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Is the Maxwell construction correct in predicting the van der Waals fluid's vapor pressure?

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The Maxwell construction yields a pressure value which traditionally been associated with the vapor pressure. Here, the question is answered whether or not the two phases represented by the construct are indeed in equilibrium.

I. INTRODUCTION

Traditionally, the Physical Chemistry course started with elementary gas theory, an extension of freshman chemistry. The additional material taught involved attempting an understanding of the ideal gas law from the molecular mechanics point of view, as well as introducing non-ideal gas behavior. For the latter, the van der Waals equation of state played a special role, as it lead to not only deviations from ideal gas behavior, but also a hint at two phase behavior, i.e., liquid-gas coexistence and the existence of a second fluid phase.

In this discussion of two phase behavior the Maxwell construct was invoked to replace part of the continuous curve of a typical isotherm with a constant pressure region (and therefore two discontinuities) which better reflects the actual behavior of real gases.

The question remained, was the Maxwell construct an *ad hoc* construct, or was there some theoretical justification for its use. Since the introduction to gas theory proceeded thermodynamics traditionally, rarely if ever was the appropriateness of the construct addressed by returning to this earlier subject. The question remains, do the discontinuity points on the adjusted vdW isotherm correspond to phases with the same Gibbs free energy?

In this contribution, the proof that the Maxwell construct is indeed theoretically correct is presented.

II. MAXWELL CONSTRUCTION

The reduced van der Waals equation is

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

Given a fixed temperature (chosen to be less than the critical temperature, so the reduced temperature, $T_r < 1$), the Maxwell construction posits choosing a fixed trial pressure and locating the three intersections of this trial pressure with the van der Waals isotherm, provided, of

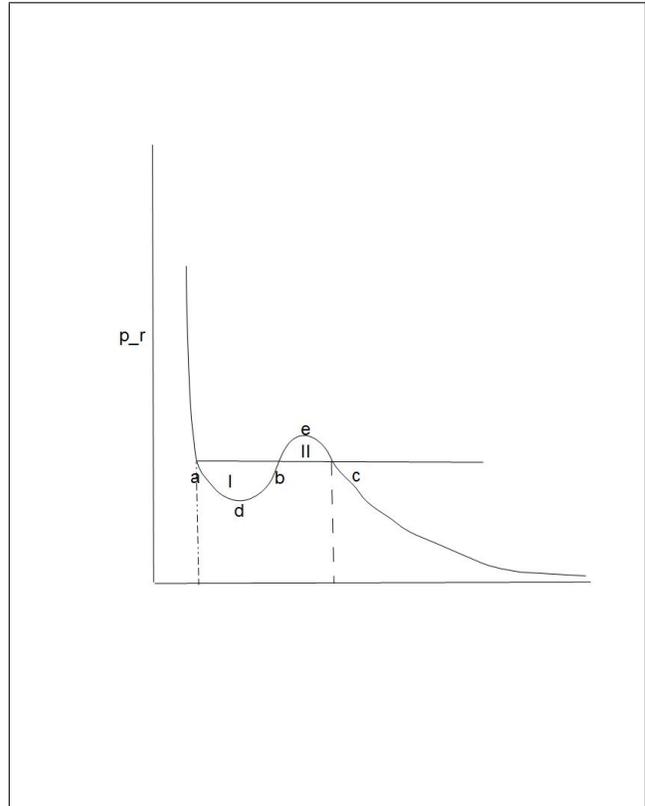


FIG. 1. A typical van der Waals isotherm whose reduced temperature is less than 1. The abscissa is v_r , the reduced volume.

course, that the trial pressure itself is lower than the critical pressure ($p_r < 1$). One sees that there are two loops connecting the three intersections, and the areas circumscribed between the vdW isotherm and the trial pressure are, according to Maxwell, to be set equal to each other by an appropriate choice of that trial pressure.

A. free energy considerations

Given

$$dG = -SdT + vdp \quad (2)$$

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(we are dropping the subscript r for the rest of this exposition), at constant temperature (where $dT = 0$), integration yields

$$G(T, p) - G(T, 0) = \int_0^p v dp \quad (3)$$

where we will choose the lower limits of both integrals to be large (infinite) volume which means zero pressure, and the Gibbs free energy at that volume [5]. The upper limit we will set at the desired ending pressure. So, we are going to do this integration twice, once to the first intersection (approaching from the large volume side), and once to the third intersection. The first intersection (c) would correspond to the vapor if the trial pressure was the actual equal area pressure, and the third intersection (a) would correspond to the liquid volume under the same conditions.

Thus., we have

$$G(T, p_e) - G(T, 0) = \int_0^{p_e} v dp \quad (4)$$

is the first integral, and

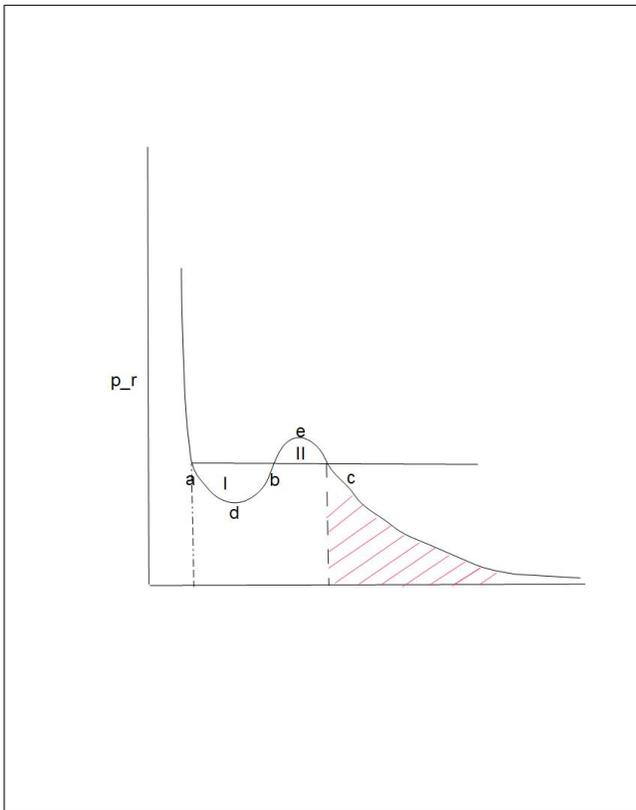


FIG. 2. The integral (from right to left) corresponding to Equation 4.

$$G(T, p_a) - G(T, 0) = \int_0^{p_a} v dp \quad (5)$$

is our second integral. We are interested in the relationship between $G(T, p_e)$ and $G(T, p_a)$, specifically, whether they are equal to each other.

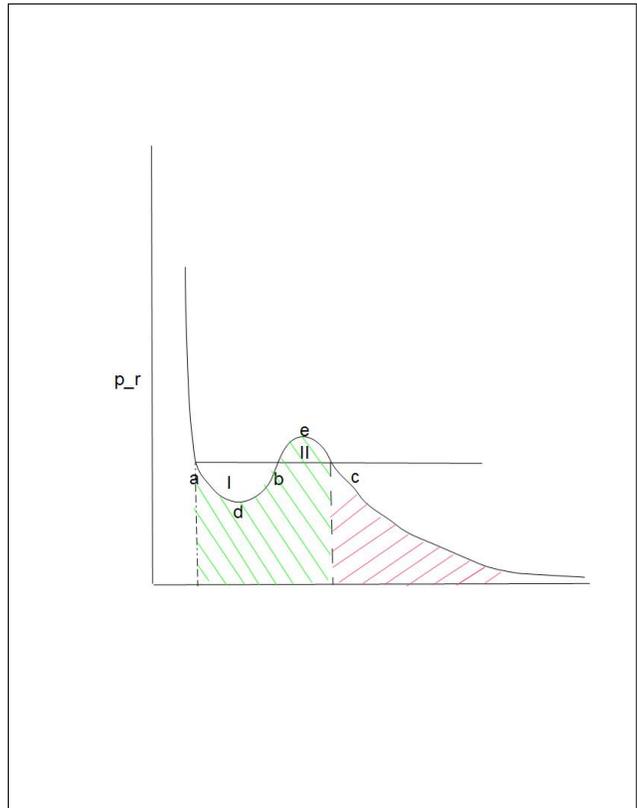


FIG. 3. The integral (from right to left) corresponding to Equation 5.

B. Dealing with the cubic

Since the van der Waals equation is a cubic, we face a conundrum here. We can not, easily, substitute for v in either of these two integrals, so that we can proceed. Winn[7] uses thermodynamic manipulations to proceed.

We instead prefer to remind the reader that integration by parts is an element of his/her past, learned in the vacuum of calculus class [6], but appropriate here.

We have

$$G(T, p_a) - G(T, 0) = (vp)|_0^{p_a} - \int_{\infty}^{v(p_a, T)} p dv \quad (6)$$

and

$$G(T, p_e) - G(T, 0) = (vp)|_0^{p_e} - \int_{\infty}^{v(p_e, T)} p dv \quad (7)$$

Although we could substitute the expression for p into each integral and proceed with the integration, we choose a slightly easier method.

Consider that the integral in Equation 5, which is to be evaluated as the area under the curve as shown in Figure 3, can be obtained by integrating from ∞ to c and then from $c \rightarrow e \rightarrow b \rightarrow d \rightarrow a$. But the path we *choose* is the straight line path, which corresponds to the path shown in Figure 4, ($c \rightarrow b \rightarrow a$). The *only* reason we can sub-

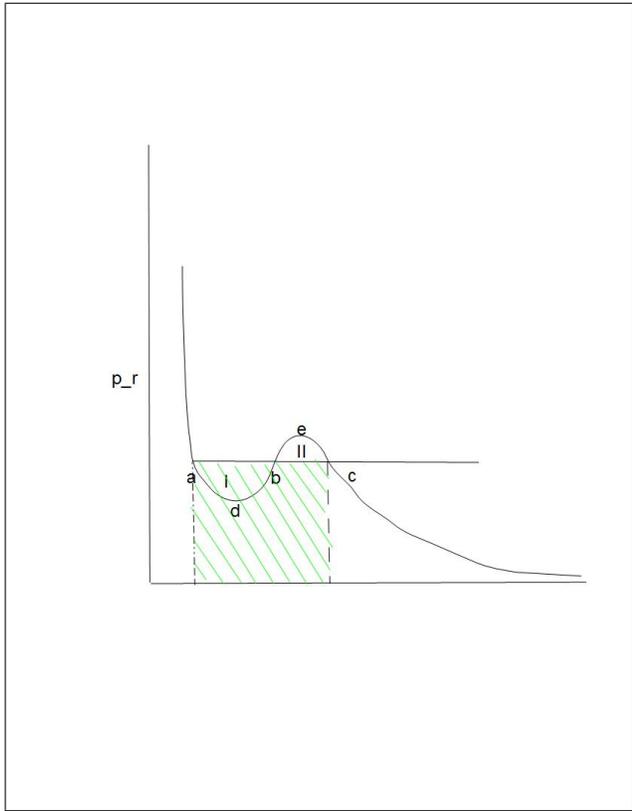


FIG. 4. The alternate path to the one in Figure 3 from $c \rightarrow b \rightarrow a$.

stitute this alternative path is the Maxwell construction! The areas “I” and “II” are equal and opposite in sign, so the integral over the curved path and the straight path from $c \rightarrow a$ have exactly the same value! Then we can write

$$G(T, p_a) - G(T, 0) = (vp)|_0^{p_a} - \int_{\infty}^{v(p_c, T)} p dv - p(v_a - v_c) \quad (8)$$

and subtracting Equation 7 from Equation 8, we obtain

$$G(T, p_c) - G(T, 0) - [G(T, p_a) - G(T, 0)] = (vp)|_0^{p_c} - \int_{\infty}^{v(p_c, T)} p dv - \left[(vp)|_0^{p_a} - \int_{\infty}^{v(p_c, T)} p dv - p(v_a - v_c) \right] \quad (9)$$

(the lower bounds cancel, no matter how they are *evaluated*) or

$$G(T, p_c) - G(T, p_a) = v_c p_c - [v_a p_a - p(v_a - v_c)] = 0 \quad (10)$$

Remember that $p_a = p_c$! We have proven that the Gibbs free energy at c and a are the same. QED.

III. CLOSING REMARKS

This paper, and the two that proceed it [1, 2] were prompted by a reading of Nahin’s [4] book which showed me, for the first time, a solution to the cubic equation. But, when I came across the paper by Lekner [3] and started doubting myself, I found that I’d made a calculus error. Luckily, digital commons allows substitution of papers, so I re-edited both papers and sent them back to

digital commons. This last one (what you are reading) was written because of Winn’s paper [7], which had as its on-line tease the following

“The cubic nature of the vdW equation can be overcome as an impediment to exploring the remarkable properties of this equation.”

Since I knew that there was nothing to “overcome”, and that any high school student could understand the cubic solution just as easily as s/he understood the quadratic solution, I felt impelled to continue writing, which is what you are now reading.

Well, high school student might be an exaggeration. I also note that Viète's work (see <https://math.berkeley.edu/~robin/Viete/> for example) was

not properly cited anywhere. Shame on me.

IV. REFERENCES

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- [1] Carl W. David. Plotting the van der waals fluid in 3d and the maxwell construction. 2015. http://digitalcommons.uconn.edu/chem_educ/89.
- [2] Carl W. David. The van der waals equation as a cubic. 2015. http://digitalcommons.uconn.edu/chem_educ/88.
- [3] John Lekner. Parametric solution of the van der waals liquid-vapor coexistence curve. *Am. J. Phys.*, 50:161, 1982.
- [4] Paul J. Nahin. *An Imaginary Tale The Story of $\sqrt{-1}$* . Princeton University Press, Princeton, NJ, 1998.
- [5] Notice that we are going to avoid the standard state discussion completely, *vide infra*.
- [6] In fact, the first time chemistry students used their calculus in the traditional curriculum, was in the derivation of the critical constants in terms of a and b , which involves differentiation (actually partial differentiation). So, two years of calculus prior to Physical Chemistry is a reasonable requirement.
- [7] John S. Winn. The fugacity of a van der waals gas. *J.Chem. Ed.*, 65:772, 1988.