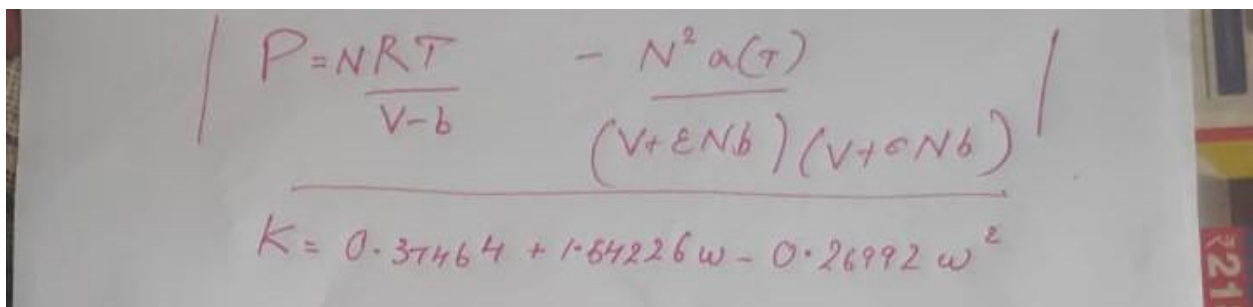# COMPUTATIONAL ASSIGNMENT
PENG ROBINSON EQUATION OF STATE FOR CHLOROFORM

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INTRODUCTION

The Peng–Robinson equation of state (PR EOS) was developed in 1976 at The University of ALberta by Ding-Yu_Peng and Donald Robinson.It has the following features

1. The parameters are expressible in terms of the critical properties and the acentric factor.
2. The model provides reasonable accuracy near the critical point, particularly for calculations of the compressibility factor and liquid density.
3. The mixing rules do not employ more than a single binary interaction parameter, which is independent of temperature, pressure, and composition.
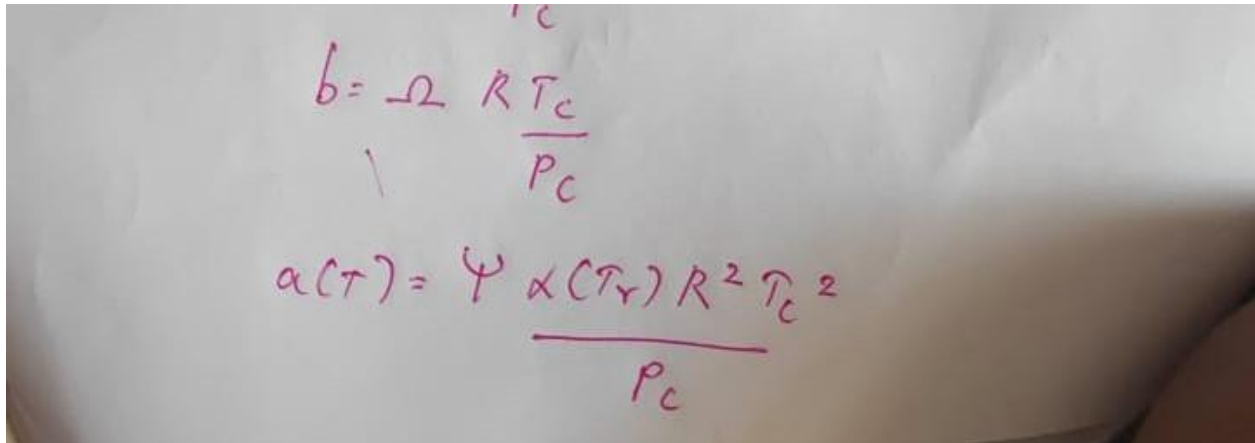4. The equation is applicable to all calculations of all fluid properties in natural gas processes.

$$P = \frac{NRT}{V-b} - \frac{N^2 a(T)}{(V+\varepsilon Nb)(V+\sigma Nb)}$$

$$K = 0.37464 + 1.54226\,\omega - 0.26992\,\omega^2$$

Improvements to the original Peng Robinson EOS were brought about through the Peng–Robinson-Stryjek-Vera equations of state.

## VALUE OF PARAMETERS FOR NITROGEN IN THE PR -EOS

$$b = \Omega \, \frac{R \, T_c}{P_c}$$

$$a(T) = \Psi \, \alpha(T_r) \, \frac{R^2 \, T_c^2}{P_c}$$

|	
ε	1-√2
σ	1+√2
Ω	0.077802
Tc	536.4 K
Pc	5.47Mpa
R	8.314413
b	6.3434e-05
ω	0.218
κ	0.6980
Ψ	0.45724
α	(1+κ*(1-sqrt(T/Tc)))^2 , T dependent
a	α* Ψ *R*R*Tc*Tc/Pc

CODE EXPLANATION AND ANALYSIS

Plotting Isotherms

This task is fairly simple.This is done in three different sections of the code.In the First Section Isotherms were plotted for temperatures 526.4:1:530.4 and in the second section 531.4:1:535.4. In both these sections the plots were obtained as expected.
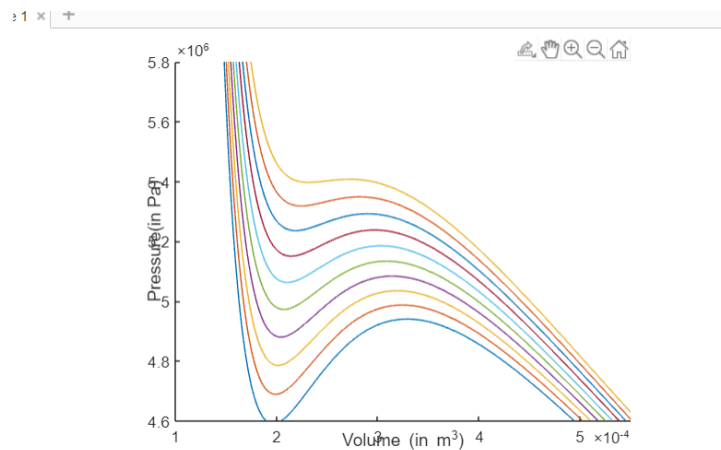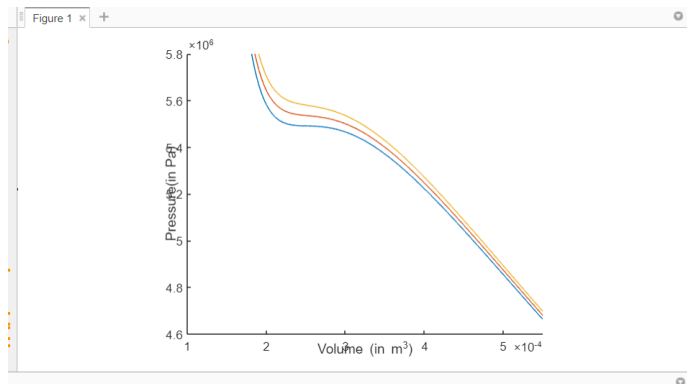

This is the case where **T < Tc**,

the isotherms followed a cubic trend and had two roots for Psat in the liquid Vapor saturation region

In the third Section isotherms were obtained for values 536.4:1:539.4. At **T=Tc,**
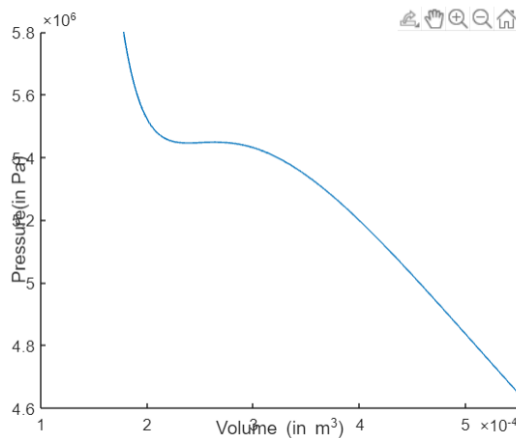
The roots merged into a distinct point.the point of inflexion is the critical point and the first and second derivatives of P w.r.t to V vanishes at this point. At **T>Tc,**

there seems to be no real root as the solid liquid and gaseous states cannot be distinguished above the critical temperature.

```
syms V;

   fplot((R*T/(V-b))-(a/((V+(eps*b))*(V+(sigma*b))))),[0.0001 0.2]);
```

Using the above code ,P vs V for the all the T above mentioned were plotted.

Dome-Shaped Curve

Procedure

In order to find the points on the saturation curve the following steps were utilised.

1)For the given temperature the value of Psat and corresponding volume values were determined.

For this we need to have an initial guess value. Antoine's equation is one of the ways in which we can determine an approximate value for Psat.But Since my choice of points were so much close to the critical temperature, Antoine's Equation could not be used as it is not so effective near the critical temperature.

Hence for a particular temperature , a guess value was taken by inspecting the isotherm with the knowledge that Psat would be present somewhere near the inflexion points.
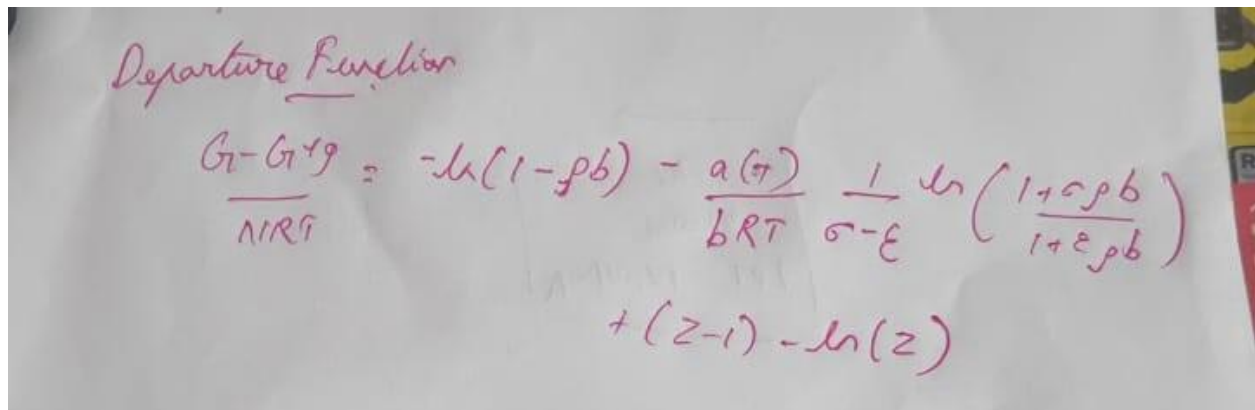
An array of Guess points of Psat were maintained for those temperatures where the corresponding points on the curve were to be determined.

Though in the code the isotherms of T 531.4-535.5 are plotted after taking the guess values of Psat for the same,this was actually determined by me beforehand by plotting the isotherms alone and this was combined just to reduce the size of the code.

Now all the below are being spoken for a particular temperature T

For the guess value of Psat, volume values were obtained using the cubic equation of volume obtained from the EOS.Since the guess values were chosen by me from the isotherms such that there would be two real roots(As it was chosen near the potential liquid-vapor saturation region) ,we assign Vmin=Vliquid and Vmax=Vgas.

Now the G departure function values were obtained for values Vliquid and Vgas (Functions for the same were made) and were compared.

Departure Function

$$\frac{G - G^{ig}}{NRT} = -\ln(1 - \rho b) - \frac{a(T)}{bRT}\frac{1}{\sigma - \varepsilon}\ln\left(\frac{1 + \sigma \rho b}{1 + \varepsilon \rho b}\right) + (Z - 1) - \ln(Z)$$

Now there could be three scenarios.

> 1)The magnitude of difference is less than my tolerance value,the this is my required Psat and the corresponding Vl and Vg
>
> If the magnitude does not meet my conditions
>
> We will either have to 2)increase or 3)decrease my psat

Now I check if I have to increase or decrease my value.I take an increased value of Psat and check the change in the magnitude of difference ,if this is less than the initial value then we are proceeding in the right way and keep on increasing in small amounts till requirements are met.Otherwise a similar process is done in the opposite direction.

Finally I have obtained my Psat and V values.

2)By now I would have stored my Psat and corresponding V values in different arrays.Using slight modifications and some copies these were plotted using a cubic spline.
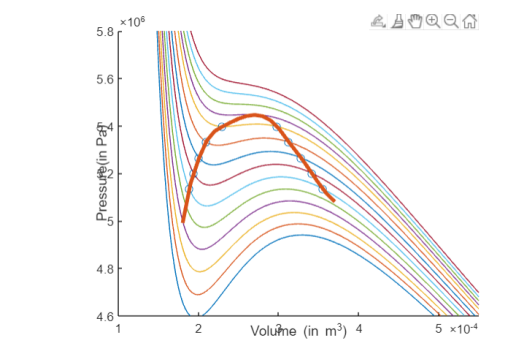

Choice of points

After a lot of experimentation and analysis , I have chosen to find Psat just at 5 temperatures and extrapolated the same to obtain my dome shaped curve.

While taking values of T less than 531.4 , I could not obtain an answer of such accuracy, for example at 530.4 the magnitude of the difference for my guess was initially 0.026 and on making changes it decreased upto 0.017 and then shot up again.So keeping a high tolerance for the same would result in an infinite loop.

At Tc=536.4K, with so many guesses ,I kept on getting solutions with a small imaginary part for two roots but never three same roots. However on extrapolating the same based on other values the dome shaped curve seems to be passing very nearly through exactly one point on the isotherm of Tc.

Comparison with real values

The value of Pc as seen from the graph is about 5.446 Mpa and the original value as per sources is found to be about 5.47Mpa.
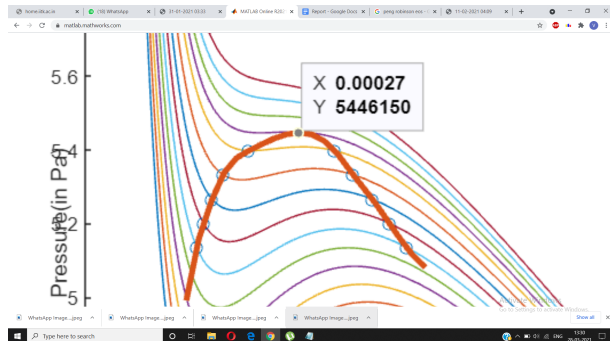
This difference points to the accuracy shown by the Peng Robinson equation at temperatures near the critical point and it is somewhat accurate.

Critical volume was found to be about 270 ml where the experimental value was about 239 ml.

References

1)https://webbook.nist.gov/chemistry/(For critical constants).

2)https://en.wikipedia.org/wiki/Equation_of_state#Peng%E2%80%93Robinson_equation_of_state(History and Development).

3)Lecture notes.(General cubic EOS,Departure Function).