2.6.1 Work of reversible isothermal expansion

Using the Leiden form of the virial approach in Eq. (1.10) we get

$$\begin{aligned} p &= nRT\left(\frac{1}{V} + \frac{n\,B}{V^2} + \frac{n^2\,C}{V^3} + \cdots\right) \quad \text{, i.e.} \\ w &= -\int_{V_1}^{V_2} pdV = -nRT\left[\int_{V_1}^{V_2}\frac{dV}{V} + nB\int_{V_1}^{V_2}\frac{dV}{V^2} + n^2C\int_{V_1}^{V_2}\frac{dV}{V^3} + \cdots\right] \quad \Rightarrow \\ w &= -nRT\left[\ln\frac{V_2}{V_1} - nB\left(\frac{1}{V_2} - \frac{1}{V_1}\right) - \frac{1}{2}n^2C\left(\frac{1}{V_2^2} - \frac{1}{V_1^2}\right) + \cdots\right] \end{aligned} \tag{2.17}$$

The first term of w represents the work of a perfect gas; for the following discussion we will neglect the third term. For an expansion $1/V_2 - 1/V_1$ is negative. We already know that $B(T)$ is positive at high T and negative at low T, i.e. at high T we find an increase of the expansion work and at low T a decrease of the expansion work for real gases compared to perfect gases. Thus repulsive forces must be dominant at high T.
We can get a corresponding result using the vdW equation (1.12) for analyzing work contributions

$$\begin{aligned} p &= \frac{nRT}{V-nb} - \frac{n^2\,a}{V^2} \quad \Rightarrow \quad w = -nRT\int_{V_1}^{V_2}\frac{dV}{V-nb} + n^2a\int_{V_1}^{V_2}\frac{dV}{V^2} \\ w &= -nRT\ln\frac{V_2-nb}{V_1-nb} - n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) \\ &\approx -nRT\ln\frac{V_2}{V_1} + n^2RTb\left(\frac{1}{V_2} - \frac{1}{V_1}\right) - n^2a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) \quad \text{(in linear order in } b\text{)} \\ &= w^0 - n^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right)(a - RTb) \quad (w^0 \text{ work of perfect gas}) \end{aligned} \tag{2.18}$$

So for a reversible compression we find $w < w^0$ for $bRT < a$ and $w > w^0$ for $bRT > a$, i.e. if attractive exceed repulsive forces ($a > bRT$) the compression of a vdW gas needs less work compared to a perfect gas. While w^0 scales with n the interaction term in linear order scales with n^2. This is a must, since at least two particles are needed for any interaction and n^2 is the essential part for the probability of two particles to meet.