Chapter 4
Equations of State

There is interplay between the fundamental forms and the equations of state. The equations of state can be obtained from any fundamental form. On the other hand, from a certain set of equations of state, the fundamental form can be obtained.

In the strict sense of thermodynamics, an equation of state is a differential of the fundamental form with respect to its natural variables as a function of these natural variables.

For example, using the energy $U(S, V, n)$ as fundamental form, then

$$- \frac{\partial U(S, V, n)}{\partial V} = p(S, V, n) = f(S, V, n)$$

that turns out as the dependence on the pressure on a function of the set $S, V, n$ is an equation of state.

Often, the energy in terms of temperature, volume, and mol number $U(T, V, n)$ is addressed as the caloric state equation, whereas the volume in terms of temperature, pressure, and mol number $V(T, p, n)$ is addressed as the thermal state equation. On the other hand, the energy exclusively expressed in terms of the corresponding natural variables $U(S, V, n)$ belongs to the type of a fundamental equation or fundamental form.

Obviously, the thermal state equation $V(T, p, n) = f(T, p, n)$ is a thermodynamic state equation arising from the Gibbs free enthalpy, because

$$\frac{\partial G(T, p, n)}{\partial p} = V(T, p, n) = f(T, p, n).$$

4.1 The Ideal Gas

If we would know any of the fundamental forms valid for the ideal gas, we could readily derive both the ideal gas law and the Poisson\(^1\) equation, namely the adiabatic

\(^{1}\) Siméon Denis Poisson, born Jun. 21, 1781, in Pithiviers, France, died Apr. 25, 1840, in Sceaux, France.
equation of change. Unfortunately, initially we do not have such a knowledge or a feeling how the fundamental form could look like.

In this section, we will show how to derive a fundamental form from the state equations. Further, we will show how to get from certain assumptions on the fundamental from the state equations. The latter approach allows getting information on the thermodynamic properties of the ideal gas.

### 4.1.1 Energy of the Ideal Gas from State Functions

We recall the thermal state equation for 1 mol of the ideal gas,

\[ p \tilde{V} = RT. \] (4.1)

In Eq. (4.1), we express the pressure and the temperature as a function of the energy \( \tilde{U}(\tilde{S}, \tilde{V}) \) and arrive at the partial differential equation (4.2):

\[- \frac{\partial \tilde{U}(\tilde{S}, \tilde{V})}{\partial \tilde{V}} \tilde{V} = R \frac{\partial \tilde{U}(\tilde{S}, \tilde{V})}{\partial \tilde{S}}. \] (4.2)

This equation has the solution

\[ \tilde{U}(\tilde{S}, \tilde{V}) = f \left( \tilde{V} e^{-\tilde{S}/R} \right). \] (4.3)

This means the energy can be any function of \( \tilde{V} e^{-\tilde{S}/R} \). Therefore, the ideal gas law as such is not sufficient to get the energy as a function of entropy and volume. The function may contain only \( \tilde{V} e^{-\tilde{S}/R} \) as argument. For example, \( f(\tilde{V} e^{-\tilde{S}/R}) = \left( \tilde{V} e^{-\tilde{S}/R} \right)^2 + 1 \) is a valid function, but \( f(\tilde{V} e^{-\tilde{S}/R}) = \tilde{V} \left( \tilde{V} e^{-\tilde{S}/R} \right)^2 + \tilde{S} \) is not a valid function. We will shortly see that the function will be \( f(x) \propto x^{1-\kappa} \). As a further state function, use the adiabatic law:

\[ p(\tilde{S}, \tilde{V}) \tilde{V}^\kappa = f(\tilde{S}) = g(\tilde{S})^{1-\kappa}, \]

where \( g(\tilde{S}) \) is some function of the entropy only. We have put in advance the exponent \( 1 - \kappa \). Again, we insert for the pressure and arrive at

\[- \frac{\partial \tilde{U}(\tilde{S}, \tilde{V})}{\partial \tilde{V}} \tilde{V}^\kappa = g(\tilde{S})^{1-\kappa}. \]

This differential equation has the solution

\[ \tilde{U}(\tilde{S}, \tilde{V}) = -\frac{(g(\tilde{S})\tilde{V})^{1-\kappa}}{1-\kappa} + h(\tilde{S}). \] (4.4)