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, ω = –0.004

$$T_r = 105.6/150.86 = 0.70; \quad P_r = 0.498/4.898 = 0.1017$$

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

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

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

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 caculations from Appendix B will be followed. From Eqn. B.30,

$$p = (3(0.08362) - (-0.9887)^2)/3 = -0.2422$$

$$q = (2(-0.9887)^3 - 9(-0.9887)(0.08362) + 27(-0.001075))/27 = -0.04511$$

From B.31, $R = -0.04511^2/4 + (-0.2422)^3/27 = -1.75\text{E-}5$, 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)

$$\theta_1 = \frac{1}{3}\text{acos}(3(-0.04511)/((-0.2422)(0.5683))) = 0.061185$$

$$\theta_2 = 0.061185 + 4.1888 = 4.250$$

$$\theta_3 = 0.061185 + 2.0944 = 2.1556$$

From B.38 (using radians)

$$x_1 = 0.5683\cos(0.061185) = 0.56724$$

$$x_2 = 0.5683\cos(4.2500) = -0.25351$$

$$x_3 = 0.5683\cos(2.1556) = -0.31372$$

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 $V = ZRT/P$

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

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

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

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