a non-viable task, but the idea is propounded anyway.

Finally, the concept generally referred to as continuity of states which, in large measure serves as justification for studying this equation of state, is introduced implying that fluids, both gases and liquids share some commonality of behavior.

Since no substance actually obeys the van der Waals equation, interest in teaching and learning about it addresses the analytic nature of the van der Waals equation and the actual behavior of phases of pure substances (van der Waals arguments have been extended to mixtures (and polymer mixtures) ([5]) also) as compared to the predictions of this particular equation of state. Thus the van der Waals equation has no discontinuities in the $p(v, T)$ space, but the real isotherm of any substance below its critical temperature shows two values of the volume in which the first derivative of the pressure with respect to the volume is discontinuous. Between these two volumes, the pressure does not change with volume, something clearly not included in the van der Waals equation. The pressure at which this occurs is, of course, the vapor pressure of the liquid. The discontinuity at the smallest volume corresponds to the volume of the liquid as it stays in equilibrium with the vapor (gas) represented by the other larger volume at the other discontinuity.

In order to reconcile the two views, the van der Waals continuous picture, and reality, the Maxwell construction is invoked. This algorithm consists of imagining a temporary pressure, finding the areas of the two loops this pressure demarcates, and adjusting the value of this pressure until the areas between the two loops and the constant pressure line are equal (and opposite in sign, i.e., cancel).

B. Intro 2

The van der Waals equation is a cubic equation in v (the molar volume) whose solution is rarely addressed ([1, 3, 6]); cubics are difficult to solve and not part of the normal armamentarium of physical chemistry students. Further, one needs analytical solutions, not numeric ones to actually carry out the Maxwell construction and obtain the vapor pressure at any predetermined temperature. There no longer exists a reason for avoiding the details of this computation, as computer assisted calculus programs and spreadsheets have made it simple to manipulate the complicated expressions that constitute the traditional cubic polynomial solutions (*vide supra*).

The Maxwell construction [4] (*vide infra*) requires that one has the three roots (if $T < T_c$) of the cu-

* This is the second of two articles published on this topic[2].

bic 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), whereupon one adds these two integrals together and forces their sum to zero through an appropriate choice of the pressure p_{trial} (at fixed and predetermined temperature).

With the roots in hand, one can produced appropriate tie lines on pseudo 3D plots of the van der Waals equation, leading to better understanding of the relationships between fluids (liquids and gases) and their positions in the phase diagram of a pure substance.

II. PRECURSOR TO GENERATING ROOTS OF THE CUBIC EQUATION

The reduced 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

$$v_r^3 + a_1 v_r^2 + a_2 v_r + a_3 = 0 \quad (1)$$

In terms of this formulation, one associates

$$a_1 = -\frac{8T_r + 1}{3} \quad (2)$$

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

and finally

$$a_3 = -\frac{1}{p_r} \quad (4)$$

In terms of the reduced cubic used as a precursor to actually solving the cubic we define

$$\eta = a_2 - \frac{a_1^2}{3} \quad (5)$$

and

$$q = -\left(+\frac{2}{27}a_1^3 - \frac{a_1 a_2}{3} + a_3\right) \quad (6)$$

Then, as shown previously ([2]), the first root is:

$$v_{r_1} = \sqrt{\frac{4\eta}{-3}} \cos \left[\frac{1}{3} \cos^{-1} \left(\frac{3q}{4\eta} \sqrt{\frac{-3}{\eta}} \right) \right] - \frac{a_1}{3}$$

which is, upon back substitution:

$$v_{r_1}(T_r, p_r) = \frac{2 \sqrt{\frac{(-\frac{8T_r}{p_r} - 1)^2}{27} - \frac{3}{p_r}} \cos \left(\frac{\arccos \left(\frac{3^{\frac{3}{2}} i \left(2 \left(\frac{-\frac{8T_r}{p_r} - 1}{\frac{p_r}{27}} \right)^3 - \frac{-\frac{8T_r}{p_r} - 1}{\frac{p_r}{3}} - \frac{1}{p_r}} \right)}{2 \left(\frac{3}{p_r} - \left(\frac{-\frac{8T_r}{p_r} - 1}{\frac{p_r}{27}} \right)^2 \right)^{\frac{3}{2}}} \right)}{3} \right)}{\sqrt{3}} - \frac{-\frac{8T_r}{p_r} - 1}{9}$$

Unfortunately, this resultant equation is enormous. More important is the fact that this root (and the others) are not in a form which can be used as limits on definite integrals, as required for the Maxwell construction.

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

III. THE MAXWELL CONSTRUCTION

In order to identify the proper p_r to use in this equation, we need to carry out the Maxwell construction [4] integrating the reduced pressure difference from the first

(as yet unknown) root to the central one (also unknown) and compare that integral to the from the the central to the largest (third) root, both of which are still unknown. Analytically, this is

$$\int_{small}^{middle} (p_{vdW} - p_{trial}) dv_r + \int_{middle}^{large} (p_{vdW} - p_{trial}) dv_r = 0$$

To make them known, choose that reduced pressure which makes these two areas equal (and opposite in sign) to each other (and the sum of the two areas equal to zero, since one is negative, the other positive) at this particular temperature. We then repeat the process for any other temperatures of interest.

The equation we are attempting to force equal to zero is:

$$\frac{8T_r}{3} \ln(3v_{r_\ell} - 1) - \left(\frac{8T_r v_{r_\ell}}{3v_{r_\ell} - 1} - \frac{6}{v_{r_\ell}} \right) - \left[\frac{8T_r}{3} \ln(3v_{r_g} - 1) - \left(\frac{8T_r v_{r_g}}{3v_{r_g} - 1} \right) + \frac{6}{v_{r_g}} \right] = 0 \quad (7)$$

and its solution is obtained by goal seeking on the value of the pressure (p_r) as the independent variable (all at fixed, pre-chosen temperature) which makes the equation true. Here, the smallest root corresponds to v_ℓ and the largest root corresponds to v_g . So, one chooses a T_r and a p_r , obtains the two relevant roots, substitutes them into Equation 7, and compares the value to zero. Choosing other values of p_r one continues until the zero value is obtained.

A few of the values obtained numerically for the vapor pressures (vp_r in reduced terms) are displayed in the on-line spreadsheet *vide supra*. The second column is the pressure, and the last column is Equation 7. This

last column is the target, and the control variable for the goal seeking is the pressure entry (second column), all at a given temperature. The detailed spreadsheet which “solves” this equation (https://docs.google.com/spreadsheets/d/1fmfaj1sYURADmGw05hma8_ujFtzE5bgDZM22iH5XAH8/pubhtml) uses goal seeking to obtain the solution of either the vapor pressure at a given temperature, or temperature for a given vapor pressure.

IV. PLOTTING THE VAN DER WAALS EQUATION IN 3D INCLUDING TIE LINES

Given the data from the spreadsheet one can easily plot the connecting lines (tie-lines) using gnuplot.

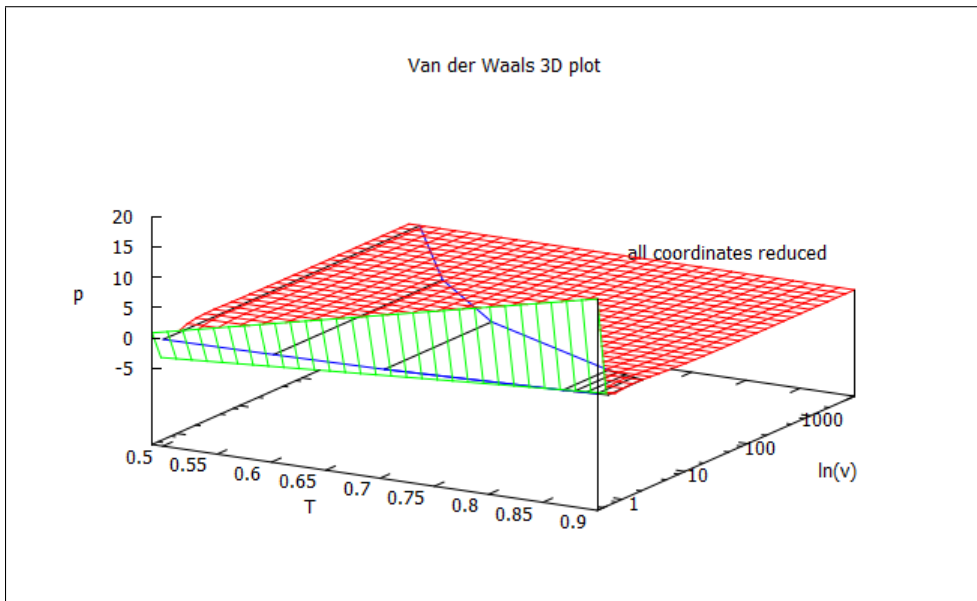


FIG. 1. A 3D plot of the van der Waals equation including tie lines.

Further, again using gnuplot, it is easy to construct the fence plot shown herein. Here is the gnuplot input data:

```
unset key

set view 35,140
set xrange [0.6 : 0.9]#Temperature (T)
set yrange [0.34 : 5.4]#Volume
set zrange [-1 : 1]#pressure
set iso 100
```

```

set samp 100
set xlabel "T_r"
set ylabel "v_r (per mole)"
set zlabel "p_r"
yf(y, a) = (abs(y-a)<.002) ? 1. : NaN# .02 originally

vdw(x,y) = 8*x/(3*y-1)-3/(y**2)

set style function impulses
#tie lines truncated on high vallues to stay inside drawing

#
      T      v_g      p      T      v_l      p
set arrow 1 from 0.9, 2.12507, 0.675167005374748 to 0.9, 0.5986, 0.675167005374748 nohead
set arrow 2 from 0.8, 2.62777, 0.495328223104105 to 0.8, 0.512, 0.495328223104105 nohead
set arrow 3 from 0.7, 3.50626, 0.344286195055004 to 0.7, 0.4641, 0.344286195055004 nohead
set arrow 4 from 0.6, 5.31219, 0.215049013324912 to 0.6, 0.4312, 0.215049013324912 nohead

set arrow 5 from 0.9, 2.12507, 0.675167005374748 to 0.8, 2.62777, 0.495328223104105 nohead lt rgb "c"
set arrow 6 from 0.8, 2.62777, 0.495328223104105 to 0.7, 3.50626, 0.344286195055004 nohead lt rgb "c"
set arrow 7 from 0.7, 3.50626, 0.344286195055004 to 0.6, 5.31219, 0.215049013324912 nohead lt rgb "c"

set arrow 8 from 0.9, 0.5986, 0.675167005374748 to 0.8, 0.512, 0.495328223104105 nohead lt rgb "c"
set arrow 9 from 0.8, 0.512, 0.495328223104105 to 0.7, 0.4641, 0.344286195055004 nohead lt rgb "c"
set arrow 10 from 0.7, 0.4641, 0.344286195055004 to 0.6, 0.4312, 0.215049013324912 nohead lt rgb "c"

#splot yf(y,1)*sin(x)**2 lw 2, yf(y,2)*sin(x+1)**2 lw 2, yf(y,3)*sin(x+2)**2 lw 2

splot yf(x,0.9)*vdw(x,y) lw 1, yf(x,0.8)*vdw(x,y) lw 1, yf(x,0.7)*vdw(x,y) lw 1, yf(x,0.6)*vdw(x,y) lw 1

```

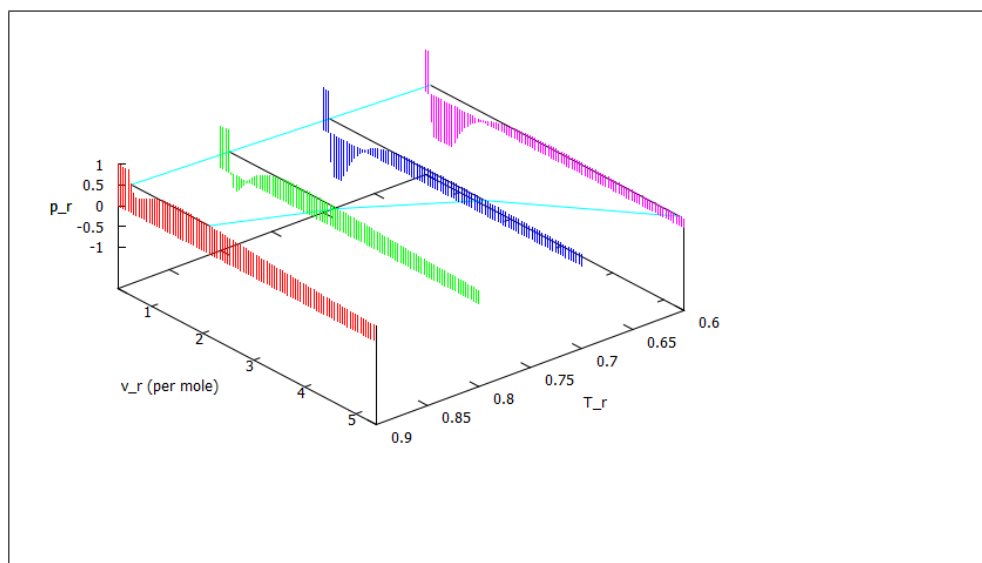


FIG. 2. A fenceplot of the van der Waals equation including tie lines. Note that the diagram when shown on a monitor, can be rotated to see the parts which have been clipped off in the rendering show here.

V. REFERENCES

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VI. CAVEATS

These materials have not been published in a journal because of reasons outlined in the material referenced here: <http://tinyurl.com/nlu6836>.

The first version of this paper had a major calculus error in it, which had to be fixed. That error was propagated into this material, so this paper had to be fixed also. If there remains errors in this work, I would appreciate knowing about them.