

Chapter 1

Review of Thermodynamics

This chapter presents a brief review of elementary thermodynamics. It complements Chapter 2, in which the connection between thermodynamics and statistical mechanical ensembles is established. The reader may wish to use this chapter as a short refresher course and may wish to consult one of the many books on thermodynamics, such as that of Callen[48] or Chapters 2 to 4 of the book by Reichl[216], for a more complete discussion of the material. The outline of the present chapter is as follows. In Section 1.1 we introduce the notion of state variables and equations of state. Section 1.2 contains a discussion of the laws of thermodynamics, definition of thermodynamic processes, and the introduction of entropy. In Section 1.3 we introduce the thermodynamic potentials that are most useful from a statistical point of view. The Gibbs–Duhem equation and a number of useful Maxwell relations are derived in Section 1.4. In Section 1.5 we turn to the response functions, such as the specific heat, susceptibility, and compressibility, which provide the common experimental probes of macroscopic systems. Section 1.6 contains a discussion of some general conditions of equilibrium and stability and we conclude, in 1.7, with a brief discussion of the thermodynamics of phase transitions and the Gibbs phase rule.

1.1 State Variables and Equations of State

A macroscopic system has many degrees of freedom, only a few of which are measurable. Thermodynamics thus concerns itself with the relation between a small number of variables which are sufficient to describe the bulk behavior of the system in question. In the case of a gas or liquid the appropriate variables are the pressure P , volume V , and temperature T . In the case of a magnetic solid the appropriate variables are the magnetic field \mathbf{H} , the magnetization \mathbf{M} , and the temperature T . In more complicated situations, such as when a liquid is in contact with its vapor, more variables are needed: the pressure P , temperature T , volume of liquid and gas V_L , V_G , interfacial area A , and surface tension σ . If the thermodynamic variables are independent of time, the system is said to be in a *steady state*. If, moreover, there are no macroscopic currents in the system, such as a flow of heat or particles through the material, the system is in *equilibrium*. Any quantity which, in equilibrium, depends only on the thermodynamic variables, rather than on the history of the sample, is called a *state function*. In subsequent sections we shall meet a number of such quantities. For a large system, the state variables can normally be taken to be either *extensive* (i.e., proportional to the size of the system) or *intensive* (i.e., independent of system size). Examples of extensive variables are the internal energy, the entropy, and the mass of the different constituents or their number, while the pressure, the temperature, and the chemical potentials are intensive. The postulate that quantities like the internal energy and entropy are extensive and independent of shape is equivalent to an assumption of additivity or, as we shall see in Section 2.1, of the existence of the *thermodynamic limit*. In the process of taking the thermodynamic limit, we let the size of the system become infinitely large, with the densities (of mass, energy, magnetic moment, polarization, etc.) remaining constant.

In equilibrium the state variables are not all independent and are connected by equations of state. The rôle of statistical mechanics is the derivation, from microscopic interactions, of such equations of state. Simple examples are the ideal gas law,

$$PV - Nk_B T = 0 \quad (1.1)$$

where N is the number of molecules in the system and k_B is Boltzmann's constant; the van der Waals equation,

$$\left(p + \frac{aN^2}{V^2}\right) (V - Nb) - Nk_B T = 0 \quad (1.2)$$

where a, b are constants; the virial equation of state

$$P - \frac{Nk_B T}{V} \left[1 + \frac{NB_2(T)}{V} + \frac{N^2 B_3(T)}{V^2} + \dots \right] = 0 \quad (1.3)$$

where the functions $B_2(T), B_3(T)$ are called virial coefficients; and in the case of a paramagnet, the Curie law,

$$M - \frac{CH}{T} = 0 \quad (1.4)$$

where C is a constant called the Curie constant. Equations (1.1), (1.2), and (1.4) are approximations, and we shall use them primarily to illustrate various principles. Equation (1.3) is, in principle, exact, but as we shall see in Chapter 4, calculation of more than a few of the virial coefficients is very difficult.

1.2 Laws of Thermodynamics

In this section we explore the consequences of the zeroth, first, and second laws of thermodynamics. The zeroth law can be thought of as the statement that matter in equilibrium can be assigned values for the temperature, pressure and chemical potentials, which in principle can be measured. Formally the law can be stated as:

If system A is in equilibrium with systems B and C then B is in equilibrium with C .

The zeroth law allows us to introduce universal scales for temperature, pressure etc.

Another way of looking at the zeroth law is through an analogy with mechanics. In equilibrium the forces are balanced. This implies that the intensive variables are constant throughout the system. In particular:

$$\begin{aligned} T &= \text{const.} \rightarrow \text{Thermal equilibrium} \\ P &= \text{const.} \rightarrow \text{Mechanical equilibrium} \\ \mu &= \text{const.} \rightarrow \text{Chemical equilibrium} \end{aligned}$$

As we shall see in the next chapter, the zeroth law has a fairly straightforward statistical interpretation and this will allow us to make contact between the thermodynamic and statistical description.