3.27 Maxwell relations, example for vdW gas

We now apply Maxwell relations to the equation of a vdW gas to find some astonishing parameter dependencies:

- Dependency of the entropy on the volume for a vdW gas:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad \Rightarrow \quad \Delta S = \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial T}\right)_V dV$$
$$\Delta S = \int_{V_1}^{V_2} \left[\left(\frac{\partial}{\partial T}\right)_V \left(\frac{n\,R\,T}{V - n\,b} - \frac{a\,n^2}{V^2}\right)\right] dV = n\,R \ln \frac{V_2 - n\,b}{V_1 - n\,b} \tag{3.65}$$

  So (astonishingly) ΔS does not depend on a.

- Internal pressure π_T of a vdW gas.
  We start with the total differential of $U(S, V)$:

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T + \left(\frac{\partial U}{\partial V}\right)_S = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p$$
$$p = \frac{n\,R\,T}{V - n\,b} - \frac{a\,n^2}{V^2} \quad \Rightarrow \quad \left(\frac{\partial p}{\partial T}\right)_V = \frac{n\,R}{V - n\,b} \tag{3.66}$$
$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = \frac{n\,R\,T}{V - n\,b} - \left(\frac{n\,R\,T}{V - n\,b} - \frac{a\,n^2}{V^2}\right) = \frac{a\,n^2}{V^2}$$

  So (astonishingly) the internal pressure π_T does not depend on b.