

## Chapter 2

# Thermodynamic Theory of Irreversible Processes

In this work, we are interested in a molecular theory (i.e., statistical mechanics) of time- and space-dependent nonequilibrium (irreversible) processes in matter regarded as composed of many discrete particles. Statistical mechanics is a mathematical model theory of macroscopic observables of gross systems by means of which we hope to theoretically describe the collective state of matter consisting of an astronomical number of discrete constituent particles. By itself, such a mathematical model theory has no physical reality unless it is underpinned by an experimentally founded phenomenological theory of processes fully consistent with the laws of thermodynamics and until verified by experiments to a satisfactory accuracy. In this particular case of theory, it must be done so by an experimentally verifiable or verified phenomenological theory of thermodynamics of irreversible processes.

For the sake of simplicity without losing the essential features of the theory we will begin the discussion with simple fluids. Once this task is accomplished, it then would be comparatively simple to generalize the theory to complex fluids consisting of non-simple molecules. We will assume in this work that the substance does not have an intrinsic angular momentum. We also assume that the system consists of an  $r$ -component non-reactive mixture. Therefore, the case of chemical reactions is excluded at the beginning, but it would be easy to modify the theory at the appropriate places to include the case of chemical reactions. After completing the formulation of the phenomenological theory under the assumptions taken, we will point out where the necessary modifications must be made to include chemical reactions. In this chapter we give a short survey of the essential features of the theory of thermodynamics of irreversible processes, subject to the assumptions mentioned, that we consider necessary in developing a theory of statistical mechanics of irreversible processes in nonequilibrium systems.

In the present work the term thermodynamics used alone without qualifiers will be reserved for equilibrium systems and processes in systems in thermal equilibrium, unless stated otherwise or modified by a suitable qualifier such as an adjective irreversible.

## 2.1 The Zeroth Law of Thermodynamics

### 2.1.1 The Zeroth Law of Thermodynamics for Temperature

If two bodies of different degrees of warmth are put into contact, the bodies eventually reach thermal equilibrium at an equal degree of warmth. This phenomenon is exploited to quantify the measure of hotness or coldness of systems. The zeroth law of thermodynamics [1–3] provides a general procedure of quantifying temperature as a measure of warmth of a system (or body).

*If two systems A and B are, respectively, in thermal equilibrium with system C, then the systems A and B are also in thermal equilibrium.*

This literal statement can be expressed mathematically and more precisely: If there exists thermal equilibrium between A and C, there is a property called temperature  $\theta$  such that if

$$\theta_A = \theta_C \quad (2.1)$$

and similarly for systems B and C

$$\theta_B = \theta_C. \quad (2.2)$$

Then there follows the equality

$$\theta_A = \theta_B. \quad (2.3)$$

In practice, these relations supply a means to devise thermometers and therewith quantify temperature precisely, as described in detail in the literature on measurements of temperature [4]. In our discussion, we will use the absolute temperature scale established in thermometry.

Although the relations (2.1)–(2.3) are mathematically impeccable and are generally used in thermodynamics textbooks [3, 5], they are not too useful from the operational standpoint, especially for irreversible thermodynamics, because there is absent the concept of time duration in which thermal equilibrium is measured between the bodies. A more useful way of saying basically the same thing is to introduce a time interval  $\Delta\tau$  in which the establishment of thermal equilibrium is monitored to a sufficient accuracy. Thus we write instead

$$\frac{\Delta_{ac}\theta}{\Delta\tau} = 0, \quad \frac{\Delta_{bc}\theta}{\Delta\tau} = 0, \quad \frac{\Delta_{ab}\theta}{\Delta\tau} = 0, \quad (2.4)$$

where  $\Delta_{ac}\theta = \theta_a - \theta_c$  and so on. These expressions make it possible to deduce more practical means of measuring temperature and the meanings of temperature for systems where nonequilibrium processes may be in progress. For example, if the

heat transfer per unit time from body  $A$  to body  $C$  is  $\mathcal{Q}_{ac}$  and the heat capacity is denoted by  $C_{ac}$  then we may write [6]

$$\frac{\Delta_{ac}\theta}{\Delta\tau} = \frac{\lambda_{ac}}{C_{ac}} \mathcal{Q}_{ac}, \quad (2.5)$$

where  $\lambda_{ac}$  is the heat transfer coefficient which is, together with the heat capacity, a characteristic of the materials involved. The  $C_{ac}$  and  $\lambda_{ac}$  are non-vanishing quantities characteristic to the material considered. Therefore, for example, the first condition in (2.4) means that  $\mathcal{Q}_{ac} = 0$  at thermal equilibrium of bodies  $A$  and  $C$ .

Determination of the parameter  $\theta$  requires thermal equilibrium between a body  $A$  and another body  $B$  (i.e., thermometer) if it is to be quantified as a well-defined value. However, the term ‘thermal equilibrium’ does not necessarily mean that body  $A$  itself is internally in thermodynamic equilibrium. It may, in fact, be a system where a number of irreversible processes are in progress at a value of temperature  $\theta$ , but the thermal equilibrium is between this body and another that is in contact with the former. The important point is that the value of  $\theta$  remains constant over the time scale  $\Delta\tau$  of measurement. This condition can be readily met if the irreversible processes in bodies  $A$  and  $B$  have reached a steady state at temperature  $\theta$  within  $\Delta\tau$ . An apt example is an animate body (e.g., a human body) where numerous irreversible processes occur, often in conditions far removed from equilibrium, yet the temperature of the body is a well-defined observable and, perhaps more precisely, a local observable, if it meets the condition expressed in (2.4). Another example is a metallic bar subjected to different temperatures at its two ends. It is well known that the temperature has a distribution between the two points. By this we mean that if infinitesimally thin imaginary slices of the metal are taken perpendicular to the direction of heat flow and each slice is put into thermal equilibrium with a thermometer, the recorded temperature values of the slices along the direction of heat flow will be different depending on the position. Even if this distribution changes in time owing to varying boundary conditions (temperatures), the distribution can be quantified as a function of time by a thermometer of an appropriate resolution power, if the relaxation of a transient temperature distribution is achieved within the time scale  $\Delta\tau$  of temperature measurement. The term thermal equilibrium used in stating the zeroth law of thermodynamics therefore must be understood in the sense that equilibrium is between the body and the thermometer over the time span  $\Delta\tau$  irrespective of possible irreversible processes within the bodies involved.

The consideration made here indicates that the zeroth law of thermodynamics is not limited to bodies in equilibrium, but also to bodies where irreversible processes may be in progress as long as the resolution power of the thermometric device permits a meaningful quantification of temperature through the relations in (2.1)–(2.3). This quantification of temperature is often used for a local elementary volume of the body at time  $t$  even if the body is in a nonequilibrium condition in another respect, and temperature becomes a field variable in such a case. If the irreversible

process of interest is such that the conditions in (2.4) are not satisfied within the time interval  $\Delta\tau$  achievable experimentally, then it is no longer possible to describe the process by means of a thermodynamic formalism on that time scale. In other words, thermodynamics has no meaning for such a process on the time scale in question.

There are other field variables to which laws similar to the zeroth law must be applied for their thermodynamic quantification. The collection of such kindred laws for the aforementioned intensive field variables may be simply called the ‘zeroth law of thermodynamics’ in a generalized sense. They will be discussed below. For this purpose, the notions of field variables are properly introduced and defined together with the notion of thermodynamic manifold, which is spanned by macroscopic observables that can be measured in principle in the laboratory on performing experiments on a set of irreversible processes. They include the conserved variables, which obey the conservation laws, and the nonconserved variables, which do not obey conservation laws, but instead are described by the constitutive equations (field equations) characteristic to the material considered.

**Definition 1** Thermodynamic manifold is spanned by the macroscopic variables

$$\mathfrak{P} := (\mathcal{E}, v, c_a, \widehat{\Phi}_a^{(s)} : a = 1, 2, \dots, r; s = 1, 2, 3, \dots).$$

The elements of this manifold  $\mathfrak{P}$  are internal energy density  $\mathcal{E}$ , volume  $v$ , concentrations (mass density fraction)  $c_a$  for conserved variables and additionally non-conserved variables (fluxes) density  $\widehat{\Phi}_a^{(s)}$ , if the fluid is monatomic. If the fluid has rotational degrees of freedom, the angular momentum and the related should be included. The species subscript  $a$  runs up to  $r$  for an  $r$ -component mixture, and the index for fluxes to  $s$ . The upper bound of index  $s$  can be as large as necessary depending on the fluid and processes of interest.

For a global system the manifold is expressible as

$$\mathfrak{P}_{\text{gl}} := (E, V, M_a, \Gamma_a^{(s)} : 1 \leq a \leq r; s \geq 1).$$

The volume integral of  $\rho\mathfrak{P}$  may be expressible by the integral

$$\mathfrak{P}_{\text{gl}} = \int_V d\mathbf{r} \rho \mathfrak{P}(\mathbf{r}, t). \quad (2.6)$$

The variables spanning manifold  $\mathfrak{P}$  are extensive in the sense that when multiplied by density  $\rho$  (i.e.,  $\rho \times \mathfrak{P}$ ) and integrated over the volume as in (2.6), they are extensive, being proportional to the mass of the system in  $V$ . In the conventional continuum mechanics the element  $v$  of manifold  $\mathfrak{P}$  is generally taken as specific volume<sup>1</sup>—inverse  $\rho$ —of the fluid. The thermodynamic manifold  $\mathfrak{P}$  alone is not

---

<sup>1</sup>This viewpoint toward volume (per mole) should be modified because it does not have a molecular representation free from macroscopic variables in its definition. It will be found more appropriate to regard it as a mean volume allowed to molecules in a randomly distributed assembly of particles. Especially, if the fluid is away from equilibrium the latter concept is more appropriate since specific

sufficient to characterize the state of a system (i.e., matter) thermodynamically. A manifold conjugate to  $\mathfrak{P}$  is required for a thermodynamic description of it. It will be called the tangent manifold  $\mathfrak{T}$ , which is defined as follows:

**Definition 2** The manifold  $\mathfrak{T}$  conjugate to  $\mathfrak{P}$  is spanned by observables  $\mathfrak{T} := (T^{-1}, p, \widehat{\mu}_a, X_a^{(s)} : a = 1, 2, \dots, r; s = 1, 2, 3, \dots)$ , each element in  $\mathfrak{T}$  being conjugate to the element of  $\mathfrak{P}$  in the same order of sequence of the two sets.

Here  $T := \theta, p, \widehat{\mu}_a, X_a^{(s)}$ , as they stand, are merely mathematical symbols for quantities conjugate to the elements of  $\mathfrak{P}$  at the moment, but they will turn out to be, respectively, temperature, pressure, chemical potentials in a generalized sense, and generalized potentials. They are intensive macroscopic variables. The variable  $\theta, p$ , and  $\widehat{\mu}_a$  are counterparts of their concepts known in equilibrium phenomena, but the quantity  $X_a^{(s)}$ , which we call the *generalized potential* for species  $a$  of process  $s$  in the nonequilibrium fluid, has no classical equivalent; they are new to the theory developed in this work. As a matter of fact, the operational meaning of parameter  $T$  has been already determined by means of the zeroth law of thermodynamics, but its quantitative determination in practice will be further clarified later. The phenomenological operational procedures for the remaining parameters  $p, \widehat{\mu}_a$ , and  $X_a^{(s)}$  can be formalized by applying the idea underlying the zeroth law of thermodynamics for temperature discussed earlier. We thus have extensions of the zeroth law of thermodynamics to parameters spanning the tangent manifold  $\mathfrak{T}$ . Their irreversible thermodynamic meanings will be clarified as the theory of irreversible processes is further developed.

### 2.1.2 The Zeroth Law of Thermodynamics Extended

The parameters  $p, \widehat{\mu}_a$ , and  $X_a^{(s)}$  and their temporal behaviors can be quantified through the relations [6] similar to (2.5)

$$\begin{aligned} \frac{\Delta p}{\Delta \tau} &= -\frac{\gamma}{\kappa} \frac{\Delta V}{\Delta \tau}, \\ \frac{\Delta \widehat{\mu}_a}{\Delta \tau} &= \frac{\nu_a}{\vartheta_a} \frac{\Delta M_a}{\Delta \tau}, \\ \frac{\Delta X_a^{(s)}}{\Delta \tau} &= \frac{\lambda_{sa}}{\omega_{sa}} \frac{\Delta \Gamma_a^{(s)}}{\Delta \tau}, \end{aligned} \tag{2.7}$$

where  $\Delta p = p_1 - p_2$ ,  $\Delta \widehat{\mu}_a = \widehat{\mu}_{a1} - \widehat{\mu}_{a2}$ ,  $\Delta X_a^{(s)} = X_{a1}^{(s)} - X_{a2}^{(s)}$  with the subscripts 1 and 2 denoting the two systems in contact, and  $\kappa, \vartheta_a$ , and  $\omega_{sa}$  are the susceptibilities

---

(Footnote 1 continued)

volume is not the same as the mean volume per molecule. For the notion of molecular representation of mean volume per molecule, see Ref. [7] and also Ref. [8]. Modification of manifold  $\mathfrak{P}$  will be discussed in a later chapter in which volume transport phenomena are discussed.

of the quantities  $V$ ,  $M_a$ , and  $\Gamma_a^{(s)}$  to the changes  $\Delta p$ ,  $\Delta\hat{\mu}_a$ , and  $\Delta X_a^{(s)}$ , respectively. The time derivatives  $(\Delta V/\Delta\tau)$ ,  $(\Delta M_a/\Delta\tau)$ , and  $(\Delta\Gamma_a^{(s)}/\Delta\tau)$  are functions of the variables in manifolds  $\mathfrak{P}$  and  $\mathfrak{T}$ , which may be empirically determined. The  $\gamma$ ,  $\nu_a$ , and  $\lambda_{sa}$  are the associated transfer coefficients. The differential equations in (2.7) are the zeroth law analogs for pressure, chemical potentials, and generalized potentials. For, as  $(\Delta V/\Delta\tau)$ ,  $(\Delta M_a/\Delta\tau)$ , and  $(\Delta\Gamma_a^{(s)}/\Delta\tau) \rightarrow 0$ , the derivatives on the left vanish:

$$\begin{aligned}\frac{\Delta p}{\Delta\tau} &= 0, \\ \frac{\Delta\hat{\mu}_a}{\Delta\tau} &= 0, \\ \frac{\Delta X_a^{(s)}}{\Delta\tau} &= 0,\end{aligned}\tag{2.8}$$

and the systems in contact reach equilibrium with regards to the variables  $p$ ,  $\hat{\mu}_a$ , and  $X_a^{(s)}$ . They thereby can be quantified experimentally, just as the temperature is measured for the system with a thermometer as the other system, since one of the systems in contact may be the instrument of measurement for the intensive variable. It should be noted, however, that the time scale for  $X_a^{(s)}$  may not be necessarily the same as for those of the conjugate variables to the conserved variables, namely,  $T$ ,  $p$ , and  $\hat{\mu}_a$ . These time scales, however, are not known *a priori* in phenomenological theories, but should be found through experiments, or calculated theoretically if molecular theories are available for them. In any case, (2.5) and (2.7) empirically establish the evolution equations for elements of manifold  $\mathfrak{T}$ . In the subsequent chapters, their evolution equations will be found derived by means of a kinetic theory. They may be also regarded as constitutive equations of the material considered. The natures of these quantities will be clarified as the theory is developed.

To carry out unambiguous discussions of thermodynamic processes it is necessary to establish sign conventions on heat transfer and work performed. We take the following sign conventions:

**Convention on heat transfer:** *Heat transfer is counted negative if heat is given up by the system to the surroundings, and positive if heat is taken up by the system from the surroundings.*

**Convention on work:** *Work is counted as positive if it is done on the system by the surroundings, and negative if it is done on the surroundings by the system.*

## 2.2 The First Law of Thermodynamics

The first law of thermodynamics was a culmination of the understanding of what is meant by heat and its relation to energy. Referring the historical account of the genesis of the idea of equivalence of heat and energy to the literature [3, 9–11], we will simply state it below.

**The First Law of Thermodynamics** may be stated in two equivalent forms:

1. *The energy of an isolated system is constant.*
2. *It is impossible to construct a perpetual machine of the first kind—a machine that, working in a cycle, expends no heat to produce an equivalent work.*

The first statement due to Clausius [12] is a little obtuse, but, more precisely put, it means that the internal energy of an isolated system is conserved over a cycle of processes restoring the system to its original state.

The second equivalent statement, in essence due to Planck [13], can be given a mathematical representation as follows. For this purpose we need the concept of internal energy.

### 2.2.1 Internal Energy

To obtain a mathematical representation of the first law of thermodynamics in the case of an infinitesimal process let us denote the differential heat change by  $dQ$  and the differential work by  $dW$  accompanying the process. The first law of thermodynamics then implies that there exists a quantity called the internal energy  $E$  whose differential  $dE$ , under the sign conventions adopted earlier for heat and work, must be given by the expression

$$dE = dQ + dW, \quad (2.9)$$

whether the process is reversible or irreversible. Thus for a cyclic process<sup>2</sup> the first law of thermodynamics may then be expressible as a vanishing circular integral

$$\oint dE = 0, \quad (2.10)$$

where the cyclic integral is to be performed over the path of a cycle in the space of macroscopic variables characterizing the thermodynamic state of the system—namely, the thermodynamic manifold  $(\mathfrak{P} \cup \mathfrak{T})$ . For by the requirement of the first law the energy of the initial state must be exactly the same as the energy of the final state in the cyclic process. If time is used as a parameter for  $E$ , then the circular integral in (2.10) may be written as an integral over a period  $\tau_c$  of the cyclic motion in the thermodynamic manifold

$$\int_0^{\tau_c} dt \frac{dE}{dt} = 0. \quad (2.11)$$

---

<sup>2</sup>A conservation law can be best stated by means of a cyclic process since the state of the system must be exactly restored on completion of the cyclic process and so must be the value of internal energy of the system. Vanishing cyclic integrals consequently play important roles in formulation of thermodynamics of irreversible processes.

It must be reiterated that the first law holds irrespective of whether the process is reversible or irreversible although in equilibrium thermodynamics it is tacitly restricted to a reversible process.

Mathematically, the vanishing circular integral (2.10) means that  $dE$  is an exact differential in the aforementioned thermodynamic manifold ( $\mathfrak{P} \cup \mathfrak{T}$ ). Equation (2.10) is also equivalent to the statement that heat is a form of energy, since on substitution of (2.9) into (2.10) we obtain

$$\oint dQ = - \oint dW = -W, \quad (2.12)$$

demonstrating that heat is equal to work (energy) with signs appropriately attached to them. It must be remarked that the mathematical representation (2.10) of the first law is for the global system performing the cycle, namely, the working substance in the whole system which goes through the cyclic process in question. We also note that  $dQ$  and  $dW$  are not by itself an exact differential<sup>3</sup> in the path of the cyclic change unlike  $dE$  is, but the sum of them,  $dE$ , is an exact differential according to the first law of thermodynamics, thus giving rise to (2.10).

### 2.2.2 Work

The meaning of work  $W$  or its differential form  $dW$  will depend on the mechanical task of the cycle (process) in question. It may consist of a number of components, including those attributable to irreversible processes involved. For example, a pressure–volume work may be performed on the system which changes the volume of the system under an external pressure, or work may be done by the system as it transfers a portion of mass to its surroundings under a material potential (chemical potential) between the system and the surroundings. Thus the system generally performs work on its surroundings under the influence of forces that drive changes in the extensive variables of  $\mathfrak{P}_{\text{gl}}$  or, more precisely, the densities of extensive variables of  $\mathfrak{P}$ . In all of these kinds of work there are always conjugate pairs of variables associated, one that drives the process of work, namely, the measure of the force, and the other that is the measure of the response by the system to the driving force. For example, in the case of pressure–volume work the pressure is the force and the volume change is the response by the system. In the case of work associated with a transfer of matter, the driving force is the chemical potential and the response is the change in mass. Similarly, in the case of work associated with nonconserved variables, *which is nonclassical*, it is possible to imagine that the system responds by adjusting the value of “flux”  $\Gamma_{ka}$  to the driving force  $X_{ka}$ . The driving forces are all in the set of variables belonging to  $\mathfrak{T}$  introduced earlier, which are conjugate to

---

<sup>3</sup>In some textbooks in thermodynamics inexact differentials are denoted with a bar on the differential sign, e.g.,  $dQ$  or  $dW$ . In this work we do not adopt such a notation.

those in  $\mathfrak{P}$ . If the aforementioned driving forces are in operation, the work done by the system per unit time can be written in the form [6]

$$\frac{dW}{dt} = -p \frac{dV}{dt} + \sum_{a=1}^r \hat{\mu}_a \frac{d_e M_a}{dt} - \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} \frac{d_e \mathfrak{P}_a^{(s)}}{dt} + \frac{d_i W}{dt}. \quad (2.13)$$

The first term on the right represents the pressure–volume work; the second the work of mass transfer; the third the work of ‘transfer’ of  $\mathfrak{P}_a^{(s)}$ , between the system and the surroundings; and the last term the internal work which is not accounted for by the first three kinds of work listed. The sign of the mass transfer suggests that it is a work done on the system by the surroundings. This convention is chosen so that the resulting mathematical formalism agrees with the conventional classical theory in the limit of equilibrium. The time derivative  $d_e/dt$  denotes the transfer (or exchange) rate of the quantity between the system and the surroundings. Since extensive quantities such as  $M_a$  and  $\mathfrak{P}_a^{(s)}$  can also change within the system owing to its inherent internal processes, their total rates of change consist of two components, one arising from the transfer of the quantity mentioned earlier, and the other arising from its internal change [6]:

$$\frac{dA}{dt} = \frac{d_e A}{dt} + \frac{d_i A}{dt} \quad (A = M_a, \mathfrak{P}_a^{(s)}), \quad (2.14)$$

where  $d_i A/dt$  stands for the internal rate of change in  $A$ , which contains basically constitutive information on the substance of interest and  $d_e A/dt$  the rate of transfer of  $A$  between the system and the surroundings. The time derivatives  $d_e A/dt$  and  $d_i A/dt$  will be referred to as the transfer time derivative and the internal time derivative of  $A$ , respectively.

In the conventional theory of macroscopic processes and thermodynamics there is no physical mechanism taken into consideration for an internal volume change and hence the transfer time derivative of volume  $d_e V/dt$  is simply equal to the total time derivative  $dV/dt$  in the case of  $V$ . Therefore there is no need to express the volume derivative as in (2.14) in the conventional theory of thermodynamics and attendant hydrodynamics. This viewpoint would be certainly plausible if we knew nothing of the fluid structure in terms of molecules and the volume inherent to molecules constituting the matter beyond the volume of the hard core of the molecules. If this average inherent volume is called the molar volume of the fluid molecule, then it is reasonable to examine the internal volume change of the fluid. The overall volume derivative of the fluid may be also written as in (2.14). The internal volume then must be regarded as belonging to the submanifold of nonconserved variables of manifold  $\mathfrak{P}$  in the terminology introduced in this work.<sup>4</sup>

---

<sup>4</sup>This modification of the viewpoint can be implemented if the notion of volume allotted to a molecule is adopted [7] via the Voronoi volume. This notion will be more easily understood if the theory is formulated as a molecular theory as will be done in a later chapter on irreversible processes

Likewise, the heat transfer rate associated with the internal energy conservation law will be denoted by  $dQ_E/dt$  by attaching the subscript  $E$  to  $Q$  because at this point in development, especially if the processes are irreversible, there is no compelling reason that the heat transfer rate in question is necessarily the same as the ‘heat transfer rate’ that will appear in the second law of thermodynamics in the form of compensated heat (see the subsection on the second law of thermodynamics below), which will be denoted by  $dQ/dt$ . Since the two quantities are not necessarily the same, we set [14]

$$\frac{dQ}{dt} = \frac{dQ_E}{dt} + \frac{dQ_n}{dt}. \quad (2.15)$$

The difference  $dQ_n/dt$  must be elucidated by some means, and it will be done when the second law of thermodynamics is discussed. It should be remarked here that this internal transfer rate  $dQ_n/dt$  is essentially in the same level as of other internal changes  $d_iA/dt$  mentioned earlier and, in fact, would be related to them in irreversible thermodynamics.

With the work made more explicit about the nature of its composition as in (2.13) and with the heat transfer rate denoted as indicated, the first law of thermodynamics may be expressed in the form

$$\frac{dE}{dt} = \frac{dQ_E}{dt} - p \frac{dV}{dt} + \sum_{a=1}^r \hat{\mu}_a \frac{d_e M_a}{dt} - \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} \frac{d_e \mathfrak{P}_a^{(s)}}{dt} + \frac{d_i W}{dt}. \quad (2.16)$$

Albeit restricted to within the bounds of the operational meanings of  $p$ ,  $\hat{\mu}_a$ , and  $X_{ka}$ , the form (2.16) will be useful for developing a generalized form of thermodynamics for global processes in a finite bounded system; see Ref. [15]. By using (2.15) the differential form (2.16) for a global irreversible process may be written as

$$\begin{aligned} \frac{dE}{dt} = \frac{dQ}{dt} - p \frac{dV}{dt} + \sum_{a=1}^r \hat{\mu}_a \frac{d_e M_a}{dt} - \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} \frac{d_e \mathfrak{P}_a^{(s)}}{dt} \\ + \left( \frac{d_i W}{dt} - \frac{dQ_n}{dt} \right). \end{aligned} \quad (2.17)$$

Before closing this subsection, we would like to examine the notion of ‘*work of the task*’. A work will be called the ‘*work of the task*’ if it is the mechanical work specifically designed for a cycle to perform. A particular work of the task is generally accompanied by other kinds of work which are not intended when the cycle of interest is designed for the task of work in question. For example, if a pressure–volume work is the work of the task, it is generally unavoidable to have the working fluid heated

---

(Footnote 4 continued)

in condensed phase where volume transport is explicitly taken into account. In phenomenological formulation, the notion must be formally accepted, but unfortunately would remain abstract.

by the viscous heating effect accompanying the compression or dilatation of the fluid, although it may be made as small as possible by a careful design of the device performing the cycle. We illustrate this point with the example of pressure–volume work for the work of the task. Over a cycle it is given by

$$W_{\text{task}} = - \oint dV p. \quad (2.18)$$

On substitution of the pressure–volume work term from (2.17) there follows the equation

$$W_{\text{task}} = -Q - W_{\text{ua}}, \quad (2.19)$$

where

$$W_{\text{ua}} = \oint (d_i W - dQ_n) + \sum_{a=1}^r \oint \hat{\mu}_a d_e M_a - \sum_{a=1}^r \sum_{s \geq 1} \oint X_a^{(s)} d_e \mathfrak{P}_a^{(s)} \quad (2.20)$$

and  $Q$  may be expressed as a difference between the input  $Q'_1$  and the output  $Q'_2$  of heat

$$Q = Q'_1 - Q'_2. \quad (2.21)$$

Therefore if it is possible to identify  $Q$  in (2.21) with that in (2.12) we find

$$W = W_{\text{task}} + W_{\text{ua}}. \quad (2.22)$$

This suggests that caution must be exercised when the first law of thermodynamics is used to calculate the work of the task in terms of heat, if there are irreversible processes involved in the course of a cycle. The expression (2.20) for unavailable work clearly indicates that its precise meaning depends on what  $W_{\text{task}}$  is. For example, if  $W_{\text{task}}$  is that of transferring a mass involving the third term on the right hand side of (2.17), then the second integral on the right hand side of (2.20) for  $W_{\text{ua}}$  is replaced by the circular integral

$$- \oint dV p,$$

the pressure–volume work, and hence the meaning of  $W_{\text{ua}}$  is accordingly altered from that of the unavailable work given in (2.20). Therefore, the unavailable work to a given task can become the available work to another task.

In equilibrium thermodynamics the unavailable work does not appear in the formulation of the theory, because *reversible processes considered in equilibrium thermodynamics are precisely the ones that have a vanishing unavailable work*, but when irreversible processes are considered, the notion of unavailable work becomes relevant and worth recognizing its presence to examine its nature.

### 2.2.3 Local Forms of Evolution Equations

The variables spanning manifold  $\mathfrak{P}$  can be endowed their evolution equations and more precise mathematical meanings in this and following subsections. These evolution equations, especially the balance equations for conserved variables, are well established in fluid (or continuum) mechanics, quite apart from the question of irreversible thermodynamics.

#### 2.2.3.1 Local Forms of the Conservation Laws

Many macroscopic processes in nature are described from the local theory viewpoint. Typical examples will be various flow processes in fluid mechanics where local field variables of fluids are assumed to obey partial differential equations—field equations. Since flow phenomena in fluids must obviously be subjected to thermodynamic laws as any macroscopic phenomena should be, it is necessary to cast the internal energy conservation law, namely, the first law of thermodynamics, in local form. In addition to the first law of thermodynamics, the system must obey the mass conservation law and the momentum conservation law as a continuum theory extension of Newton's law of motion. This is easily done by following the method of continuum mechanics [16]. We will simply accept them as phenomenological expressions for the conservation laws and present them as a proposition without going through the details of their derivations.

**Proposition 1** *For non-reacting fluids without a rotational angular momentum the local conservation laws hold for the conserved variables in the following forms:*  
*mass:*

$$\rho d_t v = \nabla \cdot \mathbf{u} \quad \text{or} \quad \frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{u}), \quad (2.23)$$

*mass fractions:*

$$\rho d_t c_a = -\nabla \cdot \mathbf{J}_a, \quad (2.24)$$

*momentum:*

$$\rho d_t \mathbf{u} = -\nabla \cdot \mathbf{P} - \rho \widehat{\mathbf{F}}, \quad (2.25)$$

*energy:*

$$\rho d_t \mathcal{E} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \widehat{\mathbf{F}}_a \cdot \mathbf{J}_a. \quad (2.26)$$

The symbol  $d_t$  stands for the substantial time derivative

$$d_t := d/dt = \partial/\partial t + \mathbf{u} \cdot \nabla \quad (2.27)$$

with  $\nabla = \partial/\partial \mathbf{r}$ . In this description, time derivative is calculated in the frame of reference moving with the fluid particle velocity.<sup>5</sup> Henceforth the symbol  $d_t$  is reserved for the substantial time derivative.

In the conservation laws presented,  $v = \rho^{-1}$  is the specific volume of the fluid;  $\rho$  is the (mass) density;  $\mathbf{u}$  is the fluid velocity;  $c_a$  is the mass fraction

$$c_a = \rho_a / \rho \quad (2.28)$$

with  $\rho_a$  denoting the (mass) density of species  $a$ ;

$$\mathbf{J}_a = \rho_a (\mathbf{u}_a - \mathbf{u}), \quad (2.29)$$

with  $\mathbf{u}_a$  denoting the velocity of species  $a$ , is the diffusion flux of species  $a$ ;  $\mathbf{Q}$  is the heat flux;  $\hat{\mathbf{F}}_a$  is the external (body) force per mass density of species  $a$  at position  $\mathbf{r}$ ; and

$$\hat{\mathbf{F}} = \sum_{a=1}^r c_a \hat{\mathbf{F}}_a, \quad (2.30)$$

the total force density. The internal energy density  $\mathcal{E}$  is related to  $E$  by the integral

$$E = \int_V d\mathbf{r} \rho \mathcal{E}(\mathbf{r}, t), \quad (2.31)$$

where the integral is over the volume  $V$  of the fluid. If the assumption of simple fluids—fluids with no internal molecular degrees of freedom such as rotational or vibrational degrees of freedom—is removed, the conserved variables should include the angular momentum and the conservation law, i.e., the angular momentum balance equation.

The pressure tensor  $\mathbf{P}$  can be decomposed into species-component pressure tensors  $\mathbf{P}_a$ :

$$\mathbf{P} = \sum_{a=1}^r \mathbf{P}_a; \quad (2.32)$$

and, similarly, the heat flux  $\mathbf{Q}$  into species-component heat fluxes  $\mathbf{Q}_a$ :

$$\mathbf{Q} = \sum_{a=1}^r \mathbf{Q}_a. \quad (2.33)$$

---

<sup>5</sup>It should be noted that fluid particle velocity is not the velocity of a molecule comprising the fluid. It is the velocity of the packet of fluid in an elementary volume of fluid at position  $\mathbf{r}$  and time  $t$ . From the molecular theory viewpoint it is the ensemble average of molecular velocities in a sufficiently small volume around the position  $\mathbf{r}$  at time  $t$ . For its molecular theory definition, see Chaps. 3, 5, 6, and 7 of this work.

Equations (2.23)–(2.26) are the local forms for the mass, mass fractions, momentum, and internal energy conservation laws, respectively. These are the field equations for local macroscopic field variables  $v$  or  $\rho$ ,  $c_a$ ,  $\mathbf{u}$ , and  $\mathcal{E}$ . We notice that these field equations contain variables  $\mathbf{J}_a$ ,  $\mathbf{P}$ , and  $\mathbf{Q}$  in addition to the conserved variables, which are so called by the terminology since they obey the conservation laws or balance equations without a dissipation term in them.

### 2.2.3.2 Local Forms for the Evolution Equations of Nonconserved Variables

The additional variables  $\mathbf{J}_a$ ,  $\mathbf{P}$ , and  $\mathbf{Q}$  are examples of nonconserved variables which we have collectively denoted by  $\Phi_a^{(s)}$ ; they span the manifold  $\mathfrak{P}$  defined in the previous subsection. In the theory of linear irreversible processes or in the conventional classical hydrodynamics they are specified by means of constitutive relations characterizing the processes in the substance of interest. The constitutive relations traditionally used in the steady-state linear theory [17, 18] of irreversible processes are not necessarily the most general forms to describe evolutions of the nonconserved variables. There is a considerable body of experimental and kinetic theory evidence that they require suitable generalizations for non-steady and nonlinear regimes. Examples for such necessity can be found in hydrodynamics, rheology [19] and other nonlinear phenomena in semiconductor physics [20], heat transport [21], plasmas [22], etc., covering the entire gamut of macroscopic physics and engineering science. The non-conserved variables  $\Phi_a^{(s)} = \rho \hat{\Phi}_a^{(s)}$  where  $1 \leq a \leq r$  and  $s \geq 1$ , for which the upper bound of  $s$  is finite in practice, but can be left unspecified at this point in development, are suitably ordered as follows:

$$\begin{aligned}\Phi_a^{(1)} &:= \Pi_a = \frac{1}{2}(\mathbf{P}_a + \mathbf{P}_a^t) - \frac{1}{3}\delta \text{Tr} \mathbf{P}_a, \\ \Phi_a^{(2)} &:= \Delta_a = \frac{1}{3}\text{Tr} \mathbf{P}_a - p_a, \\ \Phi_a^{(3)} &:= \mathbf{Q}'_a = \mathbf{Q}_a - \hat{h}_a \mathbf{J}_a, \\ \Phi_a^{(4)} &:= \mathbf{J}_a, \\ &\text{etc.}\end{aligned}$$

Here the superscript  $t$  stands for transpose of the tensor; the boldface  $\delta$  denotes the unit second rank tensor;  $p_a$  the *hydrostatic* pressure of species  $a$ ; and  $\hat{h}_a$  the enthalpy per unit mass of species  $a$ . The set of nonconserved variables can include as many nonconserved variables as necessary for proper description of the system in hand. The variable  $\Phi_a^{(4)}$  is regarded as nonconserved variable since its evolution equation is accompanied by energy dissipation represented by a source term. In some cases, the nonconserved variables may change on different, usually faster time scales and shorter spatial scales than the conserved variables. Since we are looking for a general formalism for macroscopic phenomena in this work, the conserved and nonconserved

variables will be provisionally put on formally equal footing with regard to time and spatial variables. On actual applications of the theory thus formulated, we may take into consideration the relative magnitudes of time and spatial scales of the two classes of field variables and develop approximate theories therewith. This turns out to be usually the case in practice. With this proviso, we now make the following proposition for the evolution equations for nonconserved variables  $\Phi_a^{(s)}$ . Since the nonconserved variables are also field variables, they obey partial differential equations, which take forms of balance equation, but with a source term, which will turn out related to energy dissipation because they are not conserved in time; it is a distinguishing feature from the conserved variables. It will be found convenient to assume a general form for the evolution equation for  $\Phi_a^{(s)} = \rho \widehat{\Phi}_a^{(s)}$  as below:

**Proposition 2** *The nonconserved variables  $\widehat{\Phi}_a^{(s)}$  ( $s \geq 1$ ;  $1 \leq a \leq r$ ) in manifold  $\mathfrak{P}$  obey the evolution equation*

$$\rho d_t \widehat{\Phi}_a^{(s)} = -\nabla \cdot \psi_a^{(s)} + \mathcal{Z}_a^{(s)} + \Lambda_a^{(s)}, \quad (2.34)$$

where  $\psi_a^{(s)}$  is the flux of  $\Phi_a^{(s)}$ ,  $\mathcal{Z}_a^{(s)}$  is called the kinematic term, which contains, at least, a term driving the process  $\Phi_a^{(s)}$  among other terms that nonlinearly depend on nonconserved variables and gradients of the conserved variables, and  $\Lambda_a^{(s)}$  is called the dissipation term which is responsible for energy dissipation arising from the process  $\Phi_a^{(s)}$ . The dissipation term may also be a nonlinear function of variables of the thermodynamic manifold  $\mathfrak{P}$  and its tangent manifold  $\mathfrak{T}$ .

The dissipation terms are generally algebraic functions of conserved and nonconserved variables, satisfying the constraint imposed by the local form of the second law of thermodynamics. They also depend on material parameters such as transport coefficients, density, pressure, etc. Since the kinematic and dissipation terms have different physical origins and characteristics, we have put them as separate terms in the evolution equation (2.34). It is possible to give statistical mechanical definitions for the kinematic and dissipation terms, as will be shown in later chapters on kinetic theory, and calculate them in terms of molecular properties of the fluid. However, their explicit forms in terms of conserved and nonconserved variables are not necessary for the formal theory of irreversible processes we develop axiomatically in this chapter. As will be seen, they will be subject to the constraint of the *second law of thermodynamics*. In this sense, the theory of irreversible processes developed here is fully consistent with the second law of thermodynamics at the formal theory level. Exploiting this thermodynamic consistency and, particularly, making use of the minimum principle provided by the second law of thermodynamics, we may develop a variational method of determining the kinematic and dissipation terms from the standpoint of thermodynamics of irreversible processes.

It should be noted that the linearized versions of the evolution equations for the stress tensor and heat flux were known to Maxwell [23] as transfer equations on which he based his calculation of transport coefficients under the steady-state assumption, and Chapman [24] later used their steady state form in his kinetic theory

of linear transport processes in dilute gases on the basis of the Boltzmann kinetic equation. This aspect will be discussed explicitly in chapters on kinetic theories. It is remarkable to note that the phenomenological theory of irreversible processes can make progress if the laws of thermodynamics are taken advantage of for the kinetic theory of irreversible processes. Here lies the crucial value of the thermodynamic theory of irreversible processes developed axiomatically in this chapter.

## 2.3 The Second Law of Thermodynamics

Unlike the first law of thermodynamics, which does not dictate the direction in which a reversible or irreversible macroscopic process proceeds, the second law of thermodynamics endows spontaneous natural processes with a quality of progressing in a preferred direction in time. This law is a summary of inviolable experimental facts of the unidirectional evolution in which spontaneous macroscopic processes in nature progress. It is presented as an axiom in this work. For a more detailed discussion on it the reader may be referred to *The Second Law of Thermodynamics* edited by Kestin [25] in which history and discussions of the law are given in detail.

### 2.3.1 Carnot Theorem

Historically, the unidirectional temporal evolution of natural phenomena is phrased in a theorem proposed by Carnot [26] as a conclusion of his study of cycles of heat engines. It can be stated as follows<sup>6</sup>:

#### Carnot Theorem

*The efficiency of reversible Carnot cycles is independent of the modes of operation and the materials used and is maximum. It depends only on the temperatures of the heat reservoirs.*

If the efficiency of a reversible cycle is denoted by  $\eta_{\text{rev}}$  and that of an irreversible cycle by  $\eta_{\text{irr}}$ , then regardless of the materials used and the modes of operation

$$\eta_{\text{rev}} \geq \eta_{\text{irr}} \quad \text{and} \quad \eta_{\text{rev}} = \eta'_{\text{rev}}.$$

The  $\eta_{\text{rev}}$  is a function of only the temperatures of the heat reservoirs of the Carnot cycle, and the prime denotes another reversible cycle.

Suppose two cycles (e.g., engines) of the same working material and mode of operation which operate between two heat reservoirs of different temperatures. One cycle is reversible and the other is irreversible. The reversible cycle does work  $W_{\text{rev}}$

---

<sup>6</sup>This theorem is proved in Chap.4, Ref. [3]. See also H. Poincaré, *Thermodynamique* (Georges Carré, Paris, 1892).

whereas the irreversible cycle does work  $W$ , both having received the same amount of heat from the higher temperature heat reservoir. The Carnot theorem then implies that  $W_{\text{rev}} \geq W$ . Therefore, the following can be concluded [3] as a corollary to the Carnot theorem:

*The reversible work is a maximum work, and if a cycle is irreversible, the entirety of the work that can be done by the reversible process is not all available to the irreversible cycle.*

If that amount of unavailable work is denoted by  $W_{\text{ua}}$  as we have earlier, then the reversible work  $W_{\text{rev}}$  may be decomposable into the form

$$W_{\text{rev}} = W + W_{\text{ua}} \quad (2.35)$$

for the pair of irreversible and reversible cycles under consideration. This unavailable work is intrinsic to irreversible cycles in general and was recognized in essence as *the uncompensated heat* (originally called uncompensated transformation value) by Clausius [12].

### 2.3.2 Clausius and Kelvin Principles

The theorem of Carnot led Clausius [27] and Kelvin (Thomson) [28] to formulate the second law of thermodynamics as follows.

#### Clausius Principle

*It is impossible to transfer heat from a colder to a hotter body without converting at the same time a certain amount of work into heat at the end of a cycle of change.*

#### Kelvin Principle

*In a cycle of processes it is impossible to transfer heat from a heat reservoir and convert it all into work without transferring at the same time a certain amount of heat from a hotter to a colder body.*

It can be shown [1] that these two principles are equivalent<sup>7</sup> to each other and also to the Carnot theorem. We note that the second law of thermodynamics is phrased in terms of, and for, cycles only, and for no others. Since even the present form of the second law has not as yet been given a full mathematical expression taking the uncompensated heat into consideration, it must be the goal for theory of irreversible processes before an alternative or amended form of the second law is proposed or formulated, as has been occasionally seen in the literature. Any amended form could

---

<sup>7</sup>It must be recognized that the presence and notion of unavailable work in an irreversible cycle is not as apparent in the Clausius and Kelvin principles as in the Carnot theorem, although they are equivalent to the Carnot theorem. In the end, it was the Carnot theorem that Clausius used to formulate the inequality named after him.

be liable to give rise to an unwarranted confusion in the as-yet uncompleted field of thermodynamic theory of irreversible processes.

Either one of the aforementioned literally stated forms of the second law of thermodynamics must be represented in a precise mathematical form, so that it can be used as the starting point of a thermodynamic theory of processes. Such a representation was made feasible by a combination of two important ingredients: One is Kelvin's recognition that the Carnot theorem can be the basis of a universal thermodynamic temperature scale. The other is Clausius's representation of the Carnot theorem for a Carnot cycle in the following manner.

Imagine the aforementioned pair of irreversible and reversible cycles operating between two heat reservoirs of temperatures  $T_1$  and  $T_2$  where  $T_1 > T_2$ . The two cycles take the same amount of heat  $Q_1$  from the higher temperature reservoir and perform work. The irreversible cycle does work  $W$ , discharging heat  $Q_2$  to the lower temperature reservoir, whereas the reversible cycle does a maximum work  $W_{\text{rev}}$ . The efficiency of the reversible cycle is

$$\eta_{\text{rev}} = \frac{W_{\text{rev}}}{Q_1} = 1 - \frac{T_2}{T_1},$$

whereas the efficiency of the irreversible cycle is

$$\eta_{\text{irr}} = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}.$$

By the Carnot theorem

$$1 - \frac{Q_2}{Q_1} \leq 1 - \frac{T_2}{T_1}. \quad (2.36)$$

Clausius [12] rearranges (2.36) to the form

$$-\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \geq 0 \quad (2.37)$$

and argues that this inequality can be cast in an integral form by imagining a series of infinitesimal Carnot cycles (see, for example, Sect. 4.4, Ref. [3].):

$$-\oint \frac{dQ}{T} \geq 0, \quad (2.38)$$

for which the sign convention for heat transfer introduced earlier is used.

An infinitesimal Carnot cycle is the cycle that operates between two heat reservoirs of an infinitesimally small temperature difference. The terminology *infinitesimal* does not mean that the actual physical size of the device performing the cyclic process is infinitesimal; it refers to the temperature difference of the heat reservoirs involved. Note that the temperature  $T$  refers to the heat reservoir at the point in question in the series of infinitesimal cycles making up the entire cycle under consideration. The

$dQ$  is what Clausius called *the compensated heat* which is the heat transfer involved between the system and its surroundings. Clausius also recognized another quantity which is nowadays called *the uncompensated heat* that accompanies a cyclic process when the process is irreversible. This quantity vanishes if the process is reversible. This is an amount of heat that is intrinsic to the system when the system undergoes the irreversible cyclic process in question. It is one of the central quantities that must be elucidated<sup>8</sup> in order to formulate a thermodynamic theory of irreversible processes.

### 2.3.3 Clausius Inequality

Following Clausius, we denote the uncompensated heat by  $N$  and express the Clausius inequality (2.36) as

$$N = - \oint \frac{dQ}{T} \geq 0. \quad (2.39)$$

The uncompensated heat  $N$  is always positive and vanishes only if the process is reversible, and its positivity can be regarded as an expression of the second law of thermodynamics. Clausius [12] suggested to calculate  $N$  by using (2.39) where the circular integral must be computed along an irreversible path, which includes at least one irreversible step. His suggested procedure is mathematically correct since it maintains intact the relation between the compensated and uncompensated heats. However, it ignores his original recognition that the compensated heat  $dQ/T$  and the uncompensated heat  $N$  are two physically distinctive quantities, which cannot tell us about each other.

*Here, we keep Clausius's original understanding of the uncompensated and compensated heats as two independent entities of a natural process and try to elucidate them in terms of the system properties for the irreversible process involved.* As a first step to initiate this endeavor, let us recall that there are two independent physical entities of similar kinds appearing in the guise of work-related quantities in the corollary to the Carnot theorem. According to this corollary, the reversible work is larger by  $W_{ua}$  than the irreversible work  $W$  for the pair of reversible and irreversible cycles in question and, furthermore,  $W_{ua}$  is positive semidefinite, vanishing only if the cycle is reversible. If this unavailable work is taken into account, the Carnot theorem may be written as an equation instead of an inequality as follows:

---

<sup>8</sup>In this connection, I would like to quote a passage in an article by I. Prigogine in *Science* **201**, 777 (1978) where he states "150 years after its formulation the second law of thermodynamics still appears to be more a program than a well-defined theory in the usual sense, as nothing precise (except the sign) is said about the  $S$  production". In view of the fact that entropy was not defined for irreversible processes by Clausius, we interpret that the  $S$  production here is meant for the uncompensated heat despite the notation  $S$  used for entropy in the aforementioned paper. In fact, Prigogine's use of terminology appears to be oblivious to the genesis of the notion of Clausius entropy  $S$ , as is evident from the discussion given below.

$$\frac{T_2}{T_1} = \frac{Q_2}{Q_1} - \frac{W_{\text{ua}}}{Q_1}. \quad (2.40)$$

This means that there exists a positive semidefinite quantity  $N = W_{\text{ua}}/T_2$  such that

$$\frac{Q_2}{T_2} = \frac{Q_1}{T_1} + N. \quad (2.41)$$

This  $N$  vanishes for reversible processes by the Carnot theorem. By using the notion of infinitesimal cycles and the sign convention for heat transfer introduced earlier, we may cast this equation in the form

$$N = -\left(\frac{Q_1}{T_1} - \frac{Q_2}{T_2}\right) = -\sum_i \frac{Q_i}{T_i}, \quad (2.42)$$

which gives rise to (2.39) when passage is made from the sum to the cyclic integral. Clearly, the uncompensated heat  $N$  appears as a quantity related to the work unavailable to the irreversible cycle for the purpose of its task when the work is compared with the work of the reversible cycle. The difference between available work and unavailable work is evidently intrinsic to the system and the irreversible cycle in hand, and the unavailable work should be treated as a separate entity from the compensated heat. It is reasonable to consider  $W_{\text{ua}}$  an energy dissipation to the task of work in question, as we have mentioned in an earlier subsection of this chapter.

### 2.3.4 Clausius Entropy

Since a precise mathematical representation for the uncompensated heat was not known to Clausius except that there should exist such a quantity, he limited the consideration to reversible processes for which  $N = 0$  identically, and developed thereby the theory of equilibrium thermodynamics of reversible processes, namely, thermostatics, with which we are all familiar at present through numerous textbooks on equilibrium thermodynamics. If  $N$  is thus set equal to zero for a reversible cyclic process,<sup>9</sup> then there holds the equality

$$\oint \frac{dQ}{T} = 0, \quad (2.43)$$

which implies that  $dQ/T$  must be an exact differential in  $\mathfrak{P} \cup \mathfrak{T}$  (thermodynamic manifold) for reversible processes and there exists a state function  $S_e$ . Clausius called

---

<sup>9</sup>Reversible processes are traditionally defined as those of quasistatic processes which are in continuous equilibrium with the surroundings, but it is more mathematically precise to define them as quasistatic processes for which  $N = 0$ . This will be the definition of reversible processes used throughout in this work.

it the entropy [12] of the system and defined by the differential relation

$$dS_e = \left( \frac{dQ}{T} \right)_{\text{rev}}, \quad (2.44)$$

so that

$$\oint dS_e = 0. \quad (2.45)$$

In other words, in mathematical terminology  $dS_e$  is an exact differential in the thermodynamic (variable) space characteristic of the reversible cyclic process. The differential form combined with the differential form (2.9) for the first law of thermodynamics is called the equilibrium Gibbs relation

$$dS_e = T^{-1} (dE - dW). \quad (2.46)$$

It is the fundamental equation of equilibrium thermodynamics. It is important to keep in mind that *the Clausius entropy  $S_e$  is defined for reversible processes only, but not for a nonequilibrium process. Such an entropy will be called the Clausius entropy in this work in order to distinguish it from the Boltzmann entropy defined by the  $H$  theorem in his kinetic theory.*

Before proceeding further to consider irreversible processes in a general context, we briefly mention the gist of the theory of linear irreversible processes as formulated by Onsager [29], Meixner [30], Prigogine [31], and so on. First, by interpreting the differentials of macroscopic observables in (2.46) to mean their substantial time derivatives, the equilibrium Gibbs relation for the Clausius entropy  $S_e$  is cast into a local form which may be written as

$$d_t S_e = T^{-1} (d_t \mathcal{E} - d_t \mathcal{W}), \quad (2.47)$$

where  $S_e$ ,  $\mathcal{E}$ , and  $\mathcal{W}$  are local densities of the Clausius entropy, internal energy, and work, respectively. It is important to recognize that the derivatives in (2.46) are interpreted as substantial time derivatives<sup>10</sup> in the local form (2.47), and it implies that the macroscopic quantities vary in space-time despite the fact that the Gibbs relation is originally obtained for systems in equilibrium, which is a term connoting homogeneity in space and time. The theory of linear irreversible processes [17, 29–31] assumes the validity of the local equilibrium Gibbs formula (2.47) which is combined with the conservation laws presented earlier for the conserved variables appearing in the right-hand side of (2.47). *This assumption is called the local equilibrium hypothesis.* Upon combining this assumption with a set of linear thermodynamic force-flux relations as the constitutive relations for fluxes in the conservation laws—such as stress tensors, heat fluxes, diffusion fluxes—we obtain in essence the thermodynamic theory of linear irreversible processes. The resulting field equations are the

---

<sup>10</sup>This interpretation of differentials is usually made in linear theory of irreversible thermodynamics. See [17, 30, 31].

classical hydrodynamic equations, namely, the Navier–Stokes, the Fourier, and the Fick equation in the conventional hydrodynamics [32, 33]. Therefore it may be said that the classical hydrodynamics is within the framework of the thermodynamics of linear irreversible processes.

Since the Clausius entropy can be *defined only for reversible processes* it is not clear under what conditions it is permissible to assume the local equilibrium hypothesis (2.44) when the process in question is not reversible. The thermodynamics of linear irreversible processes at first glance appears to be contradictory to the definition of the Clausius entropy. This question was first raised by Meixner [34] who was also one of the formulators of the theory of linear irreversible processes. His attempt to resolve this vexing question was not successful, however. It is one of the important objectives for the present work to find a solution to the aforementioned question.

Since the early 1960s there have appeared propositions [35–44] in varying forms that extend the thermodynamic space for systems undergoing irreversible processes to include nonconserved variables as a generalization of the local equilibrium hypothesis to nonequilibrium systems. The differential form for the nonequilibrium entropy, *which these theories postulate*, is called the extended Gibbs relation and serves as the starting equation for the subject field of extended irreversible thermodynamics.<sup>11</sup> This postulate for the extended Gibbs relation for irreversible processes, however, has not been shown to be on the support of the foundations of the thermodynamic laws although there have been efforts [35, 37, 40, 41, 43, 44] to provide its kinetic theory basis in terms of the well-known  $H$  theorem of Boltzmann. However, it becomes evident on careful examination of the properties of the Boltzmann entropy that the  $H$  theorem of Boltzmann itself should not simply be taken as an equivalent of the second law of thermodynamics as often and uncritically done in the literatures cited earlier of kinetic theory and irreversible thermodynamics. This statement will be

---

<sup>11</sup> There are basically two different versions of extended irreversible thermodynamics: one class of versions can be found in Refs. [36, 37, 41, 43, 44] and the other in Refs. [6, 35, 45, 46] and this work. In the former, it is assumed that there exists a nonequilibrium entropy which is a state function in the thermodynamic space and the nonequilibrium entropy is statistically represented by approximations of the Boltzmann entropy or its dense fluid generalization or the information entropy for dynamical systems, without a support of a kinetic equation. In the latter class (i.e., in Refs. [6, 45, 46]), it is shown from the second law of thermodynamics that there exists a quantity called *compensation function* (renamed to calortropy in this and earlier work) and its differential is an exact differential in the thermodynamics space by virtue of the second law. The compensation function, however, is not the same as the Boltzmann entropy appearing in the kinetic theory of dilute gases by Boltzmann. Since thermodynamics of irreversible processes must be securely founded on the thermodynamic laws, it is crucial to show that the basic equations are consistent with the thermodynamic laws and, for example, the extended Gibbs relation is equivalent to the second law of thermodynamics. An assumption for such a basic equation is not acceptable if the resulting theory will have anything to do with the thermodynamic laws in accounting for macroscopic processes in nature. Neither can the thermodynamic laws afford approximate representations. The basic thermodynamic equation in the formulation made in Refs. [6, 46] and in this work is a rigorous consequence of the second law of thermodynamics which mathematically extends equilibrium thermodynamics that is certainly endowed with a physical basis supported by the second law; it is not an assumption as in Refs. [35–44].

supported by the discussion in the subsequent chapters of this work when we discuss the kinetic theory foundations of thermodynamics of irreversible processes.

Besides this point, the extended Gibbs relation for the nonequilibrium entropy raises various subtle questions as to what we really mean by the nonequilibrium entropy; if it really does exist as assumed in the extended irreversible thermodynamics mentioned; whether its differential form is indeed exact in the thermodynamic space taken for description of irreversible processes in hand; what we really mean by the intensive variables appearing in the differential form and their operational thermodynamic significance; and so on. Unless these questions are satisfactorily answered and settled, the theory thus formulated is merely a mathematical formalism that has little to do with thermodynamic laws and the macroscopic reality of the processes under consideration that we hope to describe theoretically. The theory presented below is addressed to help resolve these questions and thereby put the formalism on firmer foundations of the thermodynamic laws. It is also the opinion of the present author that it is not advisable to tamper with the Clausius principle or the Kelvin principle until they are given a complete mathematical representation and such a representation is proven inadequate on application to irreversible processes, as we occasionally see in the literature on thermodynamics.

The Clausius inequality (2.38) is not the most useful mathematical form of representation for the second law of thermodynamics. To proceed further on its mathematical representation, we observe that the uncompensated heat in (2.39) may be written as a circular integral in the thermodynamic manifold over the cycle in hand:

$$N = \oint dN \geq 0, \quad (2.48)$$

where  $dN$ , or more precisely,  $dN/dt$  should be always positive except for reversible processes in which it vanishes. Otherwise, it would be possible to devise<sup>12</sup> a cyclic process in such a way that it vanishes or is negative, violating the second law of thermodynamics.

By combining (2.48) with (2.39), we obtain the equation [45, 47]

$$\oint \left( \frac{dQ}{T} + dN \right) = 0. \quad (2.49)$$

This vanishing circular integral implies that there exists a state function  $\Psi$  in the thermodynamic space such that

$$d\Psi = \frac{dQ}{T} + dN \quad (2.50)$$

---

<sup>12</sup>A simple, albeit somewhat ideal, example would be a cyclic process consisting of the irreversible segment where  $dN < 0$  and a reversible segment for the remainder of the cycle in which  $dN = 0$ . This cycle, if possible to construct, would violate the second law.

and thus even for a cyclic irreversible process

$$\oint d\Psi = 0. \quad (2.51)$$

The differential form (2.50) and the circular integral (2.51) remain valid regardless of whether the process is reversible or irreversible. Indeed, if the process is reversible, then  $dN = 0$ , or  $dN/dt = 0$ , over the differential segment of the process and we recover the Clausius entropy: namely,

$$d\Psi|_{\text{rev}} = \left. \frac{dQ}{T} \right|_{\text{rev}} = dS_e \quad (2.52)$$

and thus within a constant of integration the reversible calortropy coincides with the Clausius entropy:

$$\Psi_{\text{rev}} = S_e. \quad (2.53)$$

For irreversible processes it is clearly different from the Clausius entropy *which is defined only for reversible processes*. As will be shown in the kinetic theory chapters, it is also different from the Boltzmann entropy or the information entropy [48] for nonequilibrium processes. Since the Boltzmann entropy for a nonequilibrium system is often called the nonequilibrium entropy in the literature, it will be preferable to call  $\Psi$  by another term to remove the possibility of confusion. Henceforth it will be called by a new term [6] *calortropy* which means heat (*calor*) evolution (*tropy*).

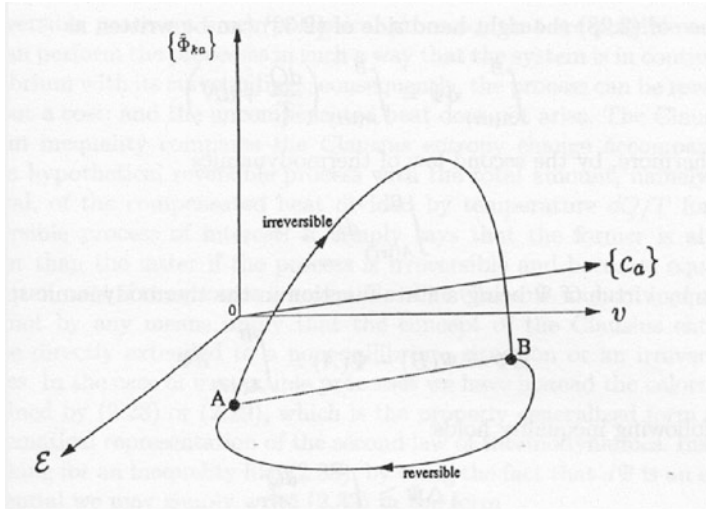
With (2.10) and (2.51), the first and the second law of thermodynamics are now expressed by a pair of vanishing circular integrals of internal energy and calortropy in the case of a cyclic process. This pair of vanishing circular integrals, equivalently, the corresponding exact differential forms (2.9) and (2.50), provides us with the starting point of a mathematical theory of thermodynamics of irreversible processes.

### 2.3.5 Clausius–Duhem Inequality

Let us now examine the relation of (2.51) to the Clausius–Duhem inequality. Clausius [12] considered a cyclic process consisting of a segment of irreversible process, which starts from state  $A$  and ends at state  $B$  that are embedded<sup>13</sup> in the equilibrium part of the thermodynamic manifold, and another segment of reversible process which

---

<sup>13</sup>In his work, Clausius made no mention of embedding the states  $A$  and  $B$  in the equilibrium part of the thermodynamic manifold. He simply constructed a cycle consisting of an irreversible segment starting from state  $A$  and ending at state  $B$  and a reversible segment starting from state  $B$  and restoring the system to state  $A$ . Since states  $A$  and  $B$  are also part of a reversible process, they must be embedded in the equilibrium part of the thermodynamic manifold. It now may be stated that there was no clear notion of thermodynamic manifold in the Clausius formulation of the second law of thermodynamics.



**Fig. 2.1** A cycle consisting of an irreversible and an reversible segment. This figure is a rendering in the thermodynamic space of the irreversible cycle from which Clausius deduced the Clausius-Duhem inequality. In the formulation of Clausius the concept of thermodynamic manifold is absent. The reversible segment is embedded in the equilibrium part of the thermodynamic manifold. This cycle is a special case, albeit somewhat ideal, because of the presence of a reversible segment. Reproduced from B.C. Eu, *Kinetic Theory and Irreversible Thermodynamics* copyright © John Wiley & Sons, Inc with permission

reversibly restores the system at state  $B$  to its original thermodynamic state  $A$ ; see Fig. 2.1. In the sense of the conditions imposed on states  $A$  and  $B$ , this cyclic process is rather special since the system must start from an equilibrium state and end at another equilibrium state but through a nonequilibrium path in the thermodynamic state space. For this cyclic process the circular integral (2.51) can be split up into reversible and irreversible segments and written as

$$\int_{A(rev)}^B d\Psi = \int_{A(irr)}^B d\Psi, \quad (2.54)$$

where the subscripts attached to the integrals, *rev* and *irr*, mean that the integration must be performed along the reversible and the irreversible path, respectively. Note that the integration over the reversible path can be reversed by virtue of the process being reversible. Since  $dN = 0$  and hence the calortropy is identified with the Clausius entropy over the reversible segment, we obtain

$$\int_{A(rev)}^B d\Psi = \int_{A(rev)}^B dS_e = S_e(B) - S_e(A) = \Delta S_e. \quad (2.55)$$

By using (2.50), the right-hand side of (2.54) can be written as

$$\int_{A(irr)}^B d\Psi = \int_{A(irr)}^B \left( \frac{dQ}{T} + dN \right). \quad (2.56)$$

Furthermore, by the second law of thermodynamics

$$\int_{A(irr)}^B dN \geq 0. \quad (2.57)$$

Since by virtue of  $\Psi$  being a state function in the thermodynamic space

$$\Delta\Psi = \Psi(B) - \Psi(A) = \int_{A(irr)}^B d\Psi,$$

the following inequality holds

$$\Delta\Psi \geq \int_{A(irr)}^B \frac{dQ}{T}. \quad (2.58)$$

The differential form for this is

$$d\Psi \geq \frac{dQ}{T}, \quad (2.59)$$

which follows from (2.50) since  $dN \geq 0$ . Therefore, it is concluded that  $\Delta\Psi \geq 0$  always for an isolated system. Equations (2.54) and (2.58) with the help of (2.55) give rise to the Clausius-Duhem inequality

$$\Delta S_e \geq \int_{A(irr)}^B \frac{dQ}{T} \quad (2.60)$$

under the sign convention adopted for heat transfer. Thus, the Clausius–Duhem inequality<sup>14</sup> is contained in the present expression for the second law of thermodynamics (2.51).

---

<sup>14</sup>Inequality (2.60), together with (2.54) and (2.55), means that for an isolated system  $\Delta S_e \geq 0$  as is generally taken in the thermodynamics literature. However, this inequality for an isolated system can be misleading and cause confusion. In applying this inequality, it must be remembered that  $\Delta S_e$  is for the reversible segment complementary to the irreversible step making up the cycle in question and the inequality (2.60) simply means that  $\Delta S_e$  for the reversible segment is always larger than the irreversible compensated heat change. If the system is isolated, the compensated heat  $dQ = 0$  everywhere in the interval of integration and hence  $\Delta S_e = 0$  identically. This conclusion is also consistent with the definition of  $dS_e$  in (2.44). It is clearly convenient to think in terms of  $\Delta\Psi \geq 0$  instead of  $\Delta S_e \geq 0$ .

Reversible processes are hypothetical processes that are possible only if one can perform the processes in such a way that the system is in continuous equilibrium with its surroundings; consequently, the process can be reversed without a cost; and the uncompensated heat does not arise. The Clausius–Duhem inequality compares the Clausius entropy change accompanying such a hypothetical reversible process with the total amount of the compensated heat divided by temperature  $dQ/T$  for the irreversible process of interest. It simply says that the former is always greater than the latter if the process is irreversible and becomes equal to the latter, only if the process is reversible. From the investigation made here we can conclude that the Clausius–Duhem inequality does not by any means imply that the concept of the Clausius entropy can be directly extended to a nonequilibrium situation or an irreversible process. In the case of irreversible processes, we have instead the calortropy  $\Psi$  defined by (2.50) or (2.51), which is a properly generalized form for mathematical representation of the second law of thermodynamics. Instead of looking for an inequality like (2.60), we may simply write, by using the fact that  $d\Psi$  is an exact differential, (2.54) in the form

$$\Delta S_e = \Delta \Psi = \Psi(B) - \Psi(A) \quad (2.61)$$

for the cyclic process considered by Clausius. Therefore, for such a special process starting from an equilibrium state and ending at another equilibrium state the calortropy change for an irreversible process can be simply computed in terms of the Clausius entropy change over a complementary reversible process which with the irreversible segment makes up the cyclic process of Clausius. We emphasize that this equality (2.61) does not mean  $S_e = \Psi$  along the same path, but  $\Delta S_e$  and  $\Delta \Psi$  are computed along two different paths, which are complementary to each other if a cyclic process is possible to construct. This conclusion appears to have considerable significance for understanding and examining from the standpoint of the second law of thermodynamics the thermodynamics of steady irreversible processes and the theory of linear irreversible processes which assumes the local equilibrium hypothesis for Clausius entropy change even if there are irreversible processes present in the system. We will return to this aspect later at a more appropriate stage. Equation (2.61) implies that there are an infinite number of reversible paths that can produce  $\Delta \Psi$  between two states  $A$  and  $B$  in the case of the particular cycle considered. Note, however, that (2.61) is for a global change, but not for a local change.

In the case of a local irreversible process, it is not possible to transcribe (2.61) into the equality

$$d\Psi = dS_e, \quad (2.62)$$

because

$$\int_{A(irr)}^B (d\Psi - dS_e) \neq \int_{A(irr)}^B d\Psi - \int_{A(rev)}^B dS_e = 0.$$

Pursuing this discussion a little further, we remark that in the linear theory of irreversible processes [17, 29–31] the entropy density change  $dS$  in a system is

written as  $dS = dQ/T + dN$  in the present notation. In the light that (2.62) holds for a global process only, this equation for  $dS$  cannot be used for local processes if  $S$  is meant for the Clausius entropy. The discussion presented earlier in connection with calortropy suggests that  $dS$  in the said equation must be interpreted as  $d\Psi$  for it to make sense from the thermodynamic standpoint.

## 2.4 Differential Form for Calortropy

The differential forms for the first and second law of thermodynamics (2.9) and (2.50) can be combined to obtain

$$d\Psi = T^{-1}(dE - dW) + dN. \quad (2.63)$$

If  $dN$  is suitably represented explicitly in terms of global thermodynamic variables, the precise meaning of calortropy  $\Psi$  will be known. Therefore, the subject of irreversible thermodynamics may be said to be centered around the meaning of uncompensated heat. Since such a representation of  $N$  requires the elements of the tangent manifold  $\mathfrak{T}$  conjugate to the manifold  $\mathfrak{P}$ , the zeroth law of thermodynamics and its extension to the variables of  $\mathfrak{T}$  other than temperature  $T$  should be made use of to render them operational. The following proposition is taken for the variables in manifold  $\mathfrak{T}$ :

**Proposition 3** *There exists a set of measurable local intensive variables, namely, temperature  $T$ , pressure  $p$ , chemical potentials  $\hat{\mu}_a$  ( $1 \leq a \leq r$ ), and generalized potentials  $X_a^{(s)}$ , which are conjugate to the internal energy  $\mathcal{E}$ , specific volume  $v$ , mass fractions  $\epsilon_a$  ( $1 \leq a \leq r$ ), and nonconserved variables<sup>15</sup>  $\hat{\Phi}_a^{(s)}$  ( $s \geq 1$ ,  $1 \leq a \leq r$ ), respectively. These intensive local variables are amenable to measurements, at least in principle, according to the zeroth law of thermodynamics and its extension.*

Thermodynamics of irreversible processes developed below will provide theories of measurements for  $\hat{\mu}_a$  and  $X_a^{(s)}$  as well as other intensive variables just as equilibrium thermodynamics gives theories of measurements of equilibrium temperature, pressure, and chemical potentials. These intensive variables are basically the constitutive parameters which must be determined as functions of their conjugate variables. Their determinations are therefore a major task of the phenomenological thermodynamics of irreversible processes that emerges in this work. The simplest example for an approximate  $X_a^{(s)}$  that can be used for studies of experimental data is the linear relations between  $X_a^{(s)}$  and  $\hat{\Phi}_a^{(s)}$ :

$$X_a^{(s)} = -\rho g_a^{(s)} \hat{\Phi}_a^{(s)}, \quad (2.64)$$

---

<sup>15</sup>If the volume transport is included, the range of index  $s$  may be taken  $s \geq 0$ , if we adopt the system of notation used in the kinetic theory chapters in this work. See Chaps. 6 and 7.

in which  $g_{sa}$  is independent of  $\widehat{\Phi}_a^{(s)}$ , but depends on  $\rho$ ,  $T$ , and  $p$ . Rigorously and more generally,  $g_a^{(s)}$  are scalar-valued functions of  $\rho$ ,  $T$ , and  $p$  as well as  $\widehat{\Phi}_a^{(s)}$  ( $r \geq a \geq 1$ ;  $s \geq 1$ ). The functions  $g_a^{(s)}$  may be given in terms of thermodynamic derivatives as will be discussed presently.

### 2.4.1 Local Differential Form for Calortropy

With the preparations made in the previous sections regarding the mathematical representation of the second law of thermodynamics and operational definitions of temperature, pressure, and so on for the intensive variables conjugate to various thermodynamic variables, we are now ready to formulate a thermodynamic theory of irreversible processes in local form. To make the presentation uncluttered with terminologies, we will first define some necessary and recurring quantities.

The calortropy  $\Psi$  for a global system can be given as a volume integral of its density  $\widehat{\Psi}$ :

$$\Psi = \int_V d\mathbf{r} \rho \widehat{\Psi}(\mathbf{r}, t). \quad (2.65)$$

Here the integration is over the volume enclosing the system. Since thermodynamic description of macroscopic processes involves a set of macroscopic variables subject to the laws of thermodynamics, it is clear that  $\widehat{\Psi}(\mathbf{r}, t)$  must be given in terms of variables spanning manifold  $\mathfrak{P} \cup \mathfrak{T}$ . *The union of this set with  $\widehat{\Psi}$  will be called the Gibbs manifold  $\mathfrak{G}$ :*

$$\begin{aligned} \mathfrak{G} &= \widehat{\Psi} \cup \mathfrak{P} \cup \mathfrak{T} \\ &= (\widehat{\Psi}, \mathcal{E}, v, \epsilon_a, \widehat{\Phi}_a^{(s)}, T, p, \widehat{\mu}_a, X_a^{(s)} : 1 \leq a \leq r; s \geq 1). \end{aligned} \quad (2.66)$$

The vanishing circular integral (2.51) may be written in a form similar to (2.11) if the circular path integral is converted into the time integration:

$$\int_0^\tau dt \frac{d\Psi}{dt} = 0, \quad (2.67)$$

where  $\tau$  is the period of the cycle. Noting that the differential form (2.50) can be cast into a derivative form

$$\frac{d\Psi}{dt} = T^{-1} \frac{dQ}{dt} + \frac{dN}{dt} \quad (2.68)$$

and the time derivatives in (2.68) are the global rates of change and by using the well-known procedure in continuum mechanics, it is possible to express the time derivatives as volume integrals of the following forms [6, 14]:

$$\frac{d\Psi}{dt} = \int_V d\mathbf{r} \left[ \frac{\partial}{\partial t} \rho \widehat{\Psi} + \nabla \cdot (\mathbf{u} \rho \widehat{\Psi}) \right], \quad (2.69)$$

$$T^{-1} \frac{dQ}{dt} = - \int_{\mathcal{B}} d\mathbf{B} \cdot \mathbf{Q}^c / T = - \int_V d\mathbf{r} \nabla \cdot [\mathbf{Q}^c / T(\mathbf{r}, t)], \quad (2.70)$$

$$\frac{dN}{dt} = \int_V d\mathbf{r} \rho \widehat{\Xi}_{\text{cal}}(\mathbf{r}, t). \quad (2.71)$$

Here  $\mathbf{u}$  is the fluid velocity. It is assumed for the derivation of (2.69) that the fluid sticks with the boundaries. The subscript  $\mathcal{B}$  to the integral in (2.70) stands for the surface of the enclosing volume whose outward normal direction is counted positive. The vector  $\mathbf{Q}^c$  also is counted positive in the normal direction to the surface. Here, it must be recalled that the differential form (2.68) pertains to one of infinitesimal Carnot cycles which operate between two heat reservoirs of a minute temperature difference and comprise the original Carnot cycle for which (2.39) holds. It is assumed that the temperature is uniform over the surface  $\mathcal{B}$  of the volume of the infinitesimal Carnot cycle which is in contact with the heat reservoir of temperature  $T$ . We remark that except for the terminal infinitesimal Carnot cycles this heat reservoir of temperature  $T$  is not the heat reservoirs of the original finite Carnot cycle, which operates between temperatures  $T_1$  and  $T_2$  and is imagined to consist of infinitesimal Carnot cycles that Clausius used in his derivation of Inequality (2.38).

The first equality in (2.70) can be achieved in this way: Let us observe that since  $T^{-1}dQ$  is the differential form for  $[(Q/T)_i - (Q/T)_{i-1}]$  [see (2.42)],  $T^{-1}dQ/dt$  may be written as the sum over the infinitesimal pistons:

$$T^{-1} \frac{dQ}{dt} = \sum_i \left( T^{-1} \frac{dQ}{dt} \right)_i,$$

which then can be written as

$$\sum_i \left( T^{-1} \frac{dQ}{dt} \right)_i = - \sum_i \int_{\mathcal{B}_i} d\mathbf{B}_i \cdot \frac{\mathbf{Q}^c(\mathcal{B}_i)}{T(\mathcal{B}_i)} = - \int_{\mathcal{B}} d\mathbf{B} \cdot \frac{\mathbf{Q}^c}{T(\mathbf{r}, t)},$$

where  $\mathcal{B} = \cup_i \mathcal{B}_i$ . From this consideration follows the second equality in (2.70). Since the index  $i$  may be regarded as a local position of the global system,  $T$  should be regarded as the local temperature that depends on position  $\mathbf{r}$ . The vector  $\mathbf{Q}^c$  is the net heat flux at the surface; it is the compensated heat flux. The quantity  $\rho \widehat{\Xi}_{\text{cal}}(\mathbf{r}, t)$  is the local rate of uncompensated heat per volume. Use of (2.69)–(2.71) in (2.68) implies, by virtue of continuity, the balance equation for the calortropy density [46, 49]:

$$\rho \frac{d\widehat{\Psi}}{dt} = - \nabla \cdot \left( \frac{\mathbf{Q}^c}{T(\mathbf{r}, t)} \right) + \rho \widehat{\Xi}_{\text{cal}}(\mathbf{r}, t). \quad (2.72)$$

We will call  $\mathbf{J}_c := \mathbf{Q}^c / T$  and  $\rho \widehat{\Xi}_{\text{cal}}$  the calortropy flux and the calortropy production, respectively.

Except that  $\rho \widehat{\Xi}_{\text{cal}}$  must be always positive and vanishes for reversible processes by virtue of Inequality  $dN/dt \geq 0$ , the precise forms for these quantities  $\mathbf{Q}^c$  and  $\widehat{\Xi}_{\text{cal}}$  are not known at this point as to permit deductions on the properties of calortropy. To this end, we reason this way. First of all, since a macroscopic system must evolve in conformation with the conservation laws, the relevant variables to characterize the macroscopic state of the system should include the conserved variables obeying the balance equations in Proposition 1. Since these balance equations require constitutive equations, it is necessary to append the set of the former with the evolution equations for nonconserved variables presented in Proposition 2. Therefore, it is evident that the space of macroscopic variables necessary to describe the calortropy is the manifold  $\mathfrak{P} \cup \mathfrak{T}$ . The desired deductions of the properties of the calortropy will be possible if the calortropy flux and the calortropy production are elucidated in manifold  $\mathfrak{P} \cup \mathfrak{T}$ . We make the following proposition for them.

**Proposition 4** *The calortropy flux  $\mathbf{J}_c := \mathbf{Q}^c/T$  is given by the bilinear form of the intensive variables  $T^{-1}$ ,  $\widehat{\mu}_a T^{-1}$ , and  $X_a^{(s)} T^{-1}$  ( $s \geq 1$ ,  $1 \leq a \leq r$ ) paired, respectively, with  $\mathbf{Q}_a$ ,  $\mathbf{J}_a$ , and  $\psi_a^{(s)}$  (flux of  $\Phi_a^{(s)}$ ) as follows:*

$$\mathbf{J}_c := \sum_{a=1}^r \frac{\mathbf{Q}_a^c}{T} = \sum_{a=1}^r T^{-1} (\mathbf{Q}_a - \widehat{\mu}_a \mathbf{J}_a + \sum_{s \geq 1} X_a^{(s)} \psi_a^{(s)}), \quad (2.73)$$

and the calortropy production  $\Xi_{\text{cal}}$  is given by the bilinear form

$$\begin{aligned} \Xi_{\text{cal}} &:= \rho \widehat{\Xi}_{\text{cal}} \\ &= -T^{-1} \sum_{a=1}^r [(\mathbf{P}_a - p_a \boldsymbol{\delta}) : \nabla \mathbf{u} + \mathbf{Q}_a^c \cdot \nabla \ln T + \mathbf{J}_a \cdot (\nabla \widehat{\mu}_a - \widehat{\mathbf{F}}_a) \\ &\quad - \sum_{s \geq 1} \psi_a^{(s)} \cdot \nabla X_a^{(s)}] + T^{-1} \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} (\mathcal{Z}_a^{(s)} + \Lambda_a^{(s)}). \end{aligned} \quad (2.74)$$

By the second law of thermodynamics, it must be such that  $\Xi_{\text{cal}} \geq 0$  always, the equality holding for reversible processes only or at equilibrium.

The inequality for the calortropy production imposes the positivity condition that the kinematic and dissipation terms  $\mathcal{Z}_a^{(s)}$  and  $\Lambda_a^{(s)}$  in the evolution equation for  $\widehat{\Phi}_a^{(s)}$  must satisfy, and thus it dictates the acceptable forms for them and hence for the evolution equations for  $\widehat{\Phi}_a^{(s)}$ . Therefore, the evolution equations for nonconserved variables are not free, but must conform to the second law of thermodynamics represented by  $\Xi_{\text{cal}} \geq 0$  in the local theory—namely, the thermodynamic consistency condition. It must be noted that the terms in the square brackets in (2.74) except for the last term involving  $\nabla X_a^{(s)}$  are formally those making up the entropy production in the theory of linear irreversible processes [17, 31]. The last term mentioned is a bilinear product of the gradient of the generalized potential and the flux  $\psi_a^{(s)}$  of nonconserved variable  $\Phi_a^{(s)}$  just as the other terms are bilinear products of the velocity

gradient and the momentum flux (i.e., the stress tensor), of the temperature gradient and the compensated heat flux, and so on. Therefore, it may be said that the gradient  $\nabla X_a^{(s)}$  induces the flux  $\psi_a^{(s)}$  of nonconserved variable  $\Phi_a^{(s)}$  just as  $\nabla \hat{\mu}_a$  induces diffusion flows of species. The occurrence of such a flux gives rise to an uncompensated heat just as do the stress, compensated heat flux, and so on. In addition to the aforementioned contribution from  $\psi_a^{(s)}$ , there are contributions to the uncompensated heat from the kinematic and dissipation terms—the last group of terms in (2.74)—in the evolution equations for the nonconserved variables in the present generalized theory. The calortropy flux proposed is also seen to include the classical terms as well as non-classical terms—the last group of terms in (2.73)—attributable to the nonconserved variables. The calortropy flux and the calortropy production proposed in Proposition 4 are mutually compatible in the sense that they give rise to an integrable differential form for  $d_t \hat{\Psi}$  as will be shown.<sup>16</sup>

Finally, a note on notation: the term  $X_a^{(s)} \hat{\Phi}_a^{(s)}$  or  $X_a^{(s)} \psi_a^{(s)}$  are made up of two tensors appropriately contracted to a scalar in the case of the former and to a vector in the case of the latter. The tensor contraction signs are omitted for brevity of notation.

Use of (2.73) and (2.74) in the calortropy balance equation (2.72) makes it possible to determine  $\hat{\Psi}$  in the Gibbs manifold  $\mathfrak{G}$  if the conservation laws listed in Proposition 1 and the evolution equations in Proposition 2 are used. In particular, if the fluxes  $\mathbf{Q}_a$ ,  $\mathbf{J}_a$ , and  $\psi_a^{(s)}$  are either replaced or rearranged by means of (2.23)–(2.25) and (2.34), then it is possible to put the balance equation for  $\hat{\Psi}$  in a Pfaffian differential form (one-form) in Gibbs manifold  $\mathfrak{G}$ :

$$d_t \hat{\Psi} = T^{-1} \left( d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a d_t \epsilon_a + \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} d_t \hat{\Phi}_a^{(s)} \right). \quad (2.75)$$

Inasmuch as the calortropy balance equation (2.72) is the local equivalent of the second law of thermodynamics, the Pfaffian differential form<sup>17</sup> (2.75) is an equivalent to the second law in the Gibbs manifold  $\mathfrak{G}$  ( $\mathfrak{G} := \mathfrak{P} \cup \mathfrak{T} \cup \hat{\Psi}$ ) under Proposition 4. *This differential form is exact in the Gibbs manifold  $\mathfrak{G}$  by virtue of the vanishing circular integral (2.51).* This can be shown as follows. From (2.67) and (2.69) we obtain

<sup>16</sup> Although (2.73) and (2.74) are sufficient for  $\mathbf{J}_c$  and  $\Xi_c$  to yield a one-form for  $d_t \hat{\Psi}$ , it is not unique. For example, a vector  $\mathbf{A}$  and its divergence  $\nabla \cdot \mathbf{A}$  can be added to  $\mathbf{J}_c$  and  $\Xi_c$ , respectively, with no effect at all on the one-form that can be obtained from the balance equation for the calortropy. In fact, the vector  $\mathbf{A}$  can be taken with  $\sum_{a=1}^r \mathbf{J}_a/m_a$  as can be seen later in Chap. 3. The formulas for  $\mathbf{J}_c$  and  $\Xi_c$  proposed in Proposition 4 therefore are minimal in the sense that they are sufficient to produce a one-form for  $d_t \hat{\Psi}$ .

<sup>17</sup> It must be noted that a Pfaffian differential form is not necessarily an exact differential unless it satisfies a set of integrability conditions [50–53]. In the case of thermodynamics, the second law of thermodynamics preempts the integrability conditions which are partial differential equations not easy to solve in general.

$$\begin{aligned}
\int_0^\tau dt \frac{d\Psi}{dt} &= \int_0^\tau dt \int_V d\mathbf{r} \left[ \frac{\partial}{\partial t} \rho \widehat{\Psi} + \nabla \cdot (\mathbf{u} \rho \widehat{\Psi}) \right] \\
&= \int_V d\mathbf{r} \int_0^\tau dt \rho \frac{d\widehat{\Psi}}{dt} = 0
\end{aligned} \tag{2.76}$$

from which, by continuity, follows the vanishing local integral

$$\int_0^\tau dt \rho \frac{d\widehat{\Psi}}{dt} = 0. \tag{2.77}$$

This implies that  $d_t \widehat{\Psi}$  is an exact differential in the Gibbs manifold  $\mathfrak{G}$  since  $\rho(d\widehat{\Psi}/dt)$  may be replaced by  $(d\rho \widehat{\Psi}/dt)$ . It is not simple to prove the exactness of a differential form like (2.75) in  $\mathfrak{G}$  if a purely mathematical approach is taken for the proof, but in the present case, the differential form  $d_t \widehat{\Psi}$  is exact by the demand of the second law of thermodynamics. Thus, when the calortropy flux and the calortropy production are suitably elucidated, the second law assures the integrability of the differential form  $d_t \widehat{\Psi}$  in  $\mathfrak{G}$ , and there exists a hypersurface of  $\widehat{\Psi}$  in manifold  $\mathfrak{G}$ . These results are collected in a theorem.

**Theorem 1** *Under Propositions 1–4 the second law of thermodynamics is expressible, for local irreversible processes in space-time, in the Pfaffian differential form in manifold  $\mathfrak{P} \cup \mathfrak{T}$*

$$d_t \widehat{\Psi} = T^{-1} \left( d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \widehat{\mu}_a d_t c_a + \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} d_t \widehat{\Phi}_a^{(s)} \right). \tag{2.78}$$

*This differential form is exact and integrable. Therefore, there exists a state function  $\widehat{\Psi}$  in the Gibbs manifold  $\mathfrak{G}$ . This function may be regarded as a hypersurface in  $\mathfrak{G}$  in conformation to the demand of the second law of thermodynamics.*

The differential form (2.78) is called the extended Gibbs relation for the reason that it reduces to the equilibrium Gibbs relation as  $X_a^{(s)} \rightarrow 0$  at equilibrium. It provides the foundation for a phenomenological theory of thermodynamics of irreversible processes in a fairly general form. We will return to further discussions on the calortropy differential after formulating the kinetic theory version of differential form (2.78). Henceforth the operator  $d_t$  may be written as  $d$  for brevity.

The necessary and sufficient conditions for integrability of the extended Gibbs relation in the Gibbs manifold is the nonequilibrium Gibbs–Duhem equation

$$\mathcal{E} d \left( \frac{1}{T} \right) + v d \left( \frac{p}{T} \right) - \sum_{a=1}^r c_a d \left( \frac{\widehat{\mu}_a}{T} \right) + \sum_{a=1}^r \sum_{q \geq 1} \widehat{\Phi}_a^{(q)} d \left( \frac{X_a^{(q)}}{T} \right) = 0. \tag{2.79}$$

If this equation is added to the extended Gibbs relation, then the resulting equation is integrable to the bilinear form for  $\Psi$  in manifold  $\mathfrak{G}$

$$\widehat{\Psi} = T^{-1} \left( \mathcal{E} + pv - \sum_{a=1}^r \widehat{\mu}_a \mathfrak{c}_a + \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} \widehat{\Phi}_a^{(s)} \right) \quad (2.80)$$

apart from a constant, which can be put equal to zero. Thus it is a sufficient condition for (2.78) to be integrable in manifold  $\mathfrak{G}$ . On the other hand, the Gibbs–Duhem equation is evidently the necessary condition for (2.78) to follow from (2.80). Therefore the statement is proved. This integrability condition [54] is a nonequilibrium generalization of the Gibbs–Duhem equation used in equilibrium thermodynamics [1], which is useful for applying the present theory to nonequilibrium phenomena. The nonequilibrium Gibbs–Duhem equation (2.79) may be rearranged to the form

$$d(pv) = \widehat{\Psi} dT + p dv + \sum_{a=1}^r \mathfrak{c}_a d\widehat{\mu}_a - \sum_{q \geq 1} \sum_{a=1}^r \widehat{\Phi}_a^{(q)} dX_a^{(q)}, \quad (2.81)$$

which then may be regarded as the differential form for the thermodynamic potential  $pv$ . The advantage of this differential form lies in the fact that the thermodynamic potential  $pv$  turns out to be given by the local grand canonical partition function appearing in nonequilibrium statistical thermodynamics, which is formulated later based on the Boltzmann kinetic equation and the irreversible kinetic equations for dense fluids treated subsequent to the Boltzmann kinetic equation in this monograph; see Chaps. 5, 6, and 7.

Before proceeding further, we examine how the present theory connects with equilibrium thermodynamics. First of all, we see that as  $X_a^{(s)}$  vanish for all  $s$  and  $a$ , equilibrium thermodynamics is recovered since  $\widehat{\Psi}$  tends to its equilibrium limit  $\widehat{\Psi}_e$  which coincides with the Clausius entropy density  $\mathcal{S}_e$ :

$$\begin{aligned} d_t \widehat{\Psi}_e &= T_e^{-1} \left( d_t \mathcal{E} + p_e d_t v - \sum_{a=1}^r \widehat{\mu}_a^e d_t \mathfrak{c}_a \right) \\ &= d_t \mathcal{S}_e, \end{aligned} \quad (2.82)$$

where

$$\begin{aligned} T_e &= \lim_{X \rightarrow 0} T = \lim_{\Phi \rightarrow 0} T, \\ p_e &= \lim_{X \rightarrow 0} p = \lim_{\Phi \rightarrow 0} p, \\ \widehat{\mu}_a^e &= \lim_{X \rightarrow 0} \widehat{\mu}_a = \lim_{\Phi \rightarrow 0} \widehat{\mu}_a. \end{aligned}$$

This consideration shows that equilibrium thermodynamics is contained in the formalism based on the concept of calortropy. Since we are not interested in equilibrium thermodynamics here, we will not dwell on this aspect further.

Other thermodynamic functions related to (2.78) and (2.81) can be defined as in equilibrium thermodynamics. For example, we may define generalized work function  $\mathcal{A}$ , generalized Gibbs free energy  $\mathcal{G}$  [6, 46], and generalized enthalpy  $\mathcal{H}$ , which will be found to be another thermodynamic potential:

$$\mathcal{A} = \mathcal{E} - T\hat{\Psi}, \quad (2.83)$$

$$\mathcal{G} = \mathcal{H} - T\hat{\Psi}, \quad (2.84)$$

$$\mathcal{H} = \mathcal{E} + pv, \quad (2.85)$$

We remark that  $\mathcal{H}$  is basically a mechanical quantity because  $\mathcal{E}$  and  $p$  are mechanically calculable from their molecular expressions. In this sense,  $\mathcal{H}$  is different from  $\mathcal{A}$  and  $\mathcal{G}$ , which is defined with  $\hat{\Psi}$  instead of  $\mathcal{S}_e$  used in equilibrium thermodynamics. Since the properties of the functions  $\mathcal{A}$  and  $\mathcal{G}$  can be discussed in complete parallel to the equilibrium thermodynamics by using the fundamental equation (2.75) we will discuss about them only briefly in this section.

### 2.4.2 Calortropy and Thermodynamic Relations

Differential forms equivalent to (2.78) and (2.81) can be easily obtained for  $\mathcal{H}$ ,  $\mathcal{A}$ , and  $\mathcal{G}$ , respectively:

$$d_t \mathcal{H} = T d_t \hat{\Psi} + v d_t p + \sum_{a=1}^r \hat{\mu}_a d_t \epsilon_a - \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} d_t \hat{\Phi}_a^{(s)}, \quad (2.86)$$

$$d_t \mathcal{A} = -\hat{\Psi} d_t T - p d_t v + \sum_{a=1}^r \hat{\mu}_a d_t \epsilon_a - \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} d_t \hat{\Phi}_a^{(s)}, \quad (2.87)$$

$$d_t \mathcal{G} = -\hat{\Psi} d_t T + p d_t v + \sum_{a=1}^r \hat{\mu}_a d_t \epsilon_a - \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} d_t \hat{\Phi}_a^{(s)}. \quad (2.88)$$

These extended Gibbs relations yield Maxwell relations between thermodynamic derivatives which are generalized to take nonequilibrium states into account. For example, there holds the relations between generalized potential derivatives

$$\left( \frac{\partial X_a^{(s)}}{\partial \hat{\Phi}_b^{(q)}} \right)_{v, \epsilon, \hat{\Phi}'} = \left( \frac{\partial X_b^{(q)}}{\partial \hat{\Phi}_a^{(s)}} \right)_{v, \epsilon, \hat{\Phi}'}, \quad \text{etc.}, \quad (2.89)$$

which relate a generalized potential  $X_a^{(s)}$  to other generalized potentials as well as other variables—these are examples for generalized Maxwell relations. These derivative relations also serve as symmetry relations between generalized potentials relating one irreversible process to another. Furthermore, there follow from (2.78) the relations between  $\hat{\Psi}$  and intensive variables  $T^{-1}$ ,  $pT^{-1}$ , etc.

$$\begin{aligned}
T^{-1} &= \left( \frac{\partial \widehat{\Psi}}{\partial \mathcal{E}} \right)_{v, c, \hat{\Phi}}, & pT^{-1} &= \left( \frac{\partial \widehat{\Psi}}{\partial v} \right)_{\mathcal{E}, c, \hat{\Phi}}, \\
\widehat{\mu}_a T^{-1} &= \left( \frac{\partial \widehat{\Psi}}{\partial c_a} \right)_{\mathcal{E}, c', \hat{\Phi}}, & X_a^{(s)} T^{-1} &= \left( \frac{\partial \widehat{\Psi}}{\partial \Phi_a^{(s)}} \right)_{\mathcal{E}, c, \hat{\Phi}}.
\end{aligned} \tag{2.90}$$

These derivatives or their analogues can be used to calculate the nonequilibrium contributions to intensive variables from the variables of the tangential manifold  $\mathfrak{T}$ , given the information on  $\widehat{\Psi}$ . We will return to this question in the kinetic theory chapters later. Other forms of generalized Maxwell relations can be obtained from the differential forms presented here in a parallel manner to equilibrium thermodynamics. Furthermore, a theory of thermodynamics of irreversible processes can be formulated on the basis of the differential forms for  $\widehat{\Psi}$ ,  $\mathcal{A}$ ,  $\mathcal{G}$ , or  $\mathcal{H}$ . Since the main objective of this section is not in developing this particular subject, but also for lack of space, we will not pursue it further; see Ref. [6] for more details of the subject. Instead, we would like to discuss the role of hydrodynamics of flow phenomena within the present framework of the thermodynamic theory of irreversible processes acquired.

## 2.5 Generalized Hydrodynamic Equations

The extended Gibbs relations suggest they can be integrated in manifold  $\mathfrak{G}$  and, for example, the calortropy may be expressed in terms of a bilinear form of the variables spanning the thermodynamic manifold  $\mathfrak{P}$  and the tangential manifold  $\mathfrak{T}$ , but such a form tells us little about the materials undergoing irreversible transport processes. To answer these questions it is necessary to examine the generalized hydrodynamic equations, especially, elucidate the kinematic terms  $\mathcal{Z}_a^{(s)}$  and the dissipation terms  $\Lambda_a^{(s)}$  therein more explicitly in terms of material functions as well as the variables of  $\mathfrak{P} \cup \mathfrak{T}$ , and then solve the evolution equations to test against measurements made in experiments on transport processes. The evolution equations (i.e., generalized hydrodynamic equations) so obtained constitute a generalized theory of hydrodynamics. To find them a little more explicitly we may first consider near-equilibrium flow phenomena, for which  $\widehat{\Psi}$  may be quadratic with respect to  $\Phi_a^{(\alpha)}$ . In such cases, the generalized potentials  $X_a^{(s)}$  now are simply proportional to  $\Phi_a^{(s)}$  as suggested by the last relation in (2.90). Phenomenologically, we may write

$$X_a^{(s)} = -g_a^{(s)} \Phi_a^{(s)}, \tag{2.91}$$

where the proportionality coefficients  $g_a^{(s)}$  are scalar functions of  $T, p, c_a$ , but may be independent of  $\Phi_a^{(s)}$  in the leading-order approximation model. However, a phenomenological theory is incapable of predicting explicit forms for  $g_a^{(s)}$ . They may be obtained more explicitly if a molecular theory model is used. For the leading members they are given by

$$g_a^{(1)} = \frac{1}{2p_a}; \quad g_a^{(2)} = \frac{3}{2p_a}; \quad g_a^{(3)} = \frac{1}{Tp_a\widehat{C}_{pa}}; \quad g_a^{(4)} = \frac{1}{\rho_a}, \quad (2.92)$$

where  $\widehat{C}_{pa}$  is the specific heat per unit mass of  $a$  at constant pressure. We will return to (2.91) in later chapters dealing with molecular theories of irreversible processes.

The kinematic term  $\mathcal{Z}_a^{(s)}$  in the generalized hydrodynamic equations should contain, at least, the thermodynamic driving force of the process, and it can be deduced that they should be of the following forms in the near-equilibrium regime of transport processes:

$$\begin{aligned} \mathcal{Z}_a^{(1)} &= -2p_a [\nabla \mathbf{u}]^{(2)}, \quad \mathcal{Z}_a^{(2)} = -p_a d_t \ln(p_a v^{5/3}/c_a), \\ \mathcal{Z}_a^{(3)} &= -Tp_a \widehat{C}_{pa} \nabla \ln T, \quad \mathcal{Z}_a^{(4)} = -p \mathbf{d}_a, \end{aligned} \quad (2.93)$$

where  $\mathbf{d}_a$  is the thermodynamic force for mass diffusion

$$\mathbf{d}_a = \nabla \left( \frac{n_a}{n} \right) + \left( \frac{n_a}{n} - \frac{\rho_a}{\rho} \right) \nabla \ln p + \frac{\rho_a}{p} (\widehat{\mathbf{F}} - \widehat{\mathbf{F}}_a). \quad (2.94)$$

This form implies that mass diffusion can be driven by gradients of concentration and pressure and by the (external) body force. We remark that  $\mathbf{d}_a$  in (2.94) can be recast into the form

$$\mathbf{d}_a = \nabla c_a + \left( \frac{n_a}{n} - \frac{\rho_a}{\rho} \right) \nabla \ln \left[ \left( \frac{n_a}{n} - \frac{\rho_a}{\rho} \right) p \right] + \frac{\rho_a}{p} (\widehat{\mathbf{F}} - \widehat{\mathbf{F}}_a), \quad (2.95)$$

if the mass fraction  $c_a$  is desired for concentrations instead of the mole fraction  $n_a/n$ . The gradients listed in (2.93) are thermodynamic driving forces of the processes in question. Here we remark that the kinematic terms in (2.93) are empirical and gleaned from experimental studies on linear transport processes in fluids [17, 18].

The dissipation terms may be deduced to be proportional to  $\Phi_a^{(s)}$ —for example, on the basis of Rayleigh dissipation principle [55]—in the case of near-equilibrium transport phenomena: for a scalar process

$$\Lambda_a^{(s)} = - \sum_{b=1}^r L_{ab}^{(s)} \Phi_a^{(s)}, \quad (2.96)$$

or for a vector process

$$\Lambda_a^{(s)} = - \sum_{\gamma=3}^4 \sum_{b=1}^r L_{ab}^{(s\gamma)} \Phi_a^{(\gamma)} \quad (s = 3, 4), \quad (2.97)$$

where  $L_{ab}^{(s)}$  are phenomenological coefficients. A scalar process can be coupled to other scalar processes, whereas a vector can be coupled to other vector processes

(e.g., heat and mass diffusions), in a manner consistent with the Curie principle [17]. The phenomenological coefficients are symmetric on account of the generalized Maxwell relations and thus in accord with the Onsager reciprocal relations [29]. Their molecular theory formulas are found in the kinetic theory chapters in this work. Putting the aforementioned forms for  $Z_a^{(s)}$  and  $\Lambda_a^{(s)}$  into the evolution equations for  $\Phi_a^{(s)}$ , we obtain the hydrodynamic equations for near equilibrium phenomena as given below:

$$\rho d_t v = \nabla \cdot \mathbf{u} \text{ or } \frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{u}), \quad (2.98)$$

$$\rho d_t c_a = -\nabla \cdot \mathbf{J}_a, \quad (2.99)$$

$$\rho d_t \mathbf{u} = -\nabla \cdot \mathbf{P} - \rho \hat{\mathbf{F}}, \quad (2.100)$$

$$\rho d_t \mathcal{E} = -\nabla \cdot \mathbf{Q} - \mathbf{P} : \nabla \mathbf{u} + \sum_{a=1}^r \mathbf{J}_a \cdot \hat{\mathbf{F}}_a, \quad (2.101)$$

for the conservation laws and

$$\rho d_t \hat{\Phi}_a^{(1)} = -2p_a [\nabla \mathbf{u}]^{(2)} - \rho \sum_{b=1}^r L_{ab}^{(1)} \hat{\Phi}_a^{(1)}, \quad (2.102)$$

$$\rho d_t \hat{\Phi}_a^{(2)} = -p_a d_t \ln(p_a v^{5/3} / c_a) - \rho \sum_{b=1}^r L_{ab}^{(2)} \hat{\Phi}_a^{(2)}, \quad (2.103)$$

$$\rho d_t \hat{\Phi}_a^{(3)} = -p_a \hat{C}_{pa} \nabla \ln T - \rho \sum_{\gamma=3}^4 \sum_{b=1}^r L_{ab}^{(3\gamma)} \hat{\Phi}_a^{(\gamma)}, \quad (2.104)$$

$$\rho d_t \hat{\Phi}_a^{(4)} = -p \mathbf{d}_a - \rho \sum_{\gamma=3}^4 \sum_{b=1}^r L_{ab}^{(4\gamma)} \hat{\Phi}_a^{(\gamma)}. \quad (2.105)$$

Equations (2.98)–(2.105) are the generalized hydrodynamic equations for linear transport processes. If  $d_t \hat{\Phi}_a^{(s)} = 0$  for all  $s$  and  $a$ , then (2.98)–(2.105) become the Navier–Stokes, Fourier, and Fick’s equations—i.e., the classical hydrodynamic equations [32, 33]—holding near-equilibrium phenomena when viewed from the thermodynamic standpoint. In other words, the conventional hydrodynamics is within the framework of thermodynamics of linear irreversible processes holding near-equilibrium flow phenomena. The evolution equations (2.98)–(2.105) should be subjected to the demand of the laws of thermodynamics according to the formalism described earlier, and we find the second law of thermodynamics require the phenomenological coefficients<sup>18</sup>  $L_{ab}^{(s)}$  or  $L_{ab}^{(s\gamma)}$  must satisfy the inequalities demanded by the second law of thermodynamics—namely, positivity conditions. In this manner,

<sup>18</sup>These phenomenological transport coefficients may be identified with their molecular theory (i.e., kinetic theory) formulas in the forms of collision bracket integrals, which appear in the kinetic theory chapters.

the classical hydrodynamic equations are made consistent with the laws of thermodynamics. Therefore they may be regarded as macroscopic evolution equations within the framework of the laws of thermodynamics.

For a class of nonlinear phenomena—e.g., rheological phenomena or nonlinear flow phenomena subjected to high spatial gradients which are observed, for example, in rarefied gas dynamics or rheology—the dissipation terms  $\Lambda_a^{(s)}$  are no longer linear, but highly nonlinear with respect to  $\Phi_a^{(s)}$  or the thermodynamic gradients—i.e., spatial gradients of variables belonging to manifold  $\mathfrak{T}$ . For example, they may be put into the form

$$\Lambda_a^{(s)} = \sum_{\gamma \geq 1} \sum_{b=1}^r L_{ab}^{(s,\gamma)} \Phi_b^{(\gamma)} \frac{\sinh \kappa}{\kappa}, \quad (2.106)$$

where  $\kappa$  is the square root of a quadratic form in  $\Phi_b^{(\gamma)}$ . This function  $\kappa$  is rather reminiscent of the Rayleigh dissipation function,<sup>19</sup> since it is quadratic with respect to  $\Phi_a^{(\alpha)}$ , which may be regarded as a generalized velocity:

$$\kappa = \sqrt{\sum_{\alpha, \gamma \geq 1} \sum_{a,b=1}^r \Phi_a^{(\alpha)} L_{ab}^{(\alpha,\gamma)} \Phi_b^{(\gamma)}}. \quad (2.107)$$

It should be noted that this form of the dissipation functions can be deduced if the calortropy production  $\sigma_{\text{ent}}$  is approximated by the formula

$$\sigma_c = k_B g^{-1} \kappa \sinh \kappa, \quad (2.108)$$

where

$$g = \frac{1}{n^2 d^2} \sqrt{\frac{m}{2k_B T}} \quad (2.109)$$

with  $m$  denoting the mean reduced mass and  $d$  the mean diameter of molecules. The dimension of factor  $g$  is inverse time or the mean intermolecular force range. With the nonlinear dissipation functions given in (2.106) in the hydrodynamic equations (2.98)–(2.105) numerous nonlinear flow phenomena [19–22] observed in the laboratory have been successfully accounted for in the fields of rheology, semiconductor carrier mobility, rarefied gas flows, and heat conduction in plasmas. Therefore, such generalized hydrodynamic equations are rather practical forms for numerous hydrodynamic phenomena observed in the laboratory conditions. In Chap. 9, we will return to some of examples of applications of the generalized hydrodynamic equations, linear and quasilinear, presented in this section.

---

<sup>19</sup>Originally, the Rayleigh dissipation function was quadratic with respect to velocities. Here we are generalizing not only the original definition for fluxes (velocities) to  $\Phi_a^{(s)}$ , but also the flux dependence of the dissipation function to a highly nonlinear form from a quadratic function of velocities.

## 2.6 Irreversible Thermodynamics of Steady States

Experiments are often performed in steady-state conditions where fluxes remain stationary in time. Such examples [56, 57] can be seen in many transport processes in fluids and solids, and rheological experiments [19], transport phenomena in semiconductors [20], rarefied gas dynamics [21], etc. In fact, linear irreversible thermodynamics discussed in the previous section can deal with such situations in more simpler and definitive fashions. Therefore, it is useful to consider them and relate the present general theory to such special cases. Here we will examine cases in which the nonconserved variables do not change in time in the frame of reference moving with the fluid velocity. That is, we consider the cases of

$$d_t \hat{\Phi}_a^{(s)} = 0.$$

However, the kinematic and dissipation terms in the evolution equation for  $\hat{\Phi}_a^{(s)}$  can be linear or nonlinear. We will separately consider the case of linear evolution equations for  $\hat{\Phi}_a^{(s)}$  in the next section.

If  $d_t \hat{\Phi}_a^{(s)} = 0$  for all  $s$  and  $a$ , then the extended Gibbs relation for calortropy becomes

$$d_t \hat{\Psi}_{ss} = T^{-1} \left( d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a d_t \epsilon_a \right), \quad (2.110)$$

where the subscript ss denotes the steady state of the nonconserved variables. Henceforth in this section we use the term steady state to mean the steady state of nonconserved variables. Since the differential form on the right-hand side of (2.110) is simply the same as the local equilibrium entropy change, the calortropy at the steady state coincides with the local equilibrium entropy  $\mathcal{S}_e$  given by the same differential form as in (2.82) except for the meanings of the coefficients  $T$ ,  $p$ , and  $\hat{\mu}_a$  to the differentials since they may depend on  $\hat{\Phi}_a^{(s)}$ :

$$d_t \hat{\Psi}_{ss} = d_t \mathcal{S}_e = T^{-1} \left( d_t \mathcal{E} + p d_t v - \sum_{a=1}^r \hat{\mu}_a d_t \epsilon_a \right). \quad (2.111)$$

In this case, the local equilibrium hypothesis, which is usually made in the linear theory of irreversible thermodynamics [17, 18, 30, 31] is a perfectly acceptable differential form for a thermodynamic description of the process in hand, provided that the steady-state evolution equations for  $\hat{\Phi}_a^{(s)}$  are given by<sup>20</sup>

---

<sup>20</sup>In actual applications of the present theory, the nonconserved variables require closure relations. For example, in the case of single-component fluids it will be found useful to take the first thirteen moments (i.e., density, pressure, three velocity components, three components of heat flux, two normal stresses, three components of shear stress) for macroscopic variables and then assume the closure relations  $\psi_a^{(1)} = \psi_a^{(3)} = 0$ . Applications discussed in a later chapter take this kind of closure relations.

$$-\nabla \cdot \boldsymbol{\psi}_a^{(s)} + \mathcal{Z}_a^{(s)} + \Lambda_a^{(s)} = 0 \quad (2.112)$$

for all  $s$  and  $a$ . See the examples for the kinematic and dissipation terms which have been already given in the previous section. In fact, the steady-state evolution equations (2.112) may give rise to nonlinear thermodynamic force–flux relations, namely, the constitutive equations for fluxes whose solutions yield nonlinear transport coefficients, if the dissipation terms are nonlinear with respect to  $\Phi_a^{(s)}$ . At this juncture of discussion, we would like to remark that the nature of (2.111) can be put in a better light if (2.111) is compared with (2.61) which was seen to hold for a cyclic process where the initial and final states  $A$  and  $B$  are embedded in the equilibrium part of the thermodynamic space. The embedded equilibrium states may be interpreted to be steady states which are characterized by (2.111) and (2.112).

The solutions of (2.112) give  $\Phi_a^{(s)}$ , for example, the stress tensor, heat flux, and diffusion fluxes, etc. as nonlinear functions of thermodynamic forces, temperature, density, etc.:

$$\mathbf{P} = \sum_{a=1}^r \mathbf{P}_a = F_p(T, \rho | \nabla \mathbf{u}, \nabla \ln T, \dots), \quad (2.113)$$

$$\mathbf{Q} = \sum_{a=1}^r \mathbf{Q}_a = F_q(T, \rho | \nabla \mathbf{u}, \nabla \ln T, \dots), \quad (2.114)$$

$$\mathbf{J}_a = F_a(T, \rho | \nabla \mathbf{u}, \nabla \ln T, \dots) \quad (1 \leq a \leq r), \quad (2.115)$$

and in general

$$\Phi_a^{(s)} = F_{sa}(T, \rho | \nabla \mathbf{u}, \nabla \ln T, \dots). \quad (2.116)$$

The functions  $F_p$ ,  $F_q$ , and  $F_a$  are generally nonlinear tensor or vector functions of thermodynamic forces,  $\nabla \mathbf{u}$ ,  $\nabla \ln T$ , and  $(\nabla \hat{\mu}_a - \hat{\mathbf{F}}_a)$ , owing to the fact that the constitutive equations (2.112) are generally nonlinear with respect to the nonconserved variables or the thermodynamic forces. On substitution of, for example, (2.113)–(2.115) into the conservation laws (2.24)–(2.26), we obtain hydrodynamic equations which generalize the classical hydrodynamic equations such as the Navier–Stokes, Fourier, and Fick equations [32, 33]. It must be noted that in the present theory the nonlinear steady-state constitutive equations (2.112) still conform to the second law of thermodynamics since they satisfy the inequality  $\Xi_{\text{cal}} \geq 0$  demanded by the second law of thermodynamics.

The deduction made here from the general theory, therefore, shows that the theory of nonlinear steady-state irreversible phenomena can be put within the framework of the present extended theory of irreversible thermodynamics in a form fully consistent with the second law of thermodynamics. If the theory for steady-state irreversible phenomena for nonlinear processes were formulated on the basis of the local equilibrium hypothesis as usually is the case in the literature on linear irreversible thermodynamics [17, 18, 56], then the form for the entropy production would not be obvious and the second law of thermodynamics would not play a role in determining

the forms for the constitutive equations for fluxes in contrast to the present theory. Some examples for application of steady-state irreversible phenomena are discussed in Refs. [6, 45, 46].

Finally, we point out that the steady-state description will be appropriate for non-conserved variables if they change on faster time scales than the conserved variables so that on the time scale of interest for the conserved variables the nonconserved variables have already relaxed to their steady-state values. There are many such situations realizable in laboratory experiments, and for such situations the steady-state theory with nonlinear constitutive equations can be sufficient. As a matter of fact, such steady-state constitutive equations coincide with those in the adiabatic approximation as will be seen later in this work, for example, Chap. 3.

The case of steady linear irreversible processes has been already discussed in the previous section, and they give rise to the traditional Navier–Stokes–Fourier hydrodynamics. Therefore there is little to add here about its relation to the linear irreversible thermodynamics.

## 2.7 Inclusion of Chemical Reactions

We now would like to take chemical reactions into consideration. Let us denote by  $R_l$  the rate of reaction  $l$ , and by  $\nu_{al}$  the associated stoichiometric coefficient times the mass of species  $a$ . This stoichiometric coefficient is counted positive for the products and negative for the reactants. In this convention the chemical reactions may be written in the form

$$\sum_{a=1}^r \nu_{al} B_a = 0, \quad (2.117)$$

where  $B_a$  denotes chemical species  $a$ . There are  $m$  chemical reactions:  $m \geq l \geq 1$ , and  $r$  chemical species are involved in the reactions. The presence of chemical reactions requires a modification of the mass fraction balance equations, whereas other macroscopic evolution equations retain the same form as (2.34) although the dissipation terms may contain reactive contributions, but they do not have to be written out explicitly for our purpose here. The mass fraction balance equation now reads

$$\rho d_t c_a = -\nabla \cdot \mathbf{J}_a + \sum_{l=1}^m \nu_{al} R_l. \quad (2.118)$$

The calortropy balance equation remains invariant to chemical reactions. Let us define the affinity  $A_l$  by the expression

$$A_l = \sum_{a=1}^r \nu_{al} \hat{\mu}_a. \quad (2.119)$$

The presence of chemical reactions then requires the following modification of Proposition 4:

**Proposition 4c** *For the system where there are  $m$  chemical reactions  $\sum_a^r \nu_{al} B_a = 0$  ( $m \geq l \geq 1$ ) the calortropy flux  $\mathbf{J}_c := \mathbf{Q}^c/T$  is given by the bilinear form of the intensive variables  $T^{-1}$ ,  $\hat{\mu}_a T^{-1}$ , and  $X_a^{(s)} T^{-1}$  ( $s \geq 1$ ,  $1 \leq a \leq r$ ) paired, respectively, with  $\mathbf{Q}_a$ ,  $\mathbf{J}_a$ , and  $\psi_a^{(s)}$  (flux of  $\Phi_a^{(s)}$ ) as follows:*

$$\mathbf{J}_c := \sum_{a=1}^r \frac{\mathbf{Q}_a^c}{T} = \sum_{a=1}^r T^{-1} (\mathbf{Q}_a - \hat{\mu}_a \mathbf{J}_a + \sum_{s \geq 1} X_a^{(s)} \psi_a^{(s)}), \quad (2.120)$$

and the calortropy production  $\Xi_{cal}$  is given by the bilinear form

$$\begin{aligned} \Xi_{cal} &:= \rho \hat{\Xi}_{cal} \\ &= -T^{-1} \sum_{a=1}^r [(\mathbf{P}_a - p_a \boldsymbol{\delta}) : \nabla \mathbf{u} + \mathbf{Q}_a^c \cdot \nabla \ln T \\ &\quad + \mathbf{J}_a \cdot (\nabla \hat{\mu}_a - \mathbf{F}_a) + \sum_{l=1}^m \nu_{al} \hat{\mu}_a R_l - \sum_{s \geq 1} \psi_a^{(s)} \cdot \nabla X_a^{(s)}] \\ &\quad + T^{-1} \sum_{a=1}^r \sum_{s \geq 1} X_a^{(s)} (\mathcal{Z}_a^{(s)} + \Lambda_a^{(s)}). \end{aligned} \quad (2.121)$$

Here contributions to  $\Lambda_a^{(s)}$  by the chemical reactions are implicit. By the second law of thermodynamics,  $\Xi_{cal} \geq 0$  always, the equality holding for reversible processes only.

Therefore, the calortropy flux formally remains the same as for nonreactive systems, but the calortropy production is modified by the presence of a term given below, since there is an energy dissipation term which arises from chemical reactions present:

$$\Xi_{cal}^{\text{chem}} := -T^{-1} \sum_{a=1}^r \sum_{l=1}^m \nu_{al} \hat{\mu}_a R_l = -T^{-1} \sum_{l=1}^m A_l R_l. \quad (2.122)$$

It is a familiar looking form for the entropy production in the linear theory [17] of irreversible processes. We emphasize that this additional term is not arbitrary, but a consequence of the modification of the mass fraction balance equations which is necessitated by the chemical reactions. When used in the calortropy balance equation, Proposition 4c gives rise to the same differential form for  $d_t \hat{\Psi}$  as (2.78) in Theorem 1. Therefore, the differential form for  $d_t \hat{\Psi}$  remains invariant in its formal structure, but the meaning of the chemical potentials changes since they now get contributions from the chemical reactions and the mass fractions become nonconserved variables joining the ranks of  $\Phi_a^{(s)}$  ( $s \geq 1$ ) whose evolution equations are also modified in

the dissipation terms. Thus hydrodynamic equations are modified, but the basic thermodynamic structure of the theory remains formally the same whether the fluid is reactive or not. If other irreversible processes, such as shearing, heat flow, and so on, are absent and chemical reactions are the only irreversible process in the system, then  $d_t \widehat{\Psi}$  becomes the local equilibrium formula for  $d_t \mathcal{S}_e$ . The local equilibrium formula also arises if the nonconserved variables are at the steady state in the moving frame of reference.

## 2.8 Inclusion of Volume Transport

In the traditional approach to continuum mechanics [16] the volume variable is described by the specific volume of the fluid, which is given by the inverse of density (or mass density in the present phenomenological theory). Recently, it has been pointed out that such a description would not yield a sufficiently general description of fluid behavior [58]. In the recent kinetic theory investigation in Ref. [8] it is shown that the specific volume is not the most appropriate quantity to describe the molar volume of a fluid, but in its place the notion of Voronoi volume [59] may be used, which may be regarded a free volume available to particles at a given state of the fluid or more generally matter. The mean Voronoi volume is a nonconserved variable, and obeys a constitutive equation with a dissipative term like other nonconserved variables we have taken into consideration in this chapter. Thus recognizing the mean Voronoi volume as a nonconserved variable on the same footing as heat flux, stress tensor, diffusion flux, etc. we extend the manifold of nonconserved variables  $\widehat{\Phi}_a^{(s)}$  to include the mean Voronoi volume, which we denote by  $\widehat{\Phi}_a^{(0)}$ , so that the set of nonconserved variables now reads  $\widehat{\Phi}_a^{(s)}$  ( $s \geq 0$ ;  $1 \leq a \leq r$ ). This requires a slight modification of Proposition 2 to the following:

**Proposition 2v** *The nonconserved variables  $\widehat{\Phi}_a^{(s)}$  ( $s \geq 0$ ;  $1 \leq a \leq r$ ) including the mean Voronoi volume obey the evolution equation*

$$\rho d_t \widehat{\Phi}_a^{(s)} = -\nabla \cdot \psi_a^{(s)} + \mathcal{Z}_a^{(s)} + \Lambda_a^{(s)}, \quad (2.123)$$

where  $\psi_a^{(s)}$  is the flux of  $\Phi_a^{(s)}$ ,  $\mathcal{Z}_a^{(s)}$  is called the kinematic term, which contains, at least, a term driving the process  $\Phi_a^{(s)}$  among other terms that nonlinearly depend on nonconserved variables and gradients of the conserved variables, and  $\Lambda_a^{(s)}$  is called the dissipation term which is responsible for energy dissipation arising from the process  $\Phi_a^{(s)}$ . The dissipation term may also be a nonlinear function of variables of manifold  $\mathfrak{P}$  as well as its tangent manifold.

Except for the fact that the set includes  $\widehat{\Phi}_a^{(0)}$  in addition to  $\widehat{\Phi}_a^{(s)}$  ( $s \geq 1$ ;  $1 \leq a \leq r$ ), that is, the range of  $\widehat{\Phi}_a^{(s)}$  should be  $s \geq 0$  and  $1 \leq a \leq r$ , Proposition 2v remains the same as Proposition 2. Of course, the evolution equation for  $\widehat{\Phi}_a^{(0)}$  and its higher-order homologues must be added to the evolution equation set for the nonconserved variables.

The form for the evolution equation for  $\widehat{\Phi}_a^{(0)}$  is not sufficiently known phenomenologically, and it is one of the aims of this work to establish it with the help of a statistical mechanical theory as will be shown in later chapters. In any case, with so modified Proposition 2 a phenomenological theory of irreversible processes in the presence of volume transport phenomena is now appropriately formulated such that it is thermodynamically consistent. The inclusion of volume transport phenomena in hydrodynamic description of flows significantly generalizes the classical hydrodynamic theory and widens our perspective toward the subject.

## 2.9 Concluding Remarks

Theory of thermodynamics is based on empirical observations of natural phenomena in macroscopic material systems in nature and laboratory. Such observations and experiences, stretching over millennia and ever made more quantitative with the progress of time, have crystallized to a set of laws axiomatic in their nature, which constitutes the laws of thermodynamic science and which all branches of macroscopic physics in matter believed to conform to and obey. Here in this chapter we have presented a summary of the subject matter in a form to cover as widely as possible according to the author's point of view on linear and nonlinear irreversible phenomena and their study in the past. In this work, the representations of the first and second laws of thermodynamics are presented as a pair of exact differentials in the Gibbs manifold  $\mathfrak{G} = \mathfrak{P} \cup \mathfrak{T} \cup \Psi$ , which includes nonequilibrium fluxes among the variables spanning the manifold of variables. Therefore the dimension of  $\mathfrak{G}$  is as large as necessary for properly describing the irreversible processes in question. The aforementioned exact differential pairs can, therefore, be expressed in a pair of circular integrals in  $\mathfrak{G}$ , if the irreversible processes are made cyclic. Moreover, the exact differential forms are on the support of generalized hydrodynamic equations attendant on the irreversible transport processes undergoing in the macroscopic material system in hand. The generalized hydrodynamic equations are in conformation with the laws of thermodynamics. Therefore they are said to be thermodynamically consistent.

The generalized hydrodynamic equations attending the differential forms mentioned tend to the classical hydrodynamic equations of Navier, Stokes, Fourier, and Fick, as the system approaches the vicinity of thermodynamic equilibrium and, therefore, the transport processes becomes linear with respect to applied thermodynamic spatial gradients or forces. In this limit the theory of irreversible thermodynamics presented tends to the thermodynamics of linear irreversible processes. Therefore the generalized hydrodynamics extends the classical hydrodynamics to nonlinear transport processes.

The present theory of irreversible processes and the generalized hydrodynamic equations are also extended to include volume transport phenomena, which the conventional hydrodynamic theory and the previous version of generalized hydrodynamic equations and theory of irreversible thermodynamics by the present author

did not take into account. In this sense, the present version is a revision of the previous theory of irreversible thermodynamics by the present author, which is intended to cover a wider range of irreversible processes.

The theory of irreversible thermodynamics presented in this chapter serves a guiding light for formulating kinetic theories of irreversible nonlinear macroscopic processes in gases and liquids in later chapters in conformation to the laws of thermodynamics. This assures us to formulate theories of transport processes, linear or nonlinear, and nonequilibrium statistical thermodynamics in gases and liquids in complete consistency with the laws of thermodynamics.

## References

1. J.G. Kirkwood, I. Oppenheim, *Chemical Thermodynamics* (McGraw-Hill, New York, 1961)
2. H.B. Callen, *Thermodynamics* (Wiley, New York, 1960)
3. B.C. Eu, M. Al-Ghoul, *Chemical Thermodynamics* (World Scientific, Singapore, 2010)
4. J.F. Schooley (ed.) in chief, *Temperature, Parts 1 and 2*, vol. 5 (American Institute of Physics, New York, 1982)
5. G.N. Lewis, M. Randall, *Thermodynamics* (McGraw-Hill, New York, 1961)
6. B.C. Eu, *Generalized Thermodynamics* (Kluwer, Dordrecht, 2002)
7. B.C. Eu, *J. Chem. Phys.* **129**, 094502, 134509 (2008)
8. J.S. Hunjan, B.C. Eu, *J. Chem. Phys.* **132**, 134510 (2010)
9. Y. Elkana, *The Discovery of Energy* (Hutchinson Educational, London, 1974)
10. R.B. Lindsay (ed.), *Energy: Historical Development of the Concept* (Dowden, Hutchinson, and Ross, Stroudsburg, PA, 1975)
11. S.G. Brush, *The Kind of Motion We Call Heat*, vols. 1, 2 (North-Holland, Amsterdam, 1976)
12. R. Clausius, *Ann. Phys.* **125**, 313 (1965). (Leipzig)
13. M. Planck, *Thermodynamics* (Dover, New York, 1945)
14. B.C. Eu, *J. Phys. Chem.* **103**, 8583 (1999)
15. B.C. Eu, *J. Phys. Chem.* **91**, 1184 (1987)
16. A.C. Eringen (ed.), *Continuum Physics*, vol. 2 (Academic, New York, 1975)
17. For example, see P. Mazur, S.R. de Groot, *Nonequilibrium Thermodynamics* (North-Holland, Amsterdam, 1962)
18. R. Haase, *Thermodynamics of Irreversible Processes* (Dover, New York, 1969)
19. H.A. Barnes, J.F. Hutton, K. Walters, *An Introduction to Rheology* (Elsevier, Amsterdam, 1989). For some examples of applications to *Rheological Phenomena* see Chapter 14 of Ref. [46]
20. D.K. Ferry, S.M. Goodnick, *Transport in Nanostructure* (Cambridge University Press, London, 1997). C.S. Ting (ed.), *Physics of Hot Electron Transport in Semiconductors* (World Scientific, Singapore, 1992)
21. For rarefied gas dynamic phenomena, see M. N. Kogan, *Rarefied Gas Dynamics* (Plenum, New York, 1967). Some examples for application of the present line of theory are also discussed in B.C. Eu, *Nonequilibrium Statistical Mechanics* (Kluwer, Dordrecht, 1998)
22. E.A. Mason, E.W. McDaniel, *Transport Properties of Ions in Gases* (Wiley, New York, 1988). J.M.G. Barthel, H. Krienke, W. Kunz, *Physical Chemistry of Electrolyte Solutions* (Springer, New York, 1998)
23. J.C. Maxwell, *Philos. Trans. R. Soc. Lond.* **157**, 49 (1867)
24. S. Chapman, *Proc. R. Soc. Lond. A* **93**, 1 (1916–17)
25. J. Kestin (ed.), *The Second Law of Thermodynamics* (Dowden, Hutchinson & Ross, Stroudsburg, PA, 1976)
26. S. Carnot, *Refléxions sur la Puissance Motrice du Feu et sur les Machines* (Bachelier, Paris, 1824). English translation (Peter Smith, Gloucester, MA, 1977)

27. R. Clausius, *Philos. Mag.* (Ser. 4) **2**, 1, 102 (1851). **24**, 81, 201 (1862)
28. L. Kelvin (W. Thomson), *Mathematical and Physical Papers of William Thomson*, vol. 1 (Cambridge University Press, Cambridge, 1882), pp. 100–106, 113–140, 174–200
29. L. Onsager, *Phys. Rev.* **37**, 405 (1931). **38**, 2265 (1931)
30. J. Meixner, *Ann. Phys.* (5) **39**, 333 (1941). J. Meixner, H.G. Reik, Thermodynamik der irreversiblen Prozesses, in *Handbuch der Physik*, vol. 3, ed. by S. Flügge (Springer, Berlin, 1959)
31. I. Prigogine, *Étude Thermodynamiques des Phénomènes Irreversible* (Desor, Liège, 1947). *Thermodynamics of Irreversible Processes* (Interscience, New York, 1967)
32. L.D. Landau, E.M. Lifshitz, *Fluid Mechanics* (Pergamon, London, 1959)
33. G.K. Batchelor, *Fluid Dynamics* (Cambridge, London, 1967)
34. J. Meixner, On the foundation of thermodynamics of processes, in *A Critical Review of Thermodynamics*. E.B. Stuart, B. Gal-Or, A.J. Brainard (eds.) (Mono Book, Baltimore, 1970), p. 544. *Rheol. Acta* **12**, 465 (1973)
35. B.C. Eu, *J. Chem. Phys.* **73**, 2958 (1980)
36. R. Nettleton, *Phys. Fluids* **4**, 1488 (1961)
37. I. Müller, *Z. Phys.* **198**, 329 (1967)
38. G. Lebon, *Bull. Acad. R. Belg. Cl. Sci.* **64**, 456 (1978)
39. G. Lebon, D. Jou, J. Casas-Vazquez, *J. Phys. A Math. Gen.* **13**, 275 (1980)
40. L.S. Garcia-Colín, G.J. Fuentes y Matinez, *J. Stat. Phys.* **29**, 387 (1982)
41. D. Jou, J. Casas-Vazquez, G. Lebon, *Extended Irreversible Thermodynamics* (Springer, Berlin, 1993)
42. I. Müller, T. Ruggeri, *Extended Thermodynamics* (Springer, Berlin, 1993)
43. L.S. Garcia-Colín, M. Lopez de Haro, R.F. Rodriguez, J. Casas-Vazquez, D. Jou, *J. Stat. Phys.* **37**, 465 (1984)
44. R.M. Velasco, L.S. Garcia-Colín, *J. Non-Equil. Thermodyn.* **18**, 157 (1993)
45. B.C. Eu, *Kinetic Theory and Irreversible Thermodynamics* (Wiley, New York, 1992)
46. B.C. Eu, *Nonequilibrium Statistical Mechanics* (Kluwer, Dordrecht, 1998)
47. B.C. Eu, *Chem. Phys. Lett.* **143**, 65 (1988)
48. W.T. Grandy, *Phys. Rep.* **62**, 175 (1980)
49. B.C. Eu, *Phys. Rev. E* **51**, 768 (1995)
50. I.N. Sneddon, *Elements of Partial Differential Equations* (McGraw-Hill, New York, 1957)
51. D.G.B. Edelen, *Applied Exterior Calculus* (Wiley, New York, 1985)
52. C. von Westenholz, *Differential Forms in Mathematical Physics* (North-Holland, Amsterdam, 1978)
53. H. Flanders, *Differential Forms* (Academic, New York, 1963)
54. M. Chen, B.C. Eu, *J. Math. Phys.* **34**, 3012 (1993). For mathematical aspects of differential forms and their integrability see Refs. [51, 52, 53] quoted above
55. L. Rayleigh, *Theory of Sound* (Dover, New York, 1949)
56. P. Glansdorff, I. Prigogine, *Thermodynamic Theory of Structure, Stability, and Fluctuations* (Wiley, New York, 1971)
57. I. Procaccia, D. Ronis, M.A. Collins, J. Ross, I. Oppenheim, *Phys. Rev. A* **19**, 1290 (1979)
58. H. Brenner, *Phys. A* **349**, 11 (2005). **349**, 60 (2005). H. Brenner, *Phys. Rev. E* **70**, 061201 (2004)
59. G.F. Voronoi, *Zeit. Reine Angew. Math.* **34**, 198 (1908)

Kinetic Theory of Nonequilibrium Ensembles, Irreversible  
Thermodynamics, and Generalized Hydrodynamics  
Volume 1. Nonrelativistic Theories

Eu, B.C.

2016, XIV, 603 p. 15 illus., 4 illus. in color., Hardcover

ISBN: 978-3-319-41146-0