

### 1.11.2 vdW equation and Leiden form

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

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

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

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

Here we have used the property of the geometrical series

$$\frac{1}{1-x} = 1 + x + x^2 + \dots \quad (1.24)$$

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

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

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.

$$\frac{dB}{dT} = \frac{a}{RT^2} > 0 \quad (1.26)$$

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

$$T_B = \frac{a}{bR} \quad (1.27)$$