6.6 SOLVING THE EQUATION OF STATE FOR Z

This example complements Example 6.3 of the textbook by providing hand calculations.

Example S6.1 Peng-Robinson Solution by Hand Calculation

Perform a hand calculation of the real roots for argon at 105.6 K and 0.498 MPa.

Solution: Looking up critical constants, \( T_c = 150.86 \), \( P_c = 4.898 \), \( \omega = -0.004 \)

\[
T_r = \frac{105.6}{150.86} = 0.70; \quad P_r = \frac{0.498}{4.898} = 0.1017
\]

From Eqn. 6.17

\[
\kappa = 0.37464 + 1.54226(-0.004) - 0.26993(-0.004)^2 = 0.36847
\]

\[
\alpha = [1 + 0.36847(1 - \sqrt{0.70})]^2 = 1.1240
\]

From Eqn. 6.16

\[
a = 0.45724 \frac{(8.314 \times 150.86)^2}{4.898} (1.124) = 165067 \frac{\text{MPa} \cdot \text{cm}^6}{\text{mol}^2}
\]

\[
b = 0.077796(8.314)(150.86)/4.898 = 19.922 \text{ cm}^3/\text{mol}
\]

using Eqns. 6.21 and 6.23

\[
A = aP/(RT)^2 = (165067)(0.498)/[(8.314)(105.6)]^2 = 0.1066
\]

\[
B = bP/RT = (19.922)(0.498)/[(8.314)(105.6)] = 0.0113
\]

Determining the coefficients of Eqn 6.25 and B.27 (from appendix B)

\[
a_2 = -(1-B) = -(1 - 0.0113) = -0.9887
\]

\[
a_1 = (A - 3B^2 - 2B) = 0.1066 - 3(0.0113)^2 - 2(0.0113) = 0.08362
\]

\[
a_0 = -(AB - B^2 - B^3) = -(0.1066(0.0113) - 0.0113^2 - 0.0113^3) = -0.001075
\]

At this point, the coefficients could be plugged into a polynomial root finding calculator program. However, the hand calculations from Appendix B will be followed. From Eqn. B.30,

\[
p = (3(0.08362) - (-0.9887)^2)/3 = -0.2422
\]

\[
q = (2(-0.9887)^3 - 9(-0.9887)(0.08362) + 27(-0.01075))/27 = -0.04511
\]

From B.31, \( R = -0.04511^2/4 + (-0.2422)^3/27 = -1.75E-5 \), so three real roots exist. Using the trigonometric method, from B.36-B37

\[
m = 2\sqrt{(-(-0.2422))/3} = 0.5683
\]
Example S6.1 Peng-Robinson Solution by Hand Calculation

Numbering roots in a manner that will result in largest to smallest \( Z \), (using radians)

\[
\theta_1 = \frac{1}{3} \arccos \left( \frac{3(-0.0511)}{(-0.2422)(0.5683)} \right) = 0.061185
\]

\[
\theta_2 = 0.061185 + 4.1888 = 4.250
\]

\[
\theta_3 = 0.061185 + 2.0944 = 2.156
\]

From B.38 (using radians)

\[
x_1 = 0.5683 \cos(0.061185) = 0.56724
\]

\[
x_2 = 0.5683 \cos(4.250) = -0.25351
\]

\[
x_3 = 0.5683 \cos(2.1556) = -0.31372
\]

and using B.29

\[
Z_1 = 0.56724 - (-0.9887)/3 = 0.8968
\]

\[
Z_2 = -0.25351 - (-0.9887)/3 = 0.07606
\]

\[
Z_3 = -0.31372 - (-0.9887)/3 = 0.01584
\]

and using \( V = \frac{ZRT}{P} \)

\[
V_1 = 0.8968(8.314)(105.6)/(0.498) = 1581 \text{ cm}^3/\text{mol}
\]

\[
V_2 = 0.07606(8.314)(105.6)/(0.498) = 134 \text{ cm}^3/\text{mol}
\]

\[
V_3 = 0.01584(8.314)(105.6)/(0.498) = 27.9 \text{ cm}^3/\text{mol}
\]

The results are in good agreement with textbook Example 6.3, recognizing limitations of roundoff errors.