Equation of State

Presented by :
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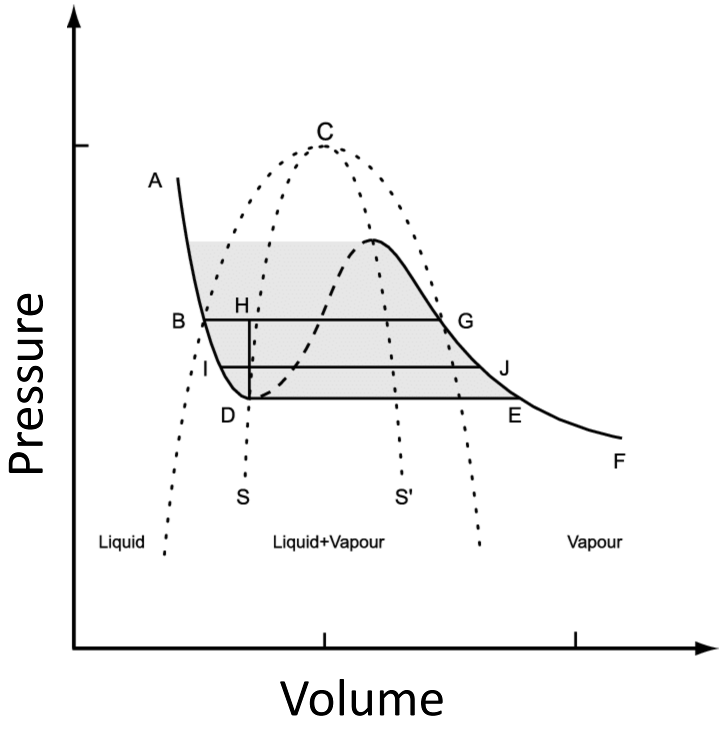
thermodynamics



$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \left(\frac{a}{P}\right)V - \left(\frac{ab}{P}\right) = 0$$

Solution of this equation give 3 roots V1, V2, V3

$$Z^3 - (1+B)Z^2 + AZ - AB = 0$$

The polynomial in Z will give three roots It may be

Case 1: all positive

Case 2: real roots but negative

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Case 4: one real two complex

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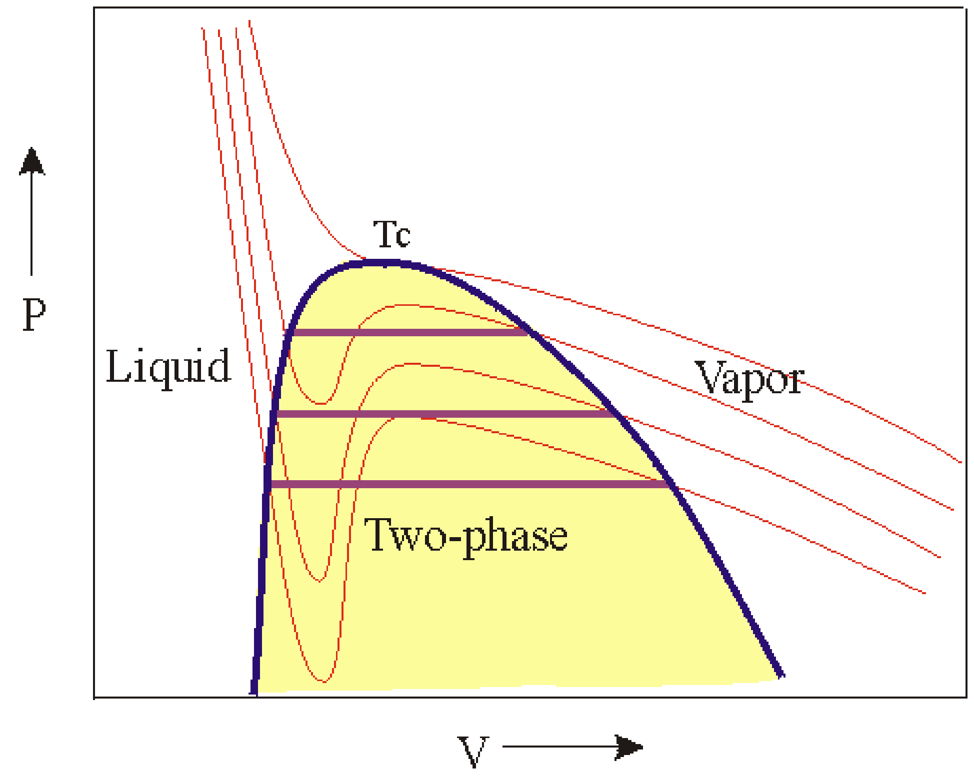
Fig : https://www.researchgate.net/figure/Schematic-pressure-volume-P-v-projection-of-the-phase-diagram-of-a-pure-substance_fig7_228710705

Pressure - Volume phase diagram
Pressure – Temperature phase diagram



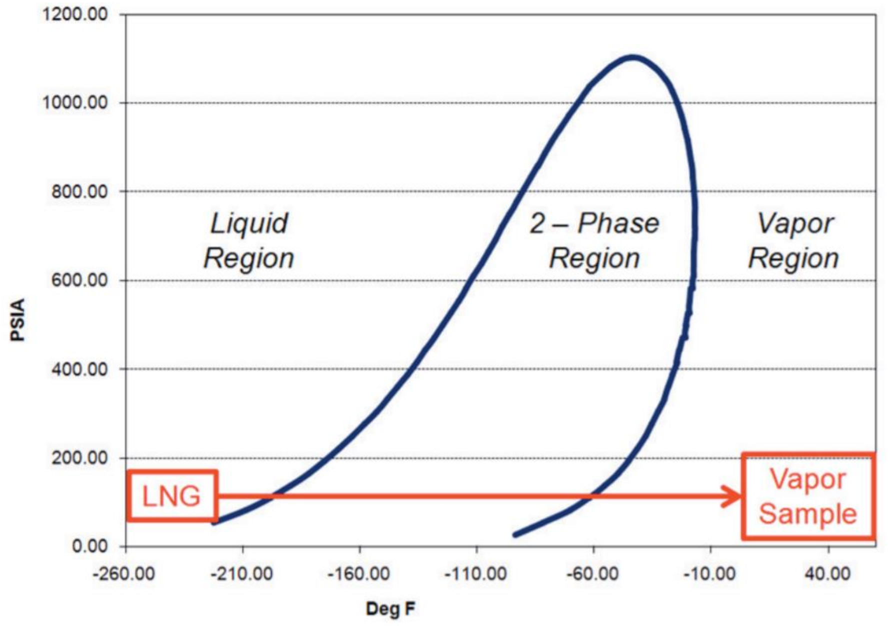


Figure 1. LNG phase diagram.

Fig 1: https://www.et.byu.edu/~rowley/ChEn273/Topics/Mass_Balances/Single_Phase_Systems/Van_der_Waals_Equation_of_State.htm
Fig 2: https://www.emerson.com/documents/automation/article-analysing-weakest-link-rosemount-en-37986.pdf

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import numpy as np
from matplotlib import pyplot as plt

def van_der_waal():
    print(   "\t ########################################################## \t"  )
    print(   "\t ####### Van Der waal EoS for single component         ####### \t"  )
    print(   "\t ########################################################## \t"  )

    MUa = 0.421875
    MUb = 0.125
    R = 10.73
    Tc = 666
    print ("\n critical temperature value in rankine : "+ str(Tc))
    Pc = 616.3
    print ("\n critical pressure value in psi : "+ str(Pc))
    M = 44
    print ("\n moleculer weight of the single component : "+ str(M))
    P = 616.3
    print ("\n pressure value in psi : "+ str(P))
    T = 460 + T0
    print ("\n temperature value rankine: "+ str(T))
    a = (MUa)*((R**2)*(Tc**2)/Pc)
    print( "\nvalue of a is  = " + str(a) + " . ")
    b = (MUb)*((R)*(Tc)/Pc)
    print("\nvalue of b is  = " + str(b) + " . ")
    print(" \n\t --------------------------------------------------- \t" )
    A = ( (a)*(P) )/ ((R**2)*(T**2))
    print("\nvalue of coefficient  A  is  = " + str(A) + " . ")
    B = ((b)*(P))/ ((R)*(T))
    print("\nvalue of coefficient B is  = " + str(B) + " . ")
    Z3 = 1
    Z2 = - (1 + B)
    Z1 = A
    Z0 = - A*B
    ########################### coefficient of polynomial #####################
    coeff = [Z3, Z2, Z1, Z0]
    ############################## roots of polynomial #######################
    Z = np.roots(coeff)
    #########coefficient or z value for gas phase that is maximum one #########
    ZG = max(Z)
    print ("\n compressibility factor Gas phase is ZG   = " + str(ZG) + " . ")
    ###### coefficient or z value for liquid phase that is minimum one  ######
    ZL = min(Z)
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    ############################## density of gas phase ######################
    ROg = ((P)*(M))/((ZG)*(R)*(T))
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Numpy and matplotlib library

Calculation of all parameter
a, b, A and B

Polynomial equation calculation for it's roots

```
P0  = 185
T = [ 116, 120, 125, 130, 135, 140, 145, 150, 155,160 ]
for i in range(len(T)):
    T0 = T[i]
    P0 = 400
    van_der_waal()


plt.figure(figsize=(12,8))
plt.legend(["liquid density", "gas density"], prop={"size":20})
plt.plot(T, density_liquid, color = 'r', label= 'liquid density ')
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plt.title('The density of the gas and liquid phases for pure propane using van der waals EoS at presssure ' + str(P0) , fontsize=23  )
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plt.legend()
plt.show()
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Pressure value
Temperature range for the simulation

Matplotlib library to generate graph

$$Z^3 - (1+B)Z^2 + AZ - AB = 0$$

Polynomial Equation

Numpy library

Roots

DENSITY

Matplotlib Library Density - pressure and temperature

$$B = \frac{bP}{RT}$$

$$A = \frac{aP}{(RT)^2}$$

$$a = \left(\frac{9}{8}\right) RT_c V_c = \left(\frac{27}{64}\right) \frac{R^2 T_c^2}{P_c}$$

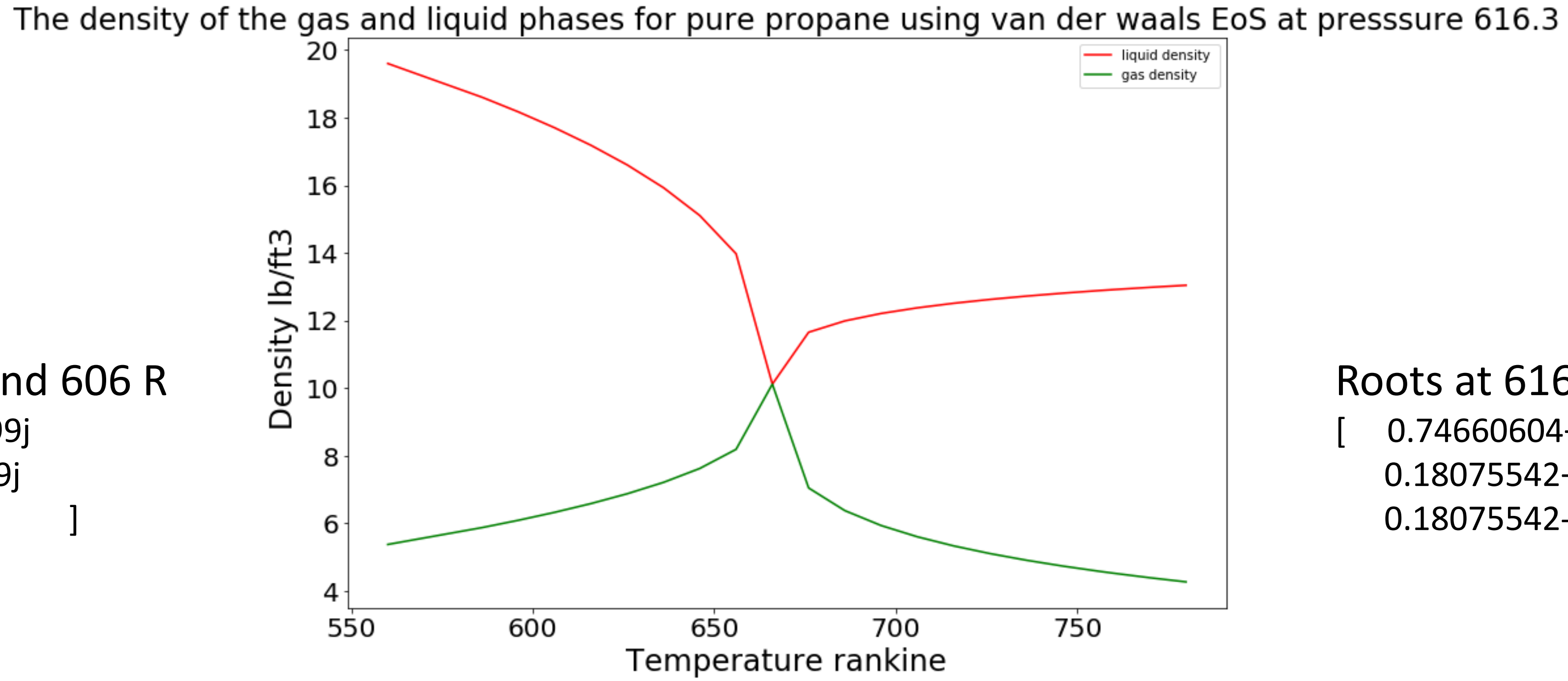
$$b = \left(\frac{1}{3}\right) V_c = \left(\frac{1}{8}\right) \frac{RT_c}{P_c}$$

R = 10.73

Tc = 666 Rankine

Pc = 616.3 psi

Effect of Temperature on Density



Roots at 616.3 psi and 606 R

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Density of Liquid phase is =
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Density of Gas phase is =
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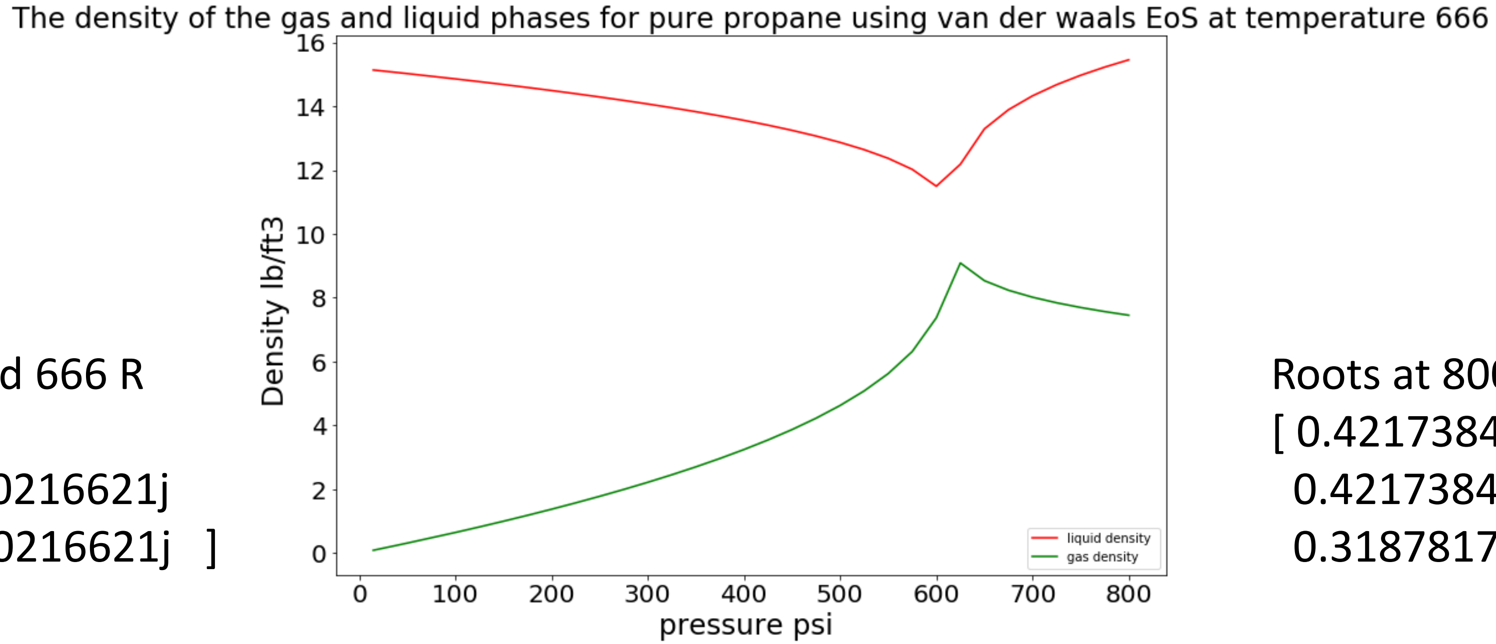
Effect of Pressure on Density



Roots at 14.7 psi and 666 R
[0.99287718 + 0.j
0.00505216 + 0.00216621j
0.00505216 - 0.00216621j]

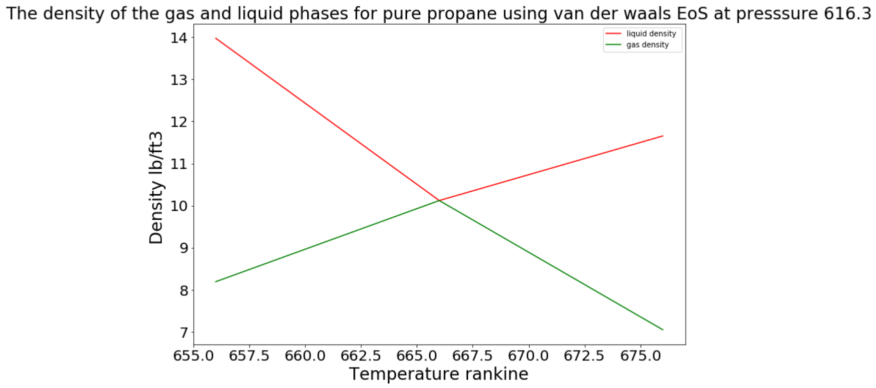
Roots at 800 psi and 666 R
[0.42173843 + 0.31760755j
0.42173843 - 0.31760755j
0.31878177 + 0. j]

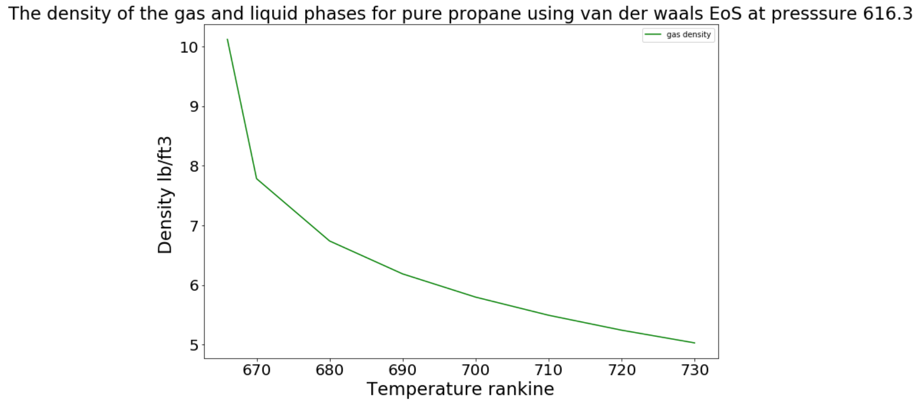
Density of Gas phase is =
(0.0911592056825045б + 0 j)

Density of Liquid phase is =
(15.132991325962657 + 6.488552123423175 j)

Density of Gas phase is =
(7.452739331777336 - 5.612593158380227 j)

Density of Liquid phase is =
(15.451663194053161 + 0 j)





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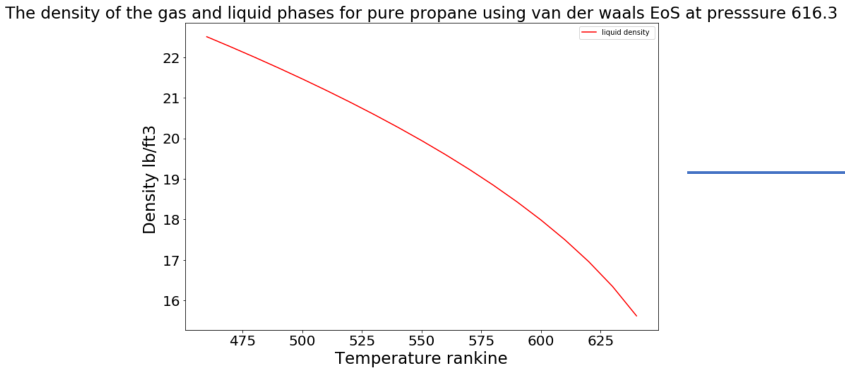

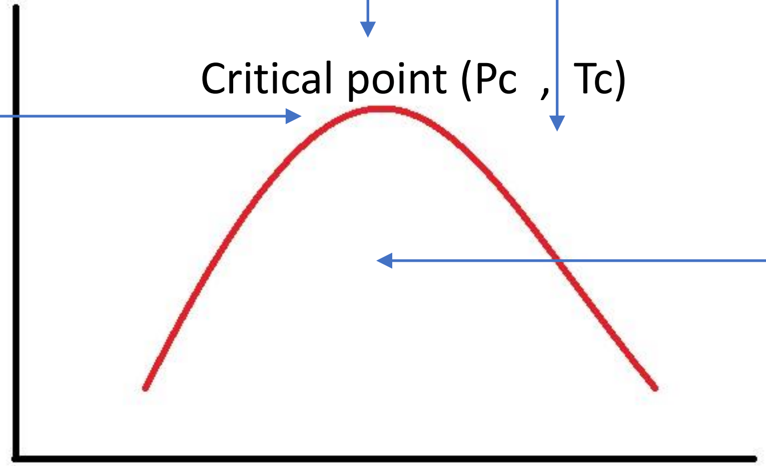

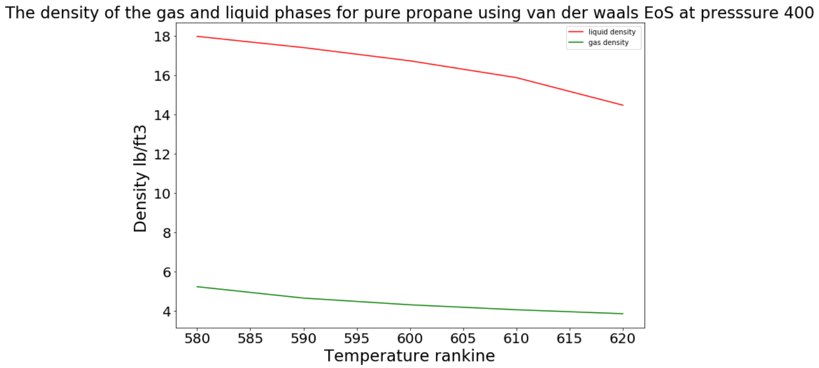

roots [0.45776103+0.39413961j
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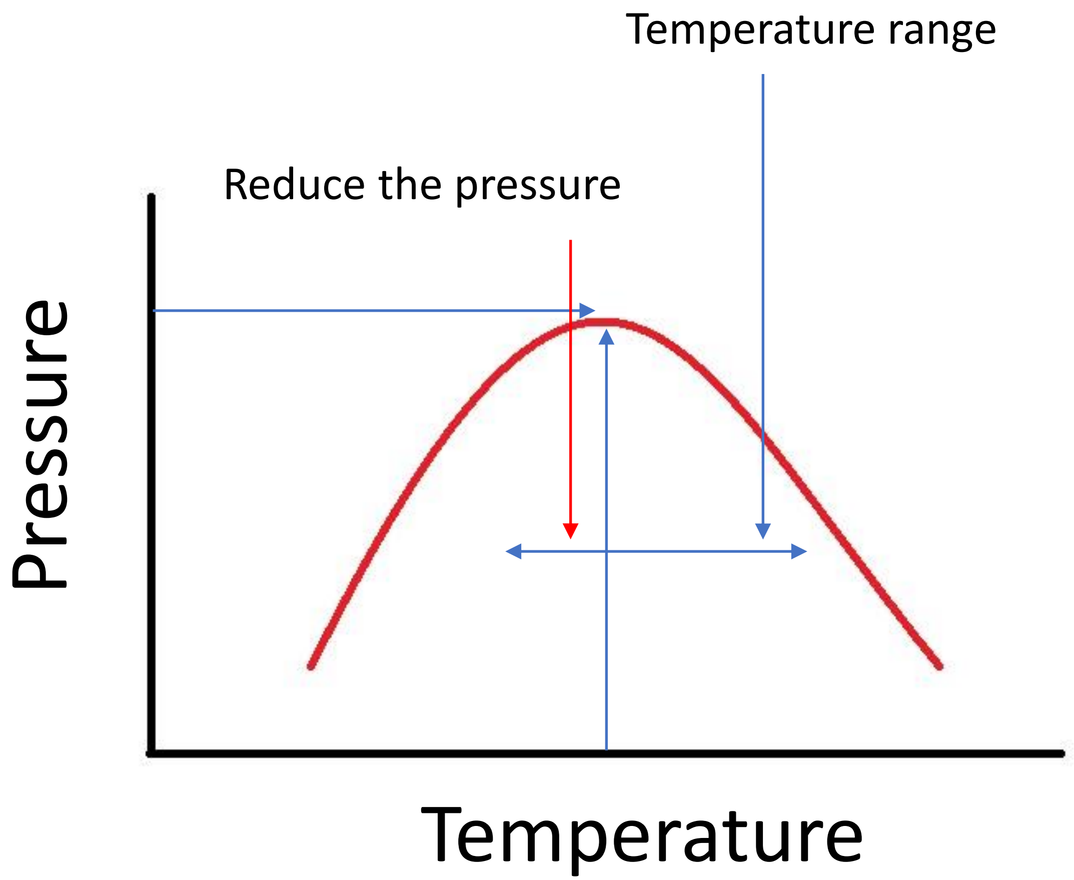
0.22024561
0.18272658]

How to build a Phase Diagram



Step 1 : Start with know point critical point

Step 2 : Reduce pressure and again calculate roots over the range of temperature

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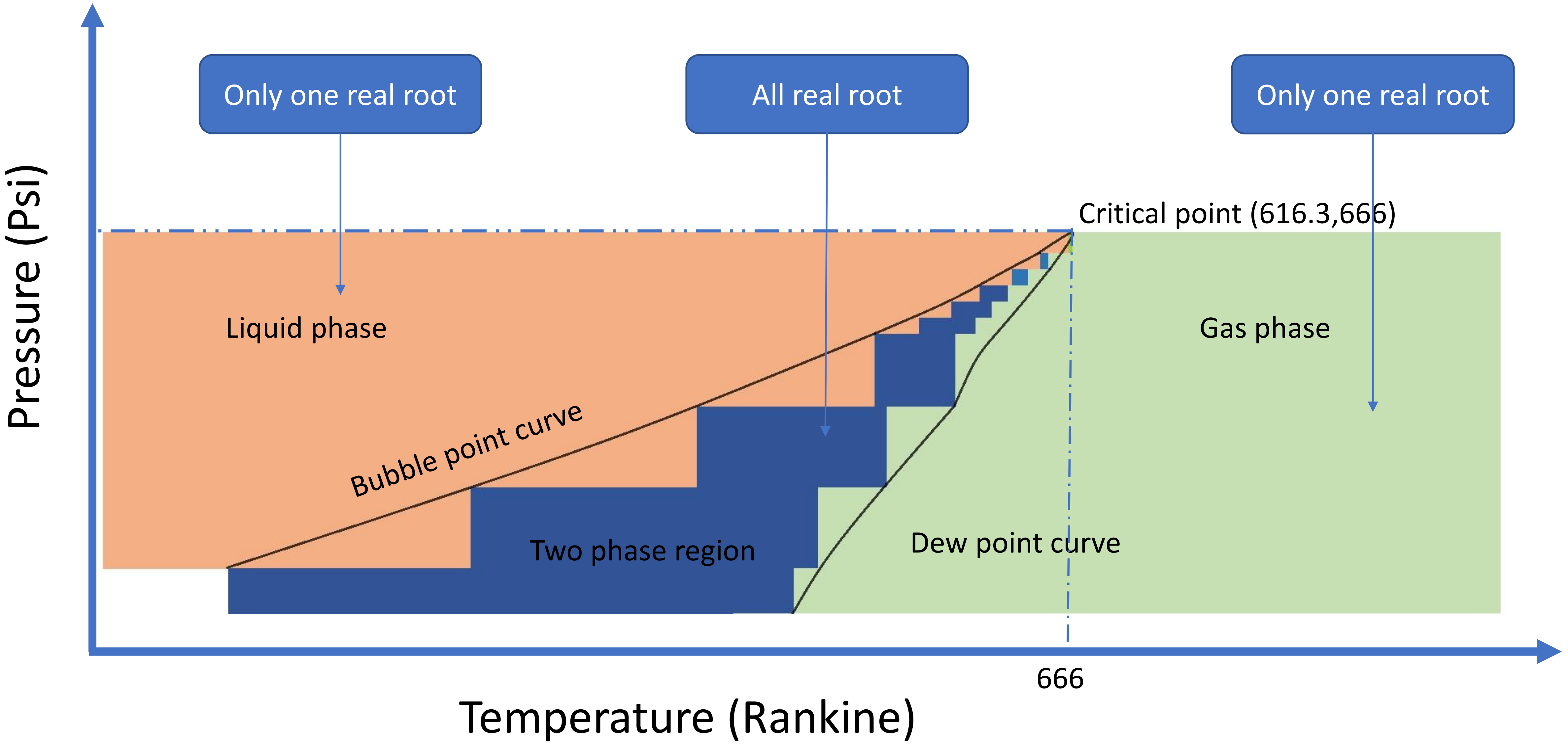
Pressure Temperature Phase Diagram



Conclusion

- If the pressure and temperature condition are in the two-phase region, then only All three roots are real only in the two-phase part.
- If the pressure and temperature condition are outside the two-phase region, then we get only real root and two complex root.
- For any condition of pressure and temperature, at least one root will have real value.
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Equation of state

Equation of State models

- Van der Waals (vdW) family
- Benedict-Webb-Rubin family
- Reference fluid EoS
- Augmented rigid body EoS

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$a = \Omega_a \frac{R^2\ Tc^2}{P_c}$$

Equation of state

- An equation of state (EOS) is an analytical expression relating the pressure p to the temperature T and the volume V.

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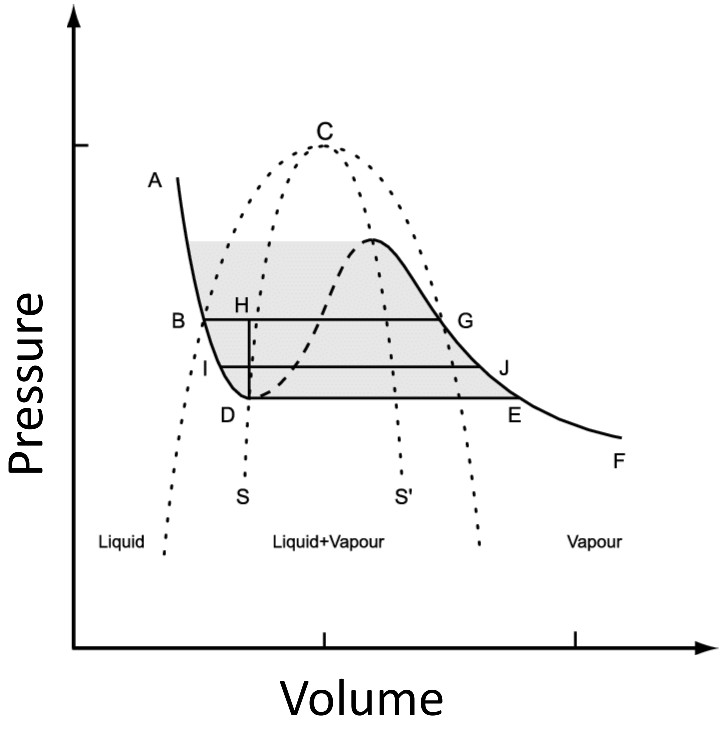

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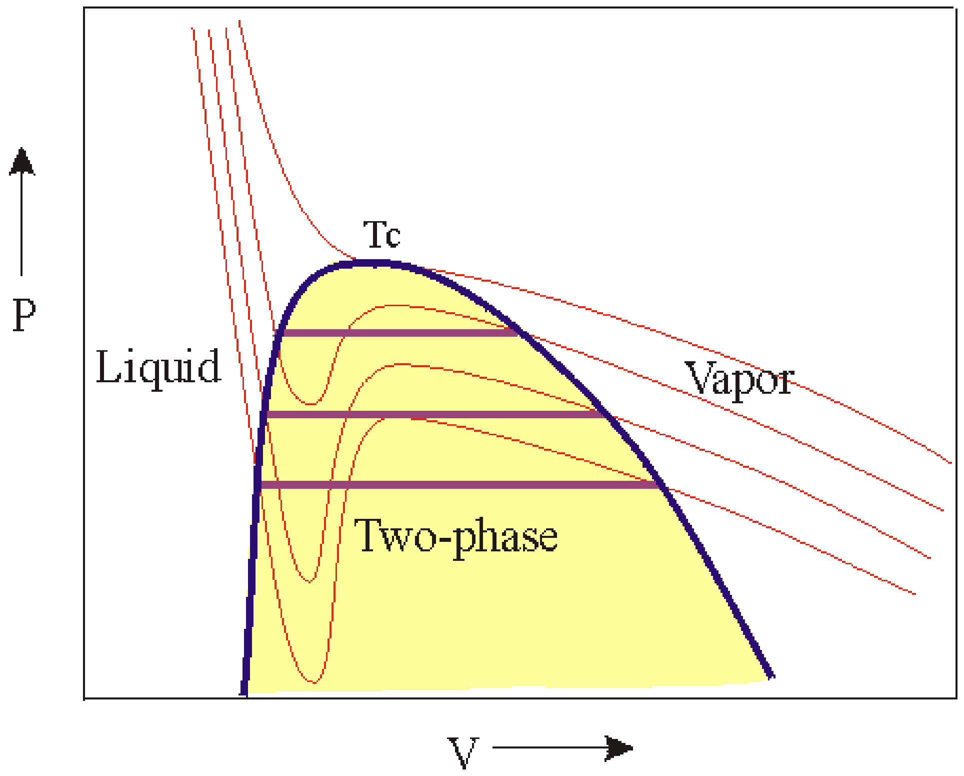

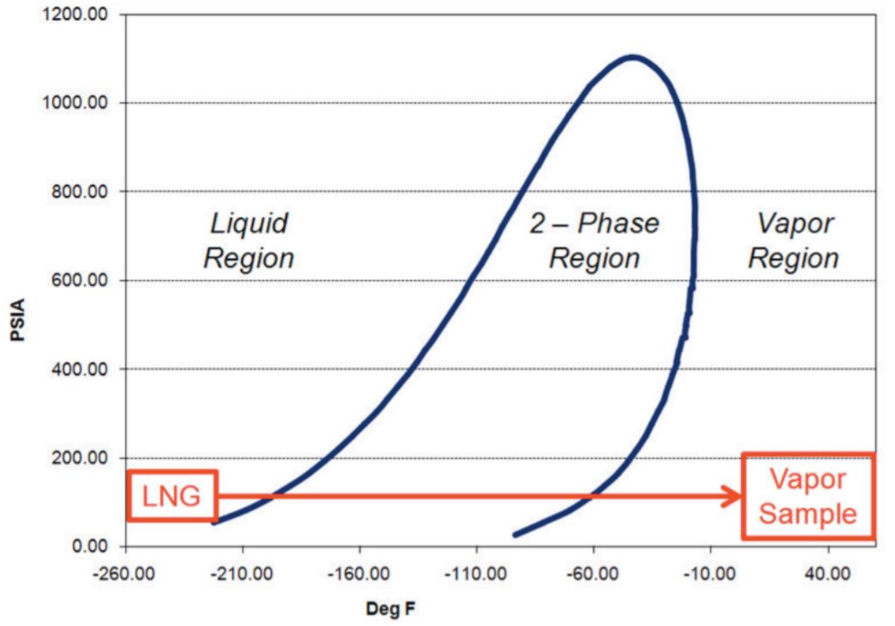

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Temperature range for the simulation

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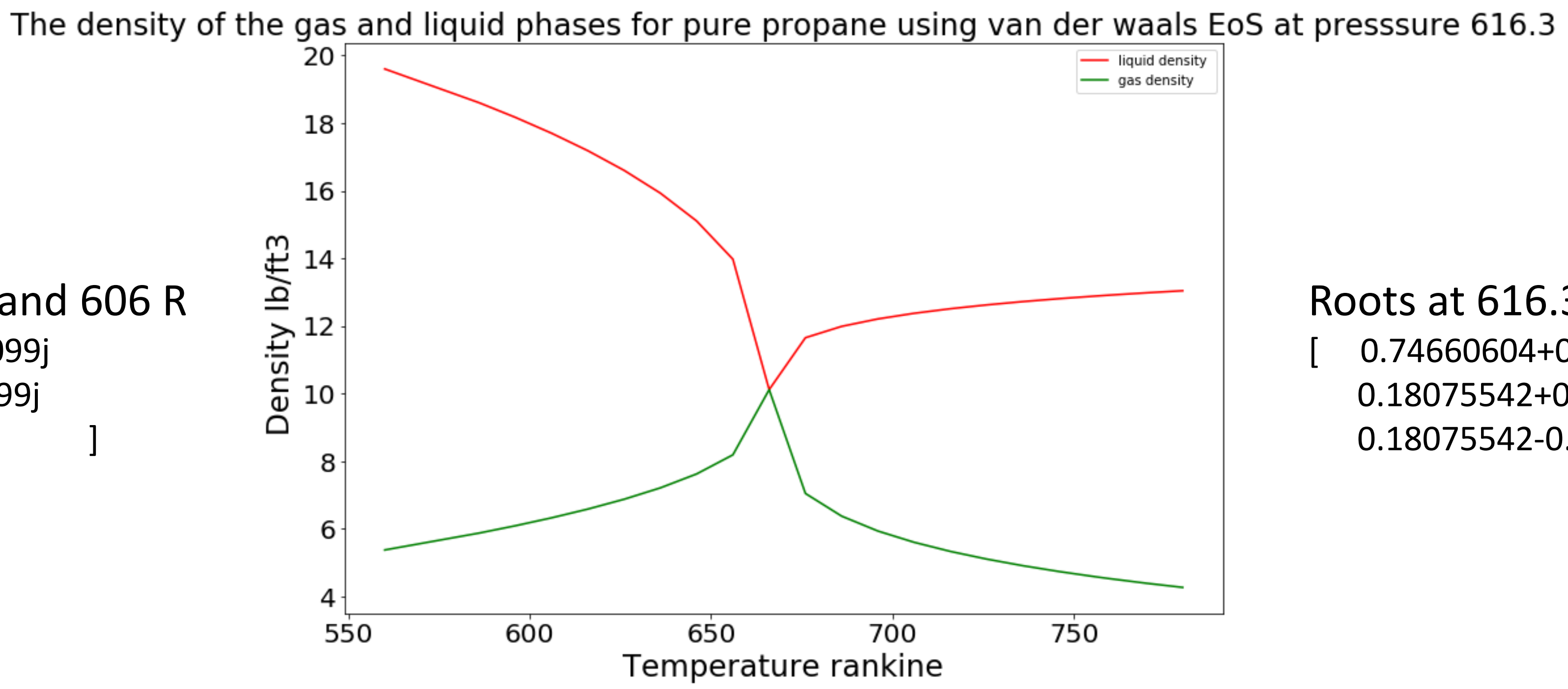

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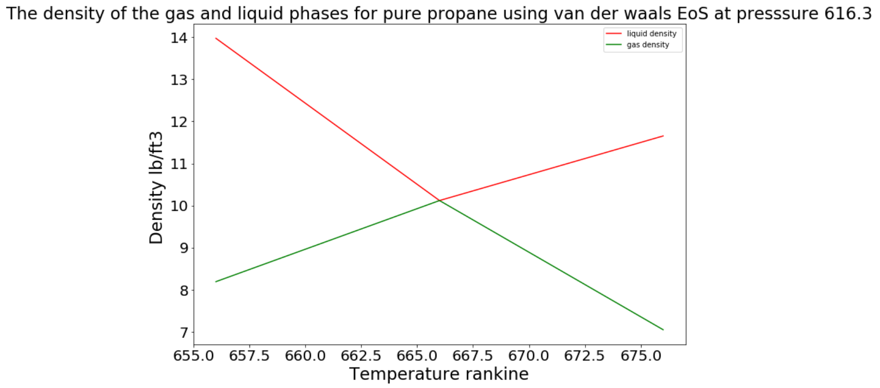

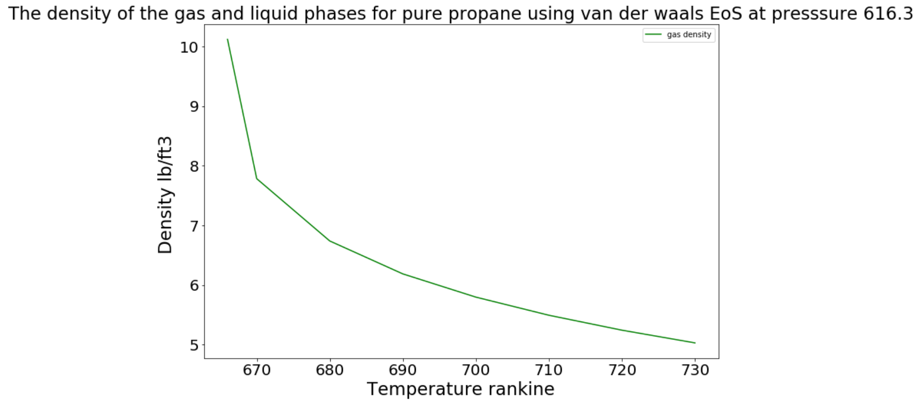

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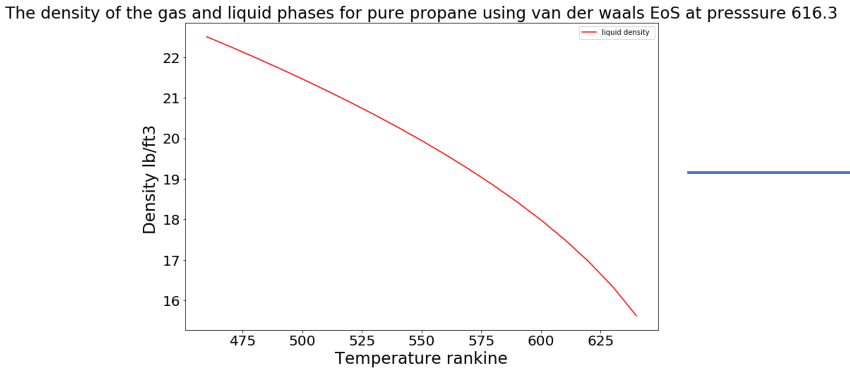

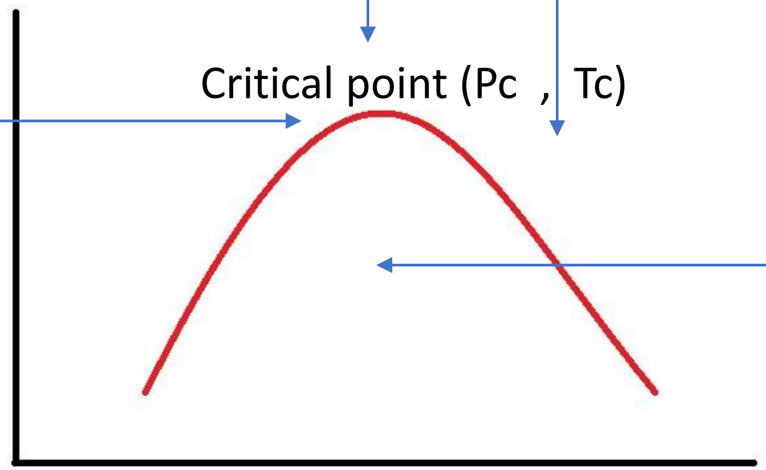

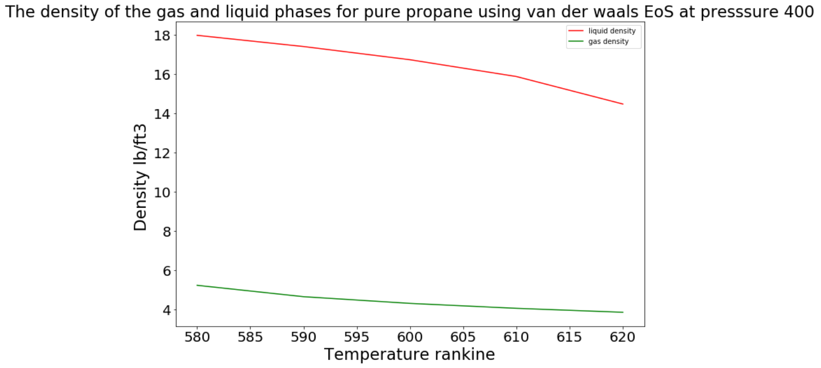

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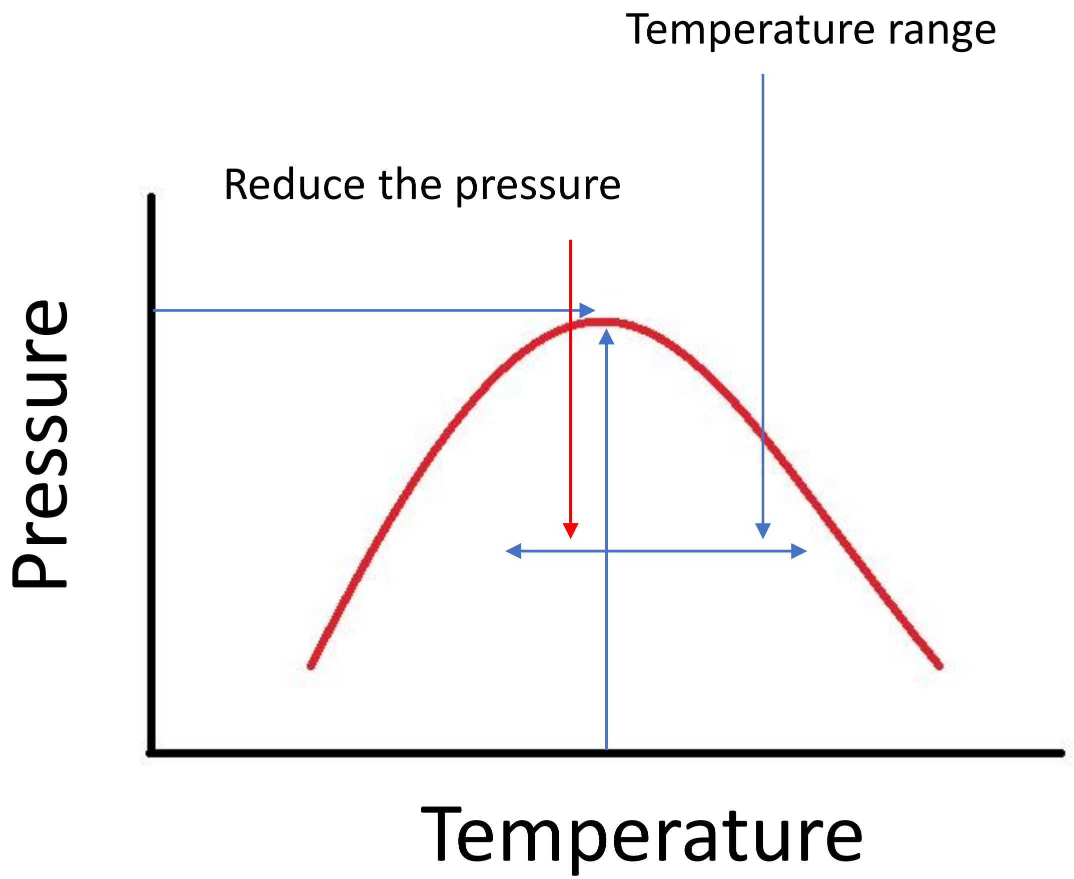

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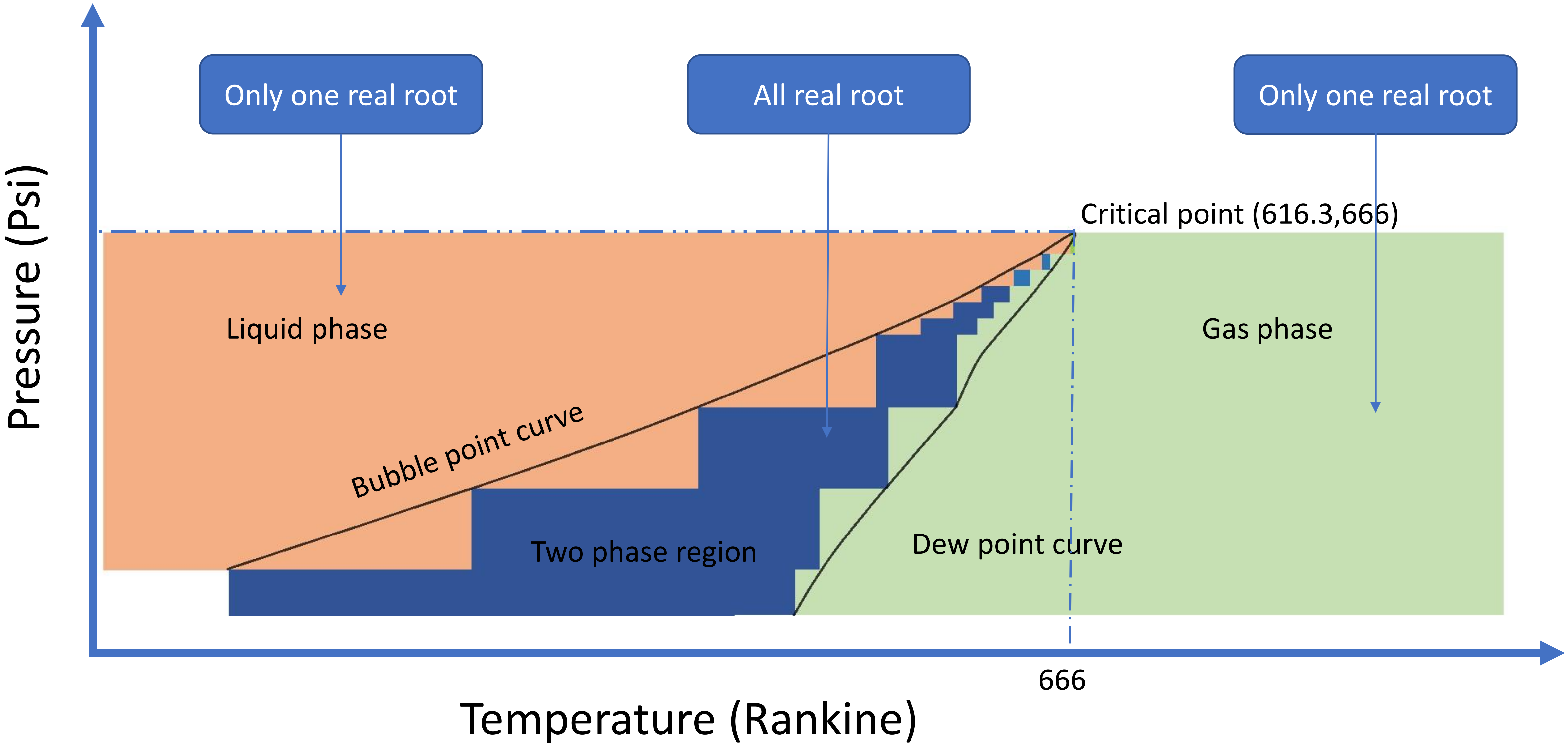

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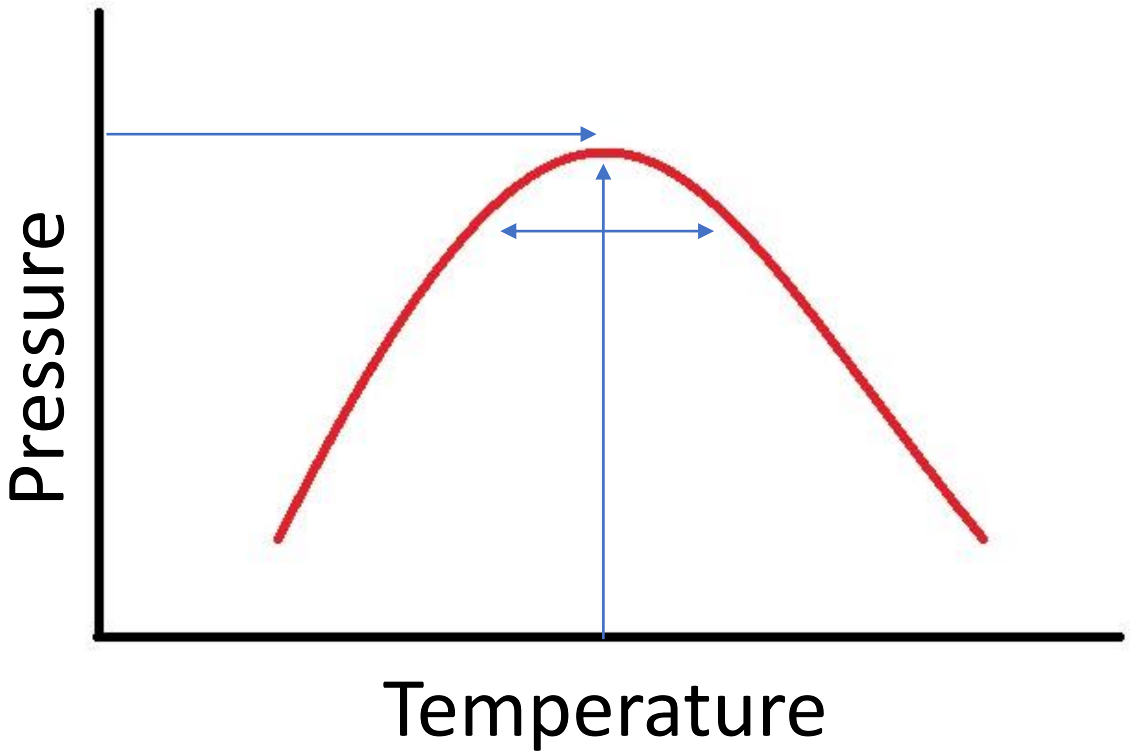

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