1.11.2 vdW equation and Leiden form

According to Eq. (1.10) the Leiden form of the virial coefficients is

$$p = \frac{RT}{V_m}\left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \cdots\right) \tag{1.22}$$

According to Eq. (1.12) the pressure can be written as

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \approx \frac{RT}{V_m}\left(1 + \frac{1}{V_m}\left(b - \frac{a}{RT}\right) + \frac{b^2}{V_m^2}\right) \tag{1.23}$$

Here we have used the property of the geometrical series

$$\frac{1}{1-x} = 1 + x + x^2 + \cdots \tag{1.24}$$

Comparing the coefficients of Eq. (1.22) and Eq. (1.23) we get

$$B = b - \frac{a}{RT} \quad \text{and} \quad C = b^2 \tag{1.25}$$

Since B contains two terms with opposite sign we find the expected behavior:

- At high T the repulsive forces are dominant, i.e. $B > 0$.
- At low T the attractive forces are dominant, i.e. $B < 0$.
- B increases with T (consistent with experimental data), i.e.

$$\frac{dB}{dT} = \frac{a}{RT^2} > 0 \tag{1.26}$$

- The Boyle temperature T_B is found for $B = 0$, i.e.

$$T_B = \frac{a}{b\,R} \tag{1.27}$$