Exploring the Use of the Peng-Robinson Equation of State in Python

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August 19, 2020

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1 Introduction

The Peng-Robinson equation of state(PREOS) is one of many cubic equations of state that describe the properties of fluids. This project aims to discover methods in which the PREOS can be used to calculate vapor pressure. It is intended to function with all fluids known to have an acentric factor. This document uses propane as an example to examine the capabilities and limitations of the Python program. *cv6Enterprise.py* is written in Python3, and displays all of its results in the terminal of any UNIX operating system and Matplotlib.

1.1 Modules used:

Numpy provided many of the mathematical functions used in the program.
Cmath was used to handle complex arithmetic.
Matplotlib was used to provide custom plots of related functions.
Scipy was used to find roots to a function.
The contents of *cv6Enterprise.py* is included in the repository on GitHub.

2 Equations

2.1 PREOS

The equation of state describes that pressure can be expressed in terms of molar volume:

$$P = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}(\underline{V} + b) + b(\underline{V} - b)} \tag{1}$$

By substituting pressure for the compressibility factor, Z, the compressibility factor can also be expressed in an equation where it is cubic in molar volume:

$$Z = \frac{\underline{V}}{\underline{V} - b} - \left(\frac{a\underline{V}}{RT}\right)\left[\frac{1}{\underline{V}(\underline{V} + b) + b(\underline{V} - b)}\right] \tag{2}$$

Unlike the van der Waals equation of state, the parameter, a is a function of temperature. a and b are given by the following equations:

$$\begin{aligned} a &= a_c\alpha \\ a_c &= 0.45724R^2\frac{T_c^2}{P_c} \\ a &= \left[1 + \kappa\left(1 - T_r^{0.5}\right)\right]^2 \\ \kappa &= 0.37464 + 1.524226\omega - 0.269932\omega^2 \\ b &= 0.07780R\frac{T_c}{P_c} \end{aligned}$$

Where ω is the acentric factor.

2.2 Fugacity

Fugacity is derived from the expression for Gibbs free energy. After many substitutions and simplifications, fugacity expressed in terms of the PREOS is:

$$f = P\ \exp\left((Z-1) - \ln(Z-B) - \frac{A}{2B\sqrt{2}} \times \ln\left[\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B}\right]\right) \tag{3}$$

With constants A and B:

$$\begin{aligned} A &= \frac{aP}{R^2T^2} \\ B &= \frac{bP}{RT} \end{aligned}$$

3 Functions in *cv6Enterprise.py*

All properties are computed using a gas constant of,
$R = 8.314462\,MPa \cdot cm^3/mol \cdot K$. Hence, pressure and molar volume will be reported in MPa and cm^3/mol, respectively.
The temperature of interest can be adjusted by changing the globally-defined variable, T. Inputting a pressure is optional; the variable, P, is usually used with the functions $freikugel(P)$ and $fugac(P, V)$. Other constants must be manually changed, like the acentric factor, critical pressure, and critical temperature. The constants for propane were found in *Fundamentals of Chemical Engineering Thermodynamics* by Dahm and Visco. [1] The triple point pressure and temperature was also used in this program. The approximate values for propane were found on NIST. [2]

3.1 $freikugel(P)$

This function systematically solves for the molar volumes of a fluid at a given pressure. Rearranging Equation 1 into the standard form of a cubic equation($rx^3 + sx^2 + tx + u = 0$) gives:

$$(-P)\underline{V}^3 + (RT - P2b + Pb)\,\underline{V}^2 + \left(2bRT - a + 3b^2P\right)\underline{V} + \left(ab - Pb^3\right) = 0$$

Where:

$$\begin{aligned} r &= -P \\ s &= RT - Pb \\ t &= 2RTb - a + 3b^2P \\ u &= ab - RTb^2 - Pb^3 \end{aligned}$$

Let $\underline{V} = x$. Substituting ($x = y - \frac{s}{3r}$) will depress the cubic to a form:

$$y^3 + py + q = 0$$

Where:

[1] Dahm, K. ; Visco, D. Appendix C.1 Critical Point, Enthalpy of Phase Change, and Liquid Molar Volume. *Fundamentals of Chemical Engineering Thermodynamics*, 1st Ed.; Cengage Learning, 2014, pp. 735

[2] NIST Chemistry WebBook. https://webbook.nist.gov/cgi/cbook.cgi?ID=C74986&Mask=4 (Accessed August 19, 2020)

$$
\begin{aligned}
p &= \frac{1}{r}\left(t - \frac{s^3}{3r}\right) \\
q &= \frac{1}{r}\left(u + \frac{2s^3}{27r^2} - \frac{st}{3r}\right)
\end{aligned}
$$

The roots of the cubic equation can be solved for using Vieta's substitution. [3] Substituting $y = w - \frac{p}{3w}$ results:

$$w^3 + q - \frac{p^3}{27w^3} = 0$$

After multiplying by w^3, the equation is now quadratic in w^3:

$$(w^3)^2 + q(w^3) - \frac{1}{27}p^3 = 0 \tag{4}$$

Equation 4 can be solved for using the quadratic formula. It will result in two values for w^3, and theoretically, six values for w. However, the roots from each root of w^3 are identical, leaving only 3 distinct roots for w. These cubic roots can be solved for using De Moivre's theorem:

$$\text{Let } w^3 = W.$$

$$w = \sqrt[3]{W}\left[\cos\left(\frac{\pi + 2\pi k}{n}\right) + i\sin\left(\frac{\pi + 2\pi k}{n}\right)\right] \tag{5}$$

$$\text{For } n = 3 \text{ and } k \text{ is a positive integer less than } n.$$

Once the three values of w are known, molar volume can be back-solved through all the substitutions. The lowest molar volume would correspond to the liquid molar volume, and the highest molar volume would correspond to the vapor molar volume. $freikugel(P)$ will compute molar volumes at any temperature specified between the triple point pressure and critical point pressure. However, its accuracy cannot be measured. For instance, at 90 K—just 5 degrees above the triple point temperature—the liquid molar volume was computed to be 35.7 cubic centimeters/mol. This would raise in error when calculating the fugacity of a liquid, because the logarithmic term in the equation is undefined when the volume is less than b, the molar volume of a substance at maximum compression. For comparison, b for propane is equal to 56.3 cubic centimeters.

[3] https://en.wikipedia.org/wiki/Cubic_equation

3.2 *plotcubic()*

This function plots the cubic equation of state. It creates an array of 200 values from $b + 1$ to 2000 cubic centimeters/mol and used Matplotlib to plot it against Equation 1. The starting point is $b + 1$ because substituting b for $\underline{V}$ into Equation 1 would result in a divide by zero error. An error would be raised and printed in the terminal output. An example plot is included as Figure 1:

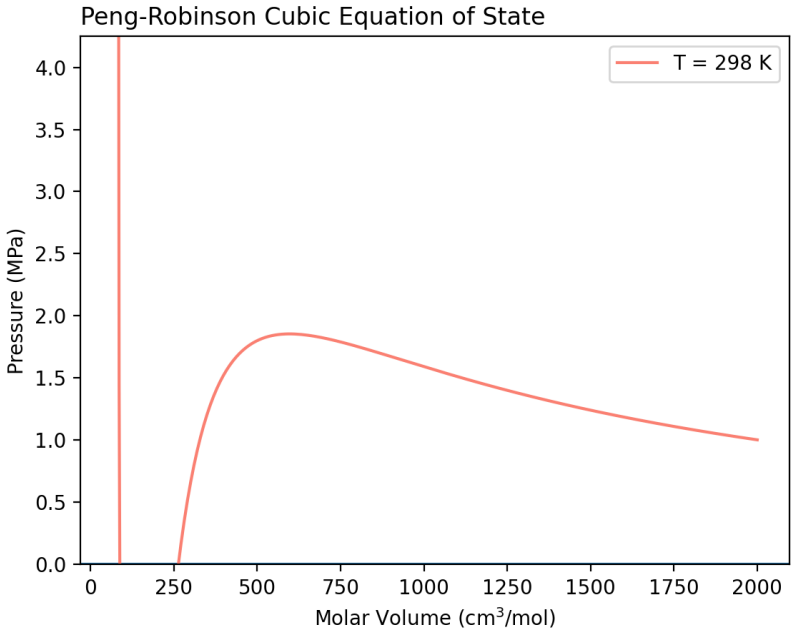

Figure 1: Plot of pressure vs molar volume at 298 K

It can be seen in Figure 1 that the function is asymptotic as it approaches the value of b from the right.

3.3 $fugac(P, V)$

This functions computes the fugacity of a substance given a molar volume and pressure, using Equation 3. It is used in conjunction with $freikugel(P)$, by taking the output of $freikugel(P)$ and using it as an input.

3.4 $plotFugacityDifference()$

This function plots the difference in fugacity: $f_l - fv$ vs pressure. A sample plot is shown in Figure 2 for a temperature of 298 K:

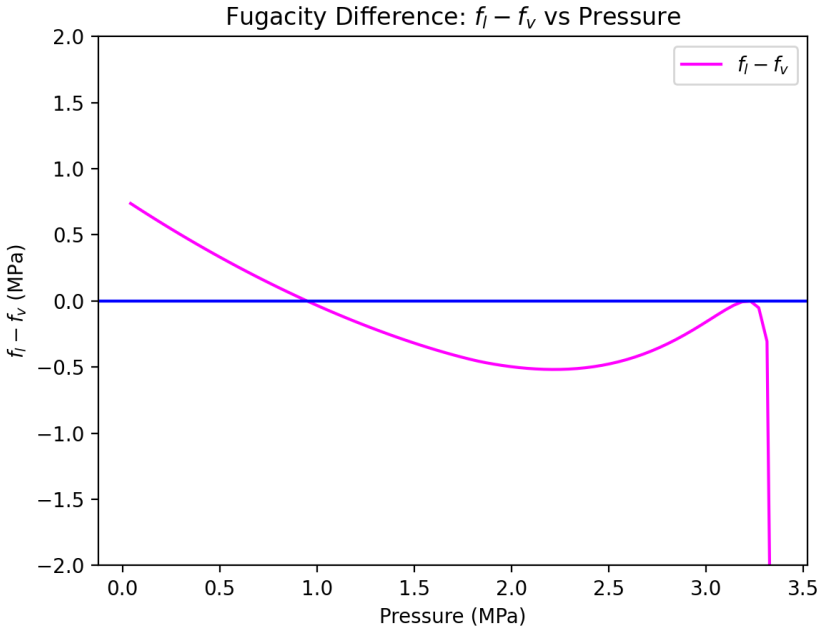

Figure 2: Fugacity difference vs pressure at 298 K

It can be seen in Figure 2 that two roots exist for the graph. One is at 0.949 MPa, and the other at about 3.3 MPa. The first-degree root is the vapor pressure at that temperature. The second-degree root has no physical meaning. When the value of the function is positive, it indicates that the substance is a vapor at that pressure since the fugacity of the vapor is computed to be lower than the fugacity of the liquid. Likewise, when the function is below the x-axis, the substance will be a liquid in that range of pressures.

3.5 $optim(P)$

This function is a combination of $freikugel(P)$ and $fugac(P, V)$. Vapor-liquid equilibrium exists when the difference between the liquid and vapor fugacity is zero.

Scipy.optimize.newton[4] helps with this

[4] https://docs.scipy.org/doc/scipy/reference/generated/scipy.optimize.newton.html

4 Appendix