

2.6.1 Work of reversible isothermal expansion

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

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

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

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

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.