

CHAPTER I

Thermodynamics of irreversible processes

Thermodynamics is a powerful generic formalism, which provides a description of physical systems involving many degrees of freedom in terms of only a small number of salient variables like the system's total energy, particle number or volume, irrespective of the actual underlying microscopic dynamics. The strength of the approach is especially manifest for the so-called equilibrium states, which in a statistical-physical interpretation are the “most probable” macroscopic states—i.e. those which correspond to the largest number of microscopic states obeying given constraints—, and are characterized by only a handful of thermodynamic variables. Accordingly, introductory courses in thermodynamics often chiefly focus on its equilibrium aspects. In that context, when considering physical transformations of a system across different macrostates, one mostly invokes “quasi-static processes”, namely fictive continuous sequences of equilibrium states between the initial and final states.

An actual physical process in a macroscopic system is however not quasi-static, but rather involves intermediary macrostates that are not at thermodynamic equilibrium. As a result, the evolution is accompanied by an increase in the total entropy of the system, or more precisely, of the smallest whole including the system under study and its environment which is isolated from the rest of the universe. That is, such an out-of-equilibrium process is irreversible.

Similar departures from equilibrium also appear spontaneously in an equilibrated system, when at least one of its key thermodynamic variables is not exactly fixed—as is the case when the system cannot exchange the corresponding physical quantity with its exterior—, but only known “on average”—as happens when the system can exchange the relevant quantity with an external reservoir. In the latter case, the thermodynamic variable will possibly fluctuate around its expectation value,⁽¹⁾ which will again momentarily drive the system out of equilibrium.

In either case, it is necessary to consider also non-equilibrated thermodynamic systems, which constitute the topic of the present chapter. In a first step, the macroscopic variables necessary to describe such out-of-equilibrium systems as well as the processes which drive them to equilibrium are presented (Sec. I.1). Making physical assumptions on how far away the systems are from equilibrium and on the processes they undergo, one can postulate constitutive equations that relate the newly introduced variables with each other (Sec. I.2), irrespective of any microscopic picture. These relations, which actually encompass several known empirical laws, involve characteristic properties of the systems, namely their transport coefficients. The calculation of the latter, like that of thermodynamic coefficients, falls outside the realm of thermodynamics and necessitates more microscopical approaches, as will be presented in the following chapters.

For simplicity, the discussion is restricted to non-relativistic systems. *...but I am willing to change that, if I find the time.*

⁽¹⁾The standard deviation of these fluctuations is readily computed in statistical mechanics, by taking second derivatives of the logarithm of the relevant partition function, and involves thermodynamic coefficients like the compressibility or the specific heat.

I.1 Description of irreversible thermodynamic processes

This section is devoted to introducing the quantities needed to describe nonequilibrated systems at the macroscopic level. First, the laws of equilibrium thermodynamics, or *thermostatistics*, are recalled (§ I.1.1), using Callen’s approach [8, Chap. 1], which is closer to statistical mechanics than that starting from the traditional principles, thereby allowing one more easily to treat macroscopic physical quantities as effective concepts. After that, the novel variables that play a role in a situation of departure from (global) thermodynamic equilibrium in a system are presented, starting with the simpler case of discrete systems (§ I.1.2), then going on to the physically richer continuous media (§ I.1.3 and I.1.4).

I.1.1 Reminder: Postulates of equilibrium thermodynamics

Instead of using the traditional laws of thermodynamics—which for the sake of completeness will be quickly recalled at the end of this subsection—it is possible to give an alternative formulation, due to Herbert Callen^(a) [8], which turns out to be totally equivalent and has the advantage of being more readily extended to out-of-equilibrium thermodynamics.

This approach takes as granted the existence of variables—namely the volume \mathcal{V} , the chemical composition N_1, N_2, \dots, N_r and the internal energy U —to characterize properties of “simple” thermodynamic systems at rest, where “simple” means macroscopically homogeneous and isotropic, chemically inert and electrically neutral. All these variables, which will hereafter be collectively represented by $\{\mathcal{X}_a\}$, are *extensive*: for a system whose volume \mathcal{V} become infinitely large, they all diverge in such a way that the ratio $\mathcal{X}_a/\mathcal{V}$ remains finite.

Remark: Interestingly enough, the extensive variables $\{\mathcal{X}_a\}$ are, with the exception of volume, all conserved quantities in isolated (and a fortiori closed) chemically inert systems, which somehow justifies the special role that they play.

Building upon the variables $\{\mathcal{X}_a\}$, thermostatistics follows from four postulates:

- According to postulate I, there exist particular macroscopic states of simple systems at rest, the *equilibrium states*, that are *fully* characterized by the variables $U, \mathcal{V}, N_1, \dots, N_r$.
- The three remaining postulates specify the characterization of the equilibrium state among all macrostates with the same values of the parameters $\{\mathcal{X}_a\}$:
 - Postulate II: For the equilibrium states of a composite system—defined as a collection of simple systems, hereafter labeled with a capital superscript (A)—, there exists a function of the extensive parameters $\{\mathcal{X}_a^{(A)}\}$ of the subsystems, the *entropy* S , which is *maximal* with respect to free variations of the variables $\{\mathcal{X}_a^{(A)}\}$.
 - Postulate III: The entropy of a composite system is the sum of the entropies of its subsystems. Additionally, S is continuous and differentiable, and is a monotonically increasing function of U .
 - Postulate IV: The entropy of any system vanishes in the state for which $\left(\frac{\partial U}{\partial S}\right)_{\mathcal{V}, N_1, \dots, N_r} = 0$.

Noting that any simple system can be in thought considered as a composite system of arbitrarily chosen subparts, the second postulate provides a variational principle for finding equilibrium states.

The generalization of these postulates to more complicated systems, e.g. magnetized systems or systems in which chemical reactions take place, is quite straightforward.

In this formulation, a special role is played by the entropy—which is actually only defined for equilibrium states. The functional relationship between S and the other characteristic variables,

^(a)H. CALLEN, 1919–1993

$S = S(\{X_a\})$, is referred to as the *fundamental equation*,⁽²⁾ and contains every information upon the thermodynamic properties of the system at equilibrium. The differential form of the relation is Gibbs'^(b) *fundamental equation*

$$dS = \sum_a \frac{\partial S}{\partial X_a} dX_a = \sum_a \mathcal{Y}_a dX_a \quad \text{with} \quad \mathcal{Y}_a \equiv \left(\frac{\partial S}{\partial X_a} \right)_{\{X_b\}_{b \neq a}}. \quad (\text{I.1})$$

The partial derivatives \mathcal{Y}_a are intensive parameters conjugate to the extensive variables. Mathematically these derivatives depend on the same set of variables $\{X_b\}$ as the entropy; the functional relationships $\mathcal{Y}_a = \mathcal{Y}_a(\{X_b\})$ are the *equations of state* of the system.

For instance, in the case of a simple multicomponent fluid, the fundamental equation reads in integral form $S = S(U, \mathcal{V}, N_1, \dots, N_r)$, and in differential form

$$dS = \frac{1}{T} dU + \frac{\mathcal{P}}{T} d\mathcal{V} - \sum_k \frac{\mu_k}{T} dN_k, \quad (\text{I.2a})$$

that is⁽³⁾

$$\mathcal{Y}_E = \frac{1}{T}, \quad \mathcal{Y}_{\mathcal{V}} = \frac{\mathcal{P}}{T}, \quad \mathcal{Y}_{N_k} = -\frac{\mu_k}{T}, \quad (\text{I.2b})$$

with T the *temperature*, \mathcal{P} the (thermodynamic) *pressure*, and μ_k the *chemical potential* for species k .

Remark: Postulate I explicitly deals with systems at rest, that is, with a vanishing total linear momentum \vec{P} . Since \vec{P} is also a conserved quantity in isolated systems, like internal energy or particle number, it is tempting to add it to the list of characteristic parameters $\{X_a\}$.

Now, a system at thermodynamic equilibrium is a fortiori in mechanical equilibrium, that is, there is no macroscopic motion internal to the system: a finite linear momentum \vec{P} is thus entirely due to some global motion of the system, with a velocity $\vec{v} = \vec{P}/M$, where M denotes the mass of the system. Equivalently, the finite value of total momentum arises from our describing the system within a reference frame in motion with velocity $-\vec{v}$ with respect to the system rest frame. The only interest in considering \vec{P} among the basic parameters is that it allows us to find the conjugate intensive parameter, which will prove useful hereafter.⁽⁴⁾

Relying momentarily on the statistical mechanical interpretation of entropy as a measure of missing information, the entropy of a system of mass M does not change whether it is at rest [energy $E = U$, entropy $S(U, \vec{P} = \vec{0}) = S_0(U)$] or in collective motion with momentum \vec{P} , in which case its energy becomes $E = U + \vec{P}^2/2M$ and its entropy $S(E, \vec{P})$. One thus has

$$S(E, \vec{P}) = S_0\left(E - \frac{\vec{P}^2}{2M}\right).$$

Differentiating this identity with respect to one of the component P^i of momentum in a given coordinate system, there comes the conjugate variable

$$\mathcal{Y}_{P^i} \equiv \frac{\partial S}{\partial P^i} = \frac{\partial S_0}{\partial P^i} = -\frac{P_i}{M} \frac{\partial S_0}{\partial U} = -\frac{v_i}{T}, \quad (\text{I.3})$$

where v_i denotes the i -th component of the velocity \vec{v} of the system. One easily checks that the other intensive parameters \mathcal{Y}_E , $\mathcal{Y}_{\mathcal{V}}$, \mathcal{Y}_{N_k} remain unchanged even if the system is in motion, which justifies a posteriori the notation convention mentioned in footnote 3.

⁽²⁾ More precisely, it is the fundamental equation in “entropy representation”.

⁽³⁾ Throughout these notes, quantities related to the internal energy U —as here its conjugate variable or later below the corresponding affinity or the internal energy per unit volume—will be denoted with the letter E , instead of U .

⁽⁴⁾ It is also more natural in order to allow the extension of the formalism to relativistic systems, since the energy alone is only a single component of a 4-vector.

^(b) J. W. GIBBS, 1839–1903

For the sake of completeness, we recall here the “classical” laws of thermodynamics, as can be found in most textbooks:

- 0th law (often unstated): thermal equilibrium at a temperature T is a transitive property;
- 1st law: a system at equilibrium is characterized by its internal energy U ; the changes of the latter are due to heat exchange Q with and/or macroscopic work W from the exterior, $\Delta U = Q + W$;
- 2nd law: a system in equilibrium is characterized by its entropy S ; in an infinitesimal process between two equilibrium states, $dS \geq \delta Q/T$, where the identity holds if and only if the process is quasi-static;
- 3rd law: for any system, $S \rightarrow S_0$ when $T \rightarrow 0^+$, where S_0 is independent of the system variables (which allows one to take $S_0 = 0$).

Callen discusses the equivalence between his postulates and these laws in Chapters 1, 2 & 4 of Ref. [8]. For instance, one sees at once that the third traditional law and the fourth postulate are totally equivalent.