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.

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

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

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