1.11.1 Critical constants and vdW equation

As illustrated in Fig. 1.4 the critical point is defined by the existence of an inflection point, i.e.

$$\left(\frac{\partial p}{\partial V_m}\right)_{T_c} = 0 = -\frac{R\,T_c}{(V_{m,c}-b)^2} + \frac{2a}{V_{m,c}^3} \quad \Rightarrow \quad \frac{R\,T_c}{(V_{m,c}-b)^2} = \frac{2a}{V_{m,c}^3} \tag{1.16}$$

$$\left(\frac{\partial^2 p}{\partial V_m^2}\right)_{T_c} = 0 = \frac{2\,R\,T_c}{(V_{m,c}-b)^3} - \frac{6a}{V_{m,c}^4} \quad \Rightarrow \quad \frac{2\,R\,T_c}{(V_{m,c}-b)^3} = \frac{6a}{V_{m,c}^4} \tag{1.17}$$

Dividing Eq. (1.16) by Eq. (1.17) we get

$$\frac{\frac{R\,T_c}{(V_{m,c}-b)^2}}{\frac{2\,R\,T_c}{(V_{m,c}-b)^3}} = \frac{\frac{2a}{V_{m,c}^2}}{\frac{6a}{V_{m,c}^4}} \quad \Rightarrow \quad \frac{V_{m,c}-b}{2} = \frac{V_{m,c}}{3} \Rightarrow V_{m,c} = 3\,b \tag{1.18}$$

Including Eq. (1.18) in Eq. (1.16) we get

$$\frac{R\,T_C}{(3b-b)^2} = \frac{2a}{27b^3} \Rightarrow T_c = \frac{8a}{27Rb} \tag{1.19}$$

Including Eq. (1.19) and Eq. (1.18) in the vdW equation we get

$$p_c = \frac{R\,T_c}{V_{m,c}-b} - \frac{a}{V_{m,c}^2} = \frac{a}{27b^2} \tag{1.20}$$

From these results e.g. the compression factor at the critical point is found:

$$Z_c = \frac{p_c\,V_{m,c}}{R\,T_c} = \frac{3}{8} \tag{1.21}$$

In general the experimental strategy for describing real (vdW) gases means

1. Calculate a and b from critical constants.
2. Compute any relevant point in phase diagram by the vdW approach.