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# Avoiding the cubic equation in finding the van der Waals Fluid's vapor pressures

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# Avoiding the cubic equation in finding the van der Waals Fluid's vapor pressures

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The van der Waals coexistence curve of liquid and vapor volumes as functions of the temperature (all in reduced coordinates) as well as the corresponding vapor pressures at these temperatures, is obtained using SageMath, a symbolic calculus/algebra computer programming language. The lack of correspondence of the coexistence locus' analytical form as obtained herein and those of Lekner remains disconcerting.

## I. INTRODUCTION

The van der Waals [1] equation represents the first attempt at understanding phase behavior which has pedagogical legs to stand on. It offers (when coupled with the Maxwell construction[2]) several opportunities to address matters which are rarely addressed with analytical mathematical precision when discussing phases and their interrelationships.

Coupled with the elementary derivation of the critical temperature, pressure and volume based on the two van der Waals constants  $a$  and  $b$ , the Maxwell construction allows treatment of the equality of chemical potentials of liquid and vapor when two phase equilibrium is established[3]. It is also very close to the first chemistry oriented application of calculus, with the attendant rationalization for 2 arduous years of mathematical preparation for Physical Chemistry study.

Further, the van der Waals treatment allows students the opportunity to learn about cubic equations, including their solution [4]. Since this is a topic not

taught in American schools, teaching it adds to the algebraic armamentarium of students in an environment which is directly applied to their presumed interest.

Finally, there is a method not widely known for obtaining the coexistence curve between vapor and liquid. This curve exists in the  $p-v-T$  space (using reduced variables throughout). Its projection onto the  $p-v$  plane is well known and drawn in every Physical Chemistry text (or used to be). Drawn, because its analytical form was, generally speaking, not known.

In my earlier papers, the vapor pressure curve for the van der Waals' fluid was established, and verified by computing the actual molar reduced vapor and liquid volumes at fixed temperatures (below the critical temperature) using the Maxwell construction employing the explicit solution of the cubic equation that the van der Waals equation actually is. After having the original paper rejected by J. Chem. Ed. and Am. J. Physics, for reasons which made no sense, the paper was released on UConn's digital commons site, and two subsequent papers were sent there (with-

out subjecting them to editorial prejudices). I then stumbled on a paper by Lekner [5] which implied that there was more known than my brute force method of solving cubic equations, and so I set out to verify Lekner's paper. This turned out to be quite difficult, hence this contribution.

The vapor pressure curve of Lekner has a completely different shape from the one normally published. It also looks different from the vapor pressure versus temperature curves that we've come to expect.

## II. INTRODUCTORY REVIEW

The van der Waals equation is

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \quad (1)$$

and the reduced van der Waals equation can be written as

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

In what follows, we will attempt to recast Lekner's calculations using the reduced equation of state form rather than the original one ne employed.

### A. Converting to reduced co ordinates

Our Maxwell construction requires us to compute  $\int p dv - \int p^{vp} dp$  But we do not want our computations to involve the van der Waals constants  $a$  and  $b$ , so

with  $p_r = p/p_c$ ,  $T_r = T/T_c$  and  $v_r = v/V_c$  the integration becomes becomes

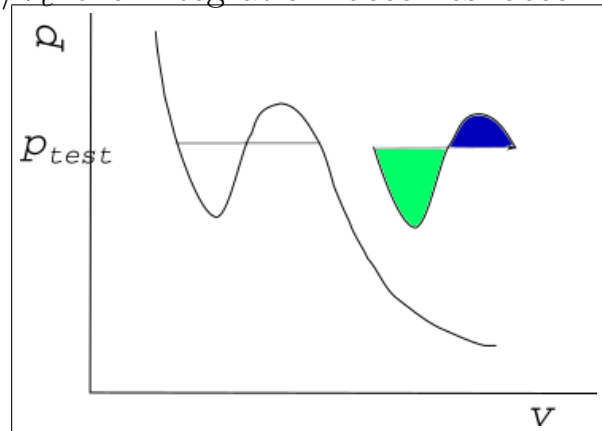


FIG. 1. The Maxwell construction. An isotherm, with  $T < t_c$  or  $T_r < 1$ .  $p_{test}$  is adjusted until the two colored areas are equal. In the case shown,  $p_{test}$  is too high (the blue area is smaller than the green one) so the two areas are not equal (and their sum is therefore not zero). 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.

$\int p_r p_c v_c dv_r - \int p_r^{vp} p_c^{vp} v_c dv_r$  i.e., the cancellation works because the resultant will be forced to zero:  $\int p_r dv_r - \int p_r^{vp} dv_r \rightarrow 0$

The right hand side pressure ( $p_r^{vp}$ ) is a constant, while the left hand side pressure ( $p_r$ ) comes from Equation (2)  $p_r = \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2}$

### B. The Maxwell construction

Figure shows the Maxwell construct which requires us to perform the following integrals:  $\int \left( \frac{8T_r}{3v_r - 1} - \frac{3}{v_r^2} \right) dv_r - \int p_r^{vp} dv_r$  from the smallest root to the center root, and from the center root to the largest root, so that the sum of these two integrals is zero. Thus, we have

$$\int_{smallest}^{central} p dv + \int_{central}^{largest} p dv - \int_{smallest}^{central} p^{vp} dv - \int_{central}^{largest} p^{vp} dv = 0$$

where we are dropping the *reduced des-*  
*ignation* and taking it for granted in

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what follows. This which means

$$\int_{v_{smallest}}^{v_{central}} \left( \frac{8T}{(3v-1)} - \frac{3}{v^2} \right) dv + \int_{v_{central}}^{v_{largest}} \left( \frac{8T}{(3v-1)} - \frac{3}{v^2} \right) dv - p^{vp}(v_{largest} - v_{smallest}) = 0 \quad (3)$$

We re-write this is slightly better form:

$$\int_{v_{small}}^{v_{central}} \left( \frac{8RT}{(3v-1)} - \frac{3}{v^2} \right) dv + \int_{v_{central}}^{v_{large}} \left( \frac{8T}{(3v-1)} - \frac{3}{v^2} \right) dv - p^{vp}(v_{largest} - v_{smallest}) = 0 \quad (4)$$

which becomes

$$\begin{aligned} & \frac{8}{3}T\ln(3v_{central} - 1) - \frac{8}{3}T\ln(3v_{small} - 1) + \frac{3}{v_{central}} - \frac{3}{v_{small}} \\ & + \frac{8}{3}T\ln(3v_{large} - 1) - \frac{8}{3}T\ln(3v_{central} - 1) - p^{vp}(v_{largest} - v_{smallest}) = 0 \quad (5) \end{aligned}$$

Combining terms, we have

$$\frac{8}{3}T\ln\left(\frac{3v_{large} - 1}{3v_{small} - 1}\right) + \frac{3}{v_{large}} - \frac{3}{v_{small}} - p^{vp}v_{large} + p^{vp}v_{small} = 0 \quad (6)$$

which we re-write as

$$\frac{8}{3}T\ln\left(\frac{3v_g - 1}{3v_\ell - 1}\right) + \frac{3}{v_g} - \frac{3}{v_\ell} - p^{vp}v_g + p^{vp}v_\ell = 0 \quad (7)$$

to emphasize the *gas* and *liquid* ends of the isotherm's intersection with the con-

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stant vapor pressure.

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

Equation 7 needs to be manipulated one more time before we're done. We note that the vapor pressure at the  $T-v_g$  and the  $T-v_\ell$  breakpoints is the same, so we can substitute for the vapor pressure using either breakpoint as we see fit. We, of course, substitute in the way which makes the most sense, combining *vapor* or *gas* values on the one hand and *liquid* values on the other. We obtain:

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

This transformation is now specific to the Maxwell construction. We see that the pressure at the terminus of the liquid part of the isotherm with the liquid vapor coexistence constant pressure locus, and the same pressure at the other end of this locus when the vapor pressure morphs into the pressure of the vapor (or gas) have been explicitly included. Thus, we have removed  $p^{vp}$  from Equation 7.

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

$$p^{vp} = \frac{8T}{3v_g - 1} - \frac{3}{v_g^2} \text{ and } p^{vp} = \frac{8T}{3v_\ell - 1} - \frac{3}{v_\ell^2} \quad (9)$$

so, combining these two we obtain an equation for  $T$  in terms of  $v_g$  and  $v_\ell$ , i.e.,

$$\frac{8T}{3v_g - 1} - \frac{3}{v_g^2} = \frac{8T}{3v_\ell - 1} - \frac{3}{v_\ell^2} \quad (10)$$

or

$$T \left( \frac{8}{3v_g - 1} - \frac{8}{3v_\ell - 1} \right) = \frac{3}{v_g^2} - \frac{3}{v_\ell^2} \quad (11)$$

```
eqn5 = eqn4.subs(vg = (exp(d)*f+1)/3)
```

```
eqn6 = eqn5.subs(vl = (exp(-d)*f+1)/3)
```

i.e.,

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

and

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

The genius of this *Ansatz* is that

so

$$T = \frac{\frac{3}{v_g^2} - \frac{3}{v_\ell^2}}{\left( \frac{8}{3v_g - 1} - \frac{8}{3v_\ell - 1} \right)} \quad (12)$$

Lekner claims that this equation for  $T$  and the earlier Equation 8 were known to Gibbs [6].

#### D. Abhorring hand calculations

The messiness of the manipulations required to continue makes it manifest that alternative methods must be employed.

And, this is the 21<sup>st</sup> century!

So we use Sage which has a cloud version which means we can use it where ever the web is available (we actually started with wxMaxima, but found Sage easier, especially for internal plotting). The central trick concerns an *Ansatz* for the term  $3v_\ell - 1$  and  $3v_g - 1$ . The relevant Sage code is

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$f(d)e^{g(d)}$  and  $f(d)e^{-g(d)}$  leads to cancellation of  $f(d)$  in the logarithms, and converts the resulting equation into a straightforward algebraic equation for  $f(d)$ . Solving this equation is non-trivial.

The Sage code displayed below obtains  $f(d)$  as

$$\left[ f = 0, f = -\frac{2e^{(2d)} \log(fe^{-d}) - 2e^{(2d)} \log(fe^d) + e^{(4d)} - 1}{(e^{(3d)} + e^d) \log(fe^{-d}) - (e^{(3d)} + e^d) \log(fe^d) + 2e^{(3d)} - 2e^d} \right] \quad (13)$$

It is hard to understand why no matter what I try, simplification of this expression fails.

```

var('p','T','vg','vl','v','d','f','yl','yg','d','p')
de = 1
p = 8*T/(3*v-1)-3/v^2

pvg = p.subs(v=vg);
pvl = p.subs(v=vl);

show(pvg)
show(pvl)

assume(v>0)
assume(3*vl-1>0)
assume(vg>vl)

int1 = p.integral(v,vl,vg)#integrate from vl to vg
show(int1)
eqn1 = int1 - (pvg*vg - pvl*vl)# subtract constant pressure integration
print ("=====")
print("eqn1 = ",eqn1)
show(eqn1)
print ("=====")

Teqn = 8*T/(3*vg-1)-3/vg^2 -(8*T/(3*vl-1)-3/vl^2)
print ("=====")
print ("T eqn = ",Teqn)
show(Teqn)
print ("=====")
eqn2 = solve(Teqn == 0,T)
print ("=====")
print("SOLUTION TO Temperature Equation, eqn2")
show(eqn2)

```

```

eqn3 = eqn1.subs(eqn2[0])
print("The relevant solution")
show(eqn3)

eqn3a = eqn3.simplify()
show(eqn3a)
print("eqn3a = ")
eqn3b = eqn3a.normalize()
print("eqn3b = ")
show(eqn3b)
print ("ratnum equivalent(?) follows")
eqn4 = eqn3b.numerator()
print("eqn4 = ")
show(eqn4)
eqn5 = eqn4.subs(vg = (exp(d)*f+1)/3)#3*vg-1=f*exp(d) so vg = (fe^d+1)/3
eqn6 = eqn5.subs(v1 = (exp(-d)*f+1)/3)#3*v1-1=f*exp(-d)

eqn7 = solve(eqn6==0,f)
eqn7 = simplify(eqn7)

print ("eqn7 = solve(eqn6==0,f)")
show(eqn7)

```

The first two parts of the following, i.e., the numerator of equation 13,

$$2e^{(2d)} \log \left( fe^{(-d)} \right) - 2de^{(2d)} \log \left( fe^d \right) + e^{(4d)} - 1$$

should be

$$2e^{(2d)} \log (f) + 2e^{(2d)} \log \left( e^{(-d)} \right) - 2e^{(2d)} \log \left( fe^d \right) + e^{(4d)} - 1$$

or

$$2e^{(2d)} \log (f) - 2de^{(2d)} - 2e^{(2d)} \log \left( fe^d \right) + e^{(4d)} - 1$$

and then the second part should read

$$\cancel{2e^{(2d)} \log (f)} - 2de^{(2d)} - \cancel{2e^{(2d)} \log (f)} - 2e^{(2d)} \log \left( e^d \right) + e^{(4d)} - 1$$

or

$$-2de^{(2d)} - 2de^{(2d)} + e^{(4d)} - 1$$

or, finally,

$$-4de^{(2d)} + e^{(4d)} - 1$$

Why Sage can't do this is beyond me.

The denominator of the expression in question should also simplify. We have

$$\left(e^{(3d)} + e^d\right) \log(f) - d\left(e^{(3d)} + e^d\right) - \left(e^{(3d)} + e^d\right) \log(fe^d) + 2e^{(3d)} - 2e^d$$

Or, again

$$\left(e^{(3d)} + e^d\right) \log(f) - d\left(e^{(3d)} + e^d\right) - \left(e^{(3d)} + e^d\right) \log(f) - d\left(e^{(3d)} + e^d\right) + 2e^{(3d)} - 2e^d$$

i.e.,

$$-2d\left(e^{(3d)} + e^d\right) + 2e^{(3d)} - 2e^d$$

So the solution we seek is

$$f = \frac{-4de^{(2d)} + e^{(4d)} - 1}{-2d\left(e^{(3d)} + e^d\right) + 2e^{(3d)} - 2e^d} \quad (14)$$

---

Using CoCalc (SageMath) in a clearly kludgy way, we have the following simplification [7]:

---

```
print ("=====")
print("eqn 8 = eqn7[1].rhs()")
eqn8 = (eqn7[1].rhs())

eqn81 = eqn8.numerator();
show(eqn81)
eqn81a= eqn81.substitute(log(f*e^(-d))==log(f) -d)
#show(eqn81a)
eqn81b = eqn81a.substitute(log(f*e^(d))==log(f) +d)
#show(eqn81b)
eqn81c = eqn81b.substitute(log(f*e^(-2*d))==log(f) -2*d)
#show(eqn81c)
eqn81d = expand(eqn81c.substitute(log(f*e^(2*d))==log(f) + 2*d))
show(eqn81d)
latex(eqn81d)
```



```

eqn82 = eqn8.denominator();
show(eqn82)
eqn82a= eqn82.substitute(log(f*e^(-d))==log(f) -d)
#show(eqn82a)
eqn82b = eqn82a.substitute(log(f*e^(d))==log(f) +d)
#show(eqn82b)
eqn82c = eqn82b.substitute(log(f*e^(-2*d))==log(f) -2*d)
#show(eqn82c)
eqn82d = expand(eqn82c.substitute(log(f*e^(2*d))==log(f) + 2*d))
show(eqn82d)
latex(eqn82d)
final = eqn81d/eqn82d
show(final)# vg = (fe^d+1)/3
latex(final)
plot(final, (d,0.0,1),axes_labels=['$d$ axis', 'f'], axes=True)
vg = ((exp(d)*final+1)/3)
vl = ((exp(-d)*final+1)/3)

print("limit vg(0) = ",limit(vg,d=0))
p = plot((vg,vl), (d,0,1),
axes_labels=['$d$ axis', '$v_g, v_{\ell}$ axis'], axes=True)
show(vg)
show(vl)
show(p)

```

The SageMath[8] output for the end results follow:

$$4de^{(2d)} - e^{(4d)} + 1 \quad (15)$$

for the numerator and

$$-2de^{(3d)} - 2de^d + 2e^{(3d)} - 2e^d \quad (16)$$

for the denominator, so we finally have

$$\frac{4de^{(2d)} - e^{(4d)} + 1}{2(de^{(3d)} + de^d - e^{(3d)} + e^d)} \quad (17)$$

This is in agreement with the hand result in Equation 14, which is heartening. However, it does not appear to agree with Lekner's result:

$$\frac{d \cosh(d) - \sinh(d)}{\cosh(d) \sinh(d) - d} \quad (18)$$

i.e.,

$$-\frac{2(de^{(-d)} + de^d + e^{(-d)} - e^d)}{4d - e^{(2d)} + e^{(-2d)}} \quad (19)$$

I need to apologize for the lack of so-

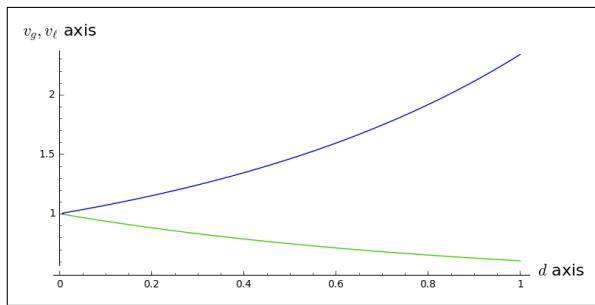


FIG. 2.  $v_g$  and  $v_l$  as functions of  $d$ . It appears disconcerting *it vide supra* that the two meet with a discontinuity, as normal behavior shows them approaching each other “smoothly”. That they both approach a value of 1 at  $d = 0$  indicates consistency with expected reduced volume behavior.

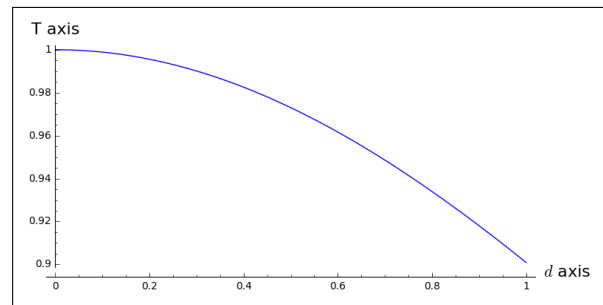


FIG. 3. The  $T(d)$  plot, showing the proper behavior at  $d = 0$ , where the reduced absolute temperature is 1.

phistication in the Sage coding. Assuming I am typical, there is a large element of trial and error in creating mathematics in this kind of environment, since each of the systems currently in use use slightly different notation for common operations in calculus and algebra. I’ve left the code in it’s naked form rather than attempting dressing it in finery.

The resultant  $v_g$  and  $v_l$  plots are shown here:

---

The SageMath code for the final plot in this paper is shown here:

```

from sage.manifolds.utilities import set_axes_labels
y=1
p1 = parametric_plot3d( (
    volume(x,y),
    Temp(x),
    pressure(x)
), (x, 0.01, 1.99) , plot_points=50,frame=False)

y=2
p2 = parametric_plot3d( (
    volume(x,y),
    Temp(x),
    pressure(x)
), (x, 0.01, 1.99) , plot_points=50,frame=False)

p3 = p1 + p2

```

```

p4 = set_axes_labels(p3, 'pressure', 'Temperature', 'volume', color='red')
#p3.set_axes_labels=(['p', 'T', '$v'])
from sage.plot.plot3d.plot3d import axes
S =axes(2,color='black')
show(p4+S)
p5 = p4+S
p5.save('vdw4-fig4.png')

```

The table of values referenced in the SageMath coding is partly reproduced herein:

$d$	$T$	$v_g$	$v_\ell$	$p$
0.01	0.99999	1.0067	0.99337	0.99996
1.01	0.89911	2.3611	0.60232	0.64426
2.01	0.70029	7.7960	0.46731	0.20088
3.01	0.52842	33.303	0.41344	0.040035

The code took lots of tinkering and fooling around to make it work, as is typical in this method of doing calculus/algebra using symbolic mathematics

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on computers.

Presumably, expensive programs such as Mathematica and Maple can allow more elegant solutions, especially to the plotting problem discussed herein. To the best of my knowledge, including the bounding box of this plot forces the axes to be labelled inappropriately. Of course, over the coming years, better plotting programs will handle these problems better than I could.

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### III. ACKNOWLEDGEMENTS

I want to thank my wife for putting up with my obsessive interest in this material.

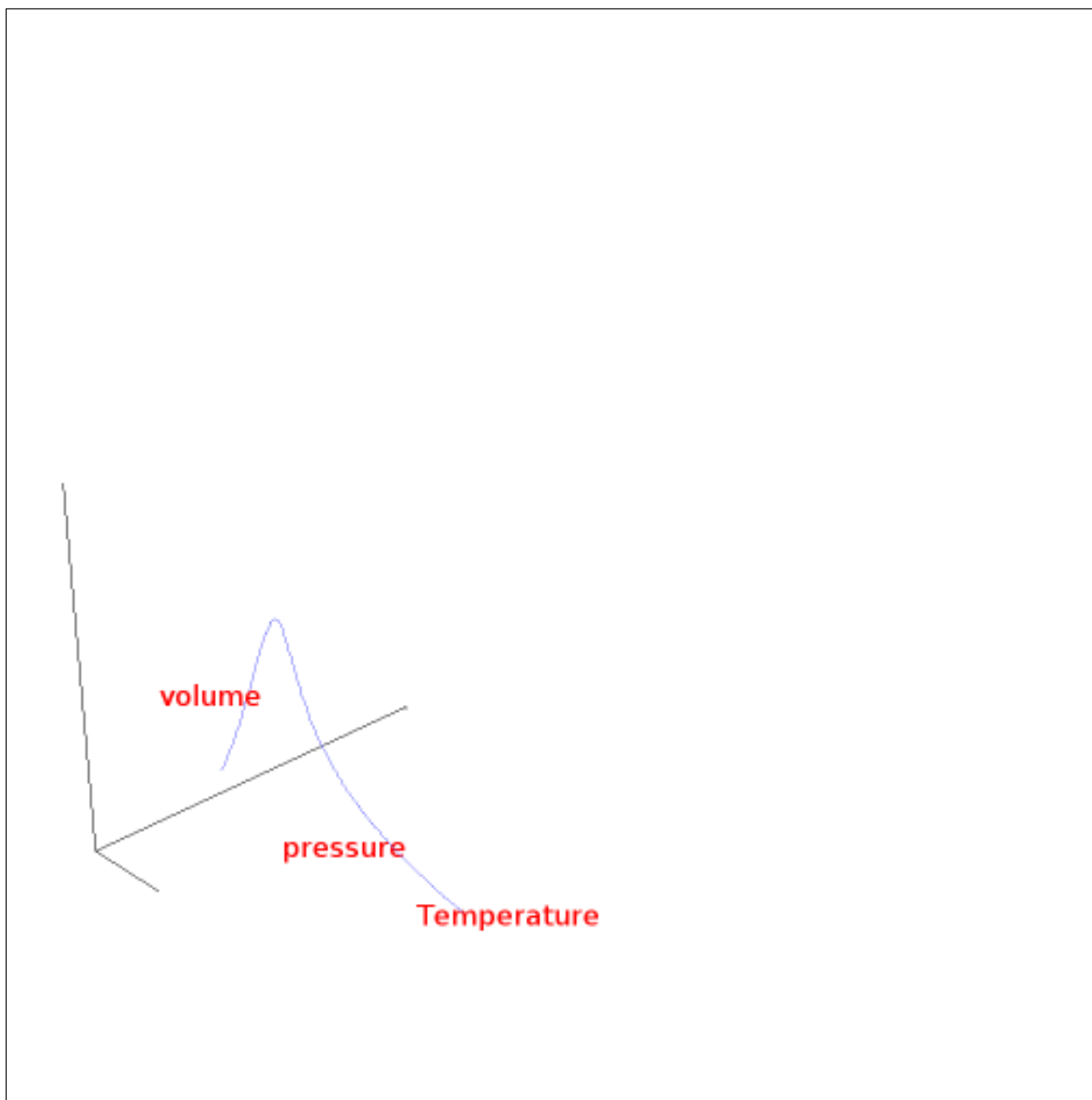


FIG. 4. The 3 dimensional  $p-v-T$  coexistence locus, showing the  $p^{vp}$  versus  $v_\ell$  and  $T$  for  $v < 1$  and versus  $v_g$  and  $T$  for  $v > 1$ . The continuity at the critical point is heartwarming. The crudity of labels and axes is the best that I could do with sagemath *parametric\_plot*. The vertical axes is the  $p$  axes.  $v$  runs left to right. On screen, one can rotate and enlarge the figure which helps.

- 
- [1] J. D. van der Waals, “Over de continuïteit van den gas- en vloeistoestand,” University of Leiden. (1873).
- [2] J. C. Maxwell, *Nature* **11**, 357 (1875).
- [3] C. David, (2016), [http://digitalcommons.uconn.edu/chem\\_educ/93](http://digitalcommons.uconn.edu/chem_educ/93).
- [4] C. David, (2015), [http://digitalcommons.uconn.edu/chem\\_educ/88](http://digitalcommons.uconn.edu/chem_educ/88).
- [5] J. Kellner, *Am. J. Phys.* **50**, 958 (2005).
- [6] Without library access, it is very difficult to verify this assertion; the reference to an unreferenced first version of Kelner’s note makes it even more mysterious that this material has never seen the light of day in textbooks (to the knowledge of the author, whose knowledge only extended up to 2009).
- [7] Several printing and showing lines are included (or excluded, i.e., commented out) to help beginning users follow the results of this code. I am assuming that students will cut and paste the code itself into their own symbolic mathematics program to validate the results shown herein. CoCalc is the successor to SageMath which provides for a paying version.
- [8] `//cloud.sagemath.com`, `note=Sage` can live on the cloud and employ `macsyma`.