5.7.1 Application of Gibbs-Duhem: rationalization of ϕ/x-curves

We now use the Gibbs-Duhem equation to calculate relations between ϕ_1 and ϕ_2 of a binary mixture. For the total derivatives we find

$$d\varphi_1 = \left(\frac{\partial\varphi_1}{\partial n_1}\right) dn_1 + \left(\frac{\partial\varphi_1}{\partial n_2}\right) dn_2 \quad \text{and} \quad d\varphi_2 = \left(\frac{\partial\varphi_2}{\partial n_1}\right) dn_1 + \left(\frac{\partial\varphi_2}{\partial n_2}\right) dn_2 \tag{5.22}$$

Using $\sum_i n_i d\varphi_i = 0$ we get

$$\begin{aligned} &\left[\left(\frac{\partial\varphi_1}{\partial n_1}\right) dn_1 + \left(\frac{\partial\varphi_1}{\partial n_2}\right) dn_2\right] n_1 + \left[\left(\frac{\partial\varphi_2}{\partial n_1}\right) dn_1 + \left(\frac{\partial\varphi_2}{\partial n_2}\right) dn_2\right] n_2 = 0 \\ \Rightarrow \; &\left[n_1 \left(\frac{\partial\varphi_1}{\partial n_1}\right) + n_2 \left(\frac{\partial\varphi_2}{\partial n_1}\right)\right] dn_1 + \left[n_1 \left(\frac{\partial\varphi_1}{\partial n_2}\right) + n_2 \left(\frac{\partial\varphi_2}{\partial n_2}\right)\right] dn_2 = 0 \end{aligned} \tag{5.23}$$

which must be true for all dn_i, so both terms of the sum must be zero, i.e.

$$\begin{aligned} &\Rightarrow \; n_1 \left(\frac{\partial\varphi_1}{\partial n_1}\right) + n_2 \left(\frac{\partial\varphi_2}{\partial n_1}\right) = 0 \quad \text{and} \quad n_1 \left(\frac{\partial\varphi_1}{\partial n_2}\right) + n_2 \left(\frac{\partial\varphi_2}{\partial n_2}\right) = 0 \\ &\Rightarrow \; x_1 \left(\frac{\partial\varphi_1}{\partial n_1}\right) = -(1-x_1) \left(\frac{\partial\varphi_2}{\partial n_1}\right) \quad \text{and} \quad x_1 \left(\frac{\partial\varphi_1}{\partial n_2}\right) = -(1-x_1) \left(\frac{\partial\varphi_2}{\partial n_2}\right) \end{aligned} \tag{5.24}$$

This implies that the slopes of φ_1 and φ_2 have opposite signs. Choosing $x_1 = 0.5$ we see that the absolute values of the slopes are equal. This is shown in Fig. 5.3 for 50 at% of the partial molar volume for water and ethanol.