1.12 Corresponding states (cs) and reduced variables

In this section we will define a universal thermal equation of state matching for all compounds: $f(p, V, T) = 0$. The basic idea is to find a representation for which the different intermolecular interactions of the different compounds can cancel out mathematically.
The strategy for the solution:

1. A special state (e.g. boiling point, critical point) represents a universal reference state for each substance which contains (all relevant) information about the intermolecular interactions.

2. Introduction of a ratio of two variables, "reduced variables":

$$\Gamma_r = \frac{\Gamma}{\Gamma_c} \tag{1.28}$$

Each of this reduced variables depends on the intermolecular interactions. Thus the intermolecular interactions (almost) cancel out.

As an example we will discuss the reduced form of the vdW equation.

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \Rightarrow p_r p_c = \frac{R T_r T_c}{V_{m,r} V_{m,c} - b} - \frac{a}{(V_{m,r} V_{m,c})^2} \tag{1.29}$$

Substituting

$$V_{m,c} = 3b \quad , \quad p_c = \frac{a}{27\, b^2} \quad , \quad T_c = \frac{8a}{27\, R\, b} \tag{1.30}$$

we finally get the universal equation

$$p_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2} \tag{1.31}$$

Although a and b are eliminated in the reduced form of the vdW equation they are still are present in form of the reduced variables.
For a later application we will need the isothermal compressibility κ which in the form of reduced variables is defined as

$$\kappa_T(V_r) = -\frac{1}{V_r}\left(\frac{\partial p_r}{\partial V_r}\right)^{-1} \quad \text{i.e.} \quad \kappa_T(1) = \left(-\frac{8\,T_r\,3}{(3\,V_r - 1)^2} + \frac{6}{V_r^3}\right)^{-1} = \frac{1}{6\,(T_r - 1)} \tag{1.32}$$

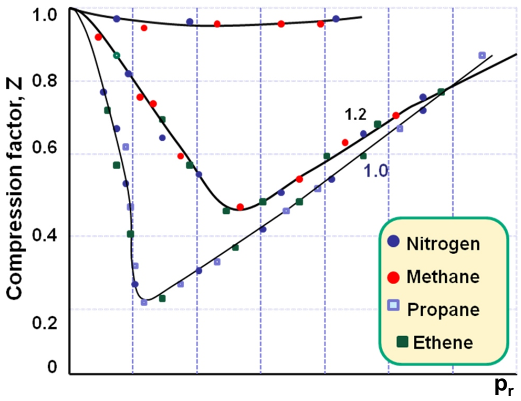

Figure 1.6: Isotherms using reduced variables for several T_r. Experimental data and theoretical curves.

How well the concept of reduced variables and corresponding states can work is shown in Fig. 1.6.

- Real gases at the same p_r and T_r exert the same V_r independent from their chemical nature, so $f(p, V, T) \rightarrow f(p_r, V_r, T_r) = 0$.
- One can adjust the conditions for each compound that the physical states of very different compounds are corresponding.
- Strong deviations may be found for strongly anisotropic molecules: polar, non-spherical molecules (here correction terms available), and for H-bonding.
- For $T < T_c$ (i.e. $T_r < 1$ not shown in diagram), the isotherms still show the vdW loops! Thus even the corresponding states do not solve all problems.