## 2.2   Description of systems by state functions

The state of a system is described unambiguously by *state functions*. Variables defining a state are called *state variables*. Properties/variables of state functions are e.g. $V$, $T$, and $p$.
For any state function the following relations hold:

1. State functions are path-independent, i.e.

$$\oint dV = 0 \tag{2.1}$$

2. Each state function represents an exact (or total) differential, e.g.

$$dV_{p,T} = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp \tag{2.2}$$

3. Mixed second derivatives are equal, e.g.

$$\left(\frac{\partial^2 V}{\partial T \partial p}\right)_{p,T} = \left(\frac{\partial^2 V}{\partial p \partial T}\right)_{T,p} \tag{2.3}$$

The three properties above are just the properties of any *exact (or total) differential*, e.g. the integral between fixed endpoints is always path-independent, from which it follows that the integral of $dV$ around any closed path must vanish. The standard test for exact differentials is to check if the cross partial derivatives are identical; if not, the differential is inexact. In this case, the integral of $dV$ is path dependent, and does not depend solely on the endpoints. Since path integrals are very difficult to measure and integrate, it is a drastic simplification to replace a path integral by a conventional integral, which is always possible for exact differentials.
Note:

- Also non-state functions are important, e.g. $w$, $q$.

- Non-state functions can occur as state functions assuming special boundary conditions (e.g. $w_T \to \Delta F$)

In thermodynamics in general a state is meant to be an equilibrium state. As an underlying model we often consider quasi-static processes, i.e. intermediate steps are considered as equilibrium states.
A set of state variables describes the system properties in an average sense.
As an example for state vs. non-state function we discuss work. The work done when climbing hills adds up, it is in general a non-state function, while the height as a state function depends only on the actual state.
Just the knowledge about the existence of an exact differential allows to calculate a third property from two others, using the famous and very general Euler chain rule:

$$dz = 0 = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \quad \Rightarrow \quad \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1 \tag{2.4}$$

As an example one finds for the compression coefficient

$$\kappa_T = -\frac{1}{V_m}\left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{V_m}\frac{1}{\left(\frac{\partial p}{\partial T}\right)_V}\left(\frac{\partial T}{\partial V}\right)_p = \frac{1}{V_m}\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial p}{\partial T}\right)_V} = \frac{1}{p}\frac{\alpha}{\beta} \tag{2.5}$$

$$\text{with} \quad \alpha = \frac{1}{V_m}\left(\frac{\partial V}{\partial T}\right)_p \text{ (expansion coefficient)} \quad \text{and} \quad \beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V \text{ (tension coefficient).} \tag{2.6}$$