The Relationship between the van der Waals Parameters and the Critical Constants

If

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

then

$$p = \frac{RT}{V - b} - \frac{a}{V^2}$$

At the critical point,

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0$$

So, differentiating our expression for pressure with respect to volume at constant temperature

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0$$

so that

$$\frac{RT_c}{(V_c - b)^2} = \frac{2a}{V_c^3}$$

Differentiating again gives

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = +\frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0$$

so that

$$\frac{2RT_c}{(V_c - b)^3} = \frac{6a}{V_c^4}$$

Dividing these two expressions gives

$$\frac{(V_c - b)}{2} = \frac{V_c}{3}$$

and so

$$V_c = 3b$$

Substitution of this result into the expression that we obtained by differentiating once

$$\frac{RT_c}{(V_c - b)^2} = \frac{2a}{V_c^3}$$

gives

$$\frac{RT_c}{(3b - b)^2} = \frac{2a}{(3b)^3}$$

which, when rearranged, gives

$$T_c = \frac{8a}{27bR}$$

Substitution of the expressions for the critical volume V_c and critical temperature T_c into the van der Waals equation gives

$$\begin{aligned} p_c &= \frac{RT_c}{V_c - b} - \frac{a}{V_c^2} \\ &= R\,\frac{1}{(3b - b)}\,\frac{8a}{27bR} - \frac{a}{9b^2} \\ &= \frac{8a}{54b^2} - \frac{a}{9b^2} \\ &= \frac{8a}{54b^2} - \frac{6a}{54b^2} \end{aligned}$$

and so

$$p_c = \frac{a}{27b^2}$$

Given these expressions for the values of the critical constants

$$\frac{T_c}{p_c} = \frac{8a}{27bR}\,\frac{27b^2}{a} = \frac{8b}{R}$$

so that

$$b = \frac{RT_c}{8p_c}$$

Similarly

$$T_c^2 = \frac{64a^2}{729b^2R^2}$$

$$\frac{T_c^2}{p_c} = \frac{64a^2}{729b^2R^2}\frac{27b^2}{a}$$
$$= \frac{64a}{27R^2}$$

Hence

$$a = \frac{27R^2T_c^2}{64p_c}$$