CHAPTER 2

Multiscale Equilibrium and Nonequilibrium Thermodynamics in Chemical Engineering

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Contents

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Advances in Chemical Engineering, Volume 39
ISSN: 0065-2377, DOI 10.1016/S0065-2377(10)39002-8

Abstract An important challenge brought to chemical engineering by new emerging technologies, in particular then by nano- and biotechnologies, is to deal with complex systems that cannot be dealt with and cannot be fully understood on a single scale. This review introduces a unifying thermodynamic framework for multiscale investigations of complex macroscopic systems.

1. INTRODUCTION

Recent interest of chemical engineers in combining nano, micro, and macro scales (called nano-engineering and bioengineering) provides a renewed motivation for investigating macroscopic systems simultaneously on several different levels (scales) of description. Such investigation needs a setting that unifies levels such as the level of classical thermodynamics, the level of hydrodynamics, and the level of particle theory. While each level has its own unique flavor, an investigation of the relations among the levels shows universal features. These features are then suggested to constitute the framework for multiscale investigations. We argue that the framework obtained in this way is in fact a framework of an abstractly formulated thermodynamics. The path leading to such abstract theory begins with the Gibbs formulation of classical thermodynamics (see, e.g., Callen, 1960). The first step toward more microscopic (mesoscopic) analysis is made by recognizing *the maximum entropy principle* as an essence of thermodynamics and as the universal passage to more macroscopic levels (Jaynes, 1967; Jaynes et al., 1978). The subsequent step is a realization that minimization of a convex function subjected to constraints is, from the mathematical point of view, a *Legendre transformation* and that the natural mathematical setting for Legendre transformations is *contact geometry* (Arnold, 1989; Hermann, 1984). Finally, in this geometrical environment we introduce the time evolution representing the approach to a more macroscopic level of description as a continuous sequence of Legendre transformation. This is then the passage from equilibrium to nonequilibrium thermodynamics in the setting of multiscale analysis.

The viewpoint sketched above has been so far developed and applied mainly in the context of mechanics and thermodynamics of complex fluids (Grmela, 2009 and references cited therein, also Section 3.1.6 of this review). The coupling between macroscopic (hydrodynamic) flow behavior and the behavior of a microstructure (e.g., macromolecules in polymeric fluids or suspended particles or membranes in various types in suspensions) is naturally expressed in the multiscale setting. In this review we shall include in illustrations also multicomponent systems undergoing chemical reactions. The motivation for this type of applications comes from three sources:

i. Importance of such systems in chemical engineering.
ii. Inclusion of multicomponent systems into equilibrium thermodynamic considerations played an important role in arriving at the Gibbs formulation of equilibrium thermodynamics. In fact, the extension from viewing a system (e.g., air) as a single component system to viewing it as a multicomponent system (e.g., viewing air as a mixture of several gases) can well be the first example of the multiscale analysis (recall, e.g., the so-called Gibbs paradox arising in such consideration).
iii. Chemically reacting systems have also played an important role in the development of nonequilibrium thermodynamics. One of the key new concepts introduced in nonequilibrium thermodynamics is the concept of a *thermodynamic force* driving macroscopic systems to equilibrium. Chemical affinity is one of the first and one of the most important examples of such force. Having identified the thermodynamic forces, the next step that has to be made in nonequilibrium thermodynamics is to construct with them the time evolution agreeing with the observed approach to equilibrium. The usual linear (Onsager) construction is not satisfactory in chemical kinetics since it does not lead to the mass action law that generates the well-established governing equations of chemical kinetic. This difficulty has certainly been one of the reasons for a rather low standing of nonequilibrium thermodynamics in chemical kinetics in particular and in chemical engineering in general. But this apparent difficulty is not really a difficulty at all. It can be overcome by a simple mathematical construction that does not require any additional physical insight and that has moreover been suggested long time ago by Marcelin and de Donder in their viewpoint of chemical kinetics (de Donder et al. 1936; Feinberg, 1972; Gorban and Karlin, 2003, 2005). As we shall see below (Section 3.1.2), the formulation of chemical kinetics that appears naturally in multiscale nonequilibrium thermodynamics does not only include the mass action law as a particular case but it extends it to systems with complex equilibrium behavior and to more microscopic levels.

The review is organized as follows: In Section 2 we present the multiscale equilibrium thermodynamics in the setting of contact geometry. The time evolution (multiscale nonequilibrium thermodynamics) representing approach of a mesoscopic level L_{meso1} to the level of equilibrium thermodynamics L_{eth} is discussed in Section 3. A generalization in which the level L_{eth} is replaced by another mesoscopic level L_{meso2} is considered in Section 4. The notion of multiscale thermodynamics of systems arises in the analysis of this type of time evolution.

2. MULTISCALE EQUILIBRIUM THERMODYNAMICS

In this section we limit ourselves to equilibrium. The time evolution that is absent in this section will be taken into consideration in the next two sections. We begin the equilibrium analysis with classical equilibrium thermodynamics of a one-component system. The classical Gibbs formulation is then put into the setting of contact geometry. In Section 2.2 we extend the set of state variables used in the classical theory and introduce a mesoscopic equilibrium thermodynamics.

2.1 Classical equilibrium thermodynamics

The variables characterizing complete states at equilibrium (we shall use hereafter the symbol y to denote them) are

$$y = (e,\ n) \tag{1}$$

where (e,n) are respectively the energy and the number of moles per unit volume. The two-dimensional space with y as its elements will be denoted by the symbol N.

The fundamental thermodynamic relation is a function $N \to \mathbb{R}$; $(e, n) \mapsto s(e, n)$, where s denotes entropy per unit volume. The function $s(e,n)$ as well as all other functions introduced below are assumed to be sufficiently regular so that the operations made with them are well defined. We can see the fundamental thermodynamic relation $s = s(e,n)$ geometrically (as Gibbs did, see Gibbs, 1984) as a two-dimensional manifold, called a Gibbs manifold, imbedded in the three-dimensional space with coordinates (e,n,s) by the mapping: $(e,n) \hookrightarrow (e, n, s(e,n))$.

In view of the importance of Legendre transformations in equilibrium thermodynamics, we shall make, following Hermann (Hermann, 1984), an alternative formulation of the fundamental thermodynamic relation. We introduce a five-dimensional space (we shall use hereafter the symbol **N** to denote it) with coordinates $(e,n,e^{*}\overleftarrow{,n}^{*}\overleftarrow{,s})$ and present the fundamental thermodynamic relation as a two-dimensional manifold imbedded in the five-dimensional space **N** by the mapping

$$y \hookrightarrow \left(y, \frac{\partial s}{\partial y}(y), s(y) \right) \tag{2}$$

We shall call this manifold a Gibbs–Legendre manifold and denote it by the symbol N. The advantage of this formulation is that the space **N** is naturally equipped with 1-form $ds - e^* de - n^* dn$ and this 1-form is preserved in Legendre transformations. In the standard thermodynamic notation, the variables $y^* \overset{\leftarrow}{=} (e^*, n^*)$ are denoted $1/T$, $-\mu/T$, respectively, where T is the temperature and μ the chemical potential. The Legendre transformation of the fundamental thermodynamic relation $s = s(e,n)$ into its dual form $s^* = s^*(e^*, n^*)$, where $s^* - = P/T$, P is the pressure, is made in the following three steps: (i) we introduce thermodynamic potential $\varphi(e,n;e^*,n^*) = -s(e,n) + e^* e + n^* n$; (ii) we solve equations $\partial\varphi/\partial e = 0$, $\partial\varphi/\partial n = 0$, let their solution be $(e_{\mathrm{eth}}(y^*), n_{\mathrm{eth}}(y^*))$; and (iii) $s^*(y^*) = \varphi(e_{\mathrm{eth}}(y^*), n_{\mathrm{eth}}(y^*);\; y^*)$. The Legendre image N^* of the Gibbs–Legendre manifold N is the image of the mapping $y^* \hookrightarrow \left(y^*, \frac{\partial s^*}{\partial y^*}(y^*), s^*(y^*)\right)$.

2.2 Mesoscopic equilibrium thermodynamics

Question: *Where does the fundamental thermodynamic relation* $s = s(y)$ *come from? Given a physical system, what is the fundamental thermodynamic relation representing it in equilibrium thermodynamics?*

We shall give two answers in equilibrium theories and another answer in nonequilibrium theories (discussed in Sections 3 and 4).

Answer 1: *The only way to find the fundamental thermodynamic relation* $s = s(y)$ *inside the classical equilibrium thermodynamics is by making experimental measurements. Results of the measurements are usually presented in Thermodynamic Tables.*

The second answer is found by taking a more microscopic (i.e., more detailed) view, called a mesoscopic view, that we shall now present.

Let the state variables (1) be replaced by a state variable $x \in M$ corresponding to a more detailed (more microscopic) view than the one taken in classical equilibrium thermodynamics. Several examples of x are discussed below in the examples accompanying this section. Following closely Section 2.1, we shall now formulate equilibrium thermodynamics that we shall call a mesoscopic equilibrium thermodynamics.

The mesoscopic fundamental thermodynamic relation is now a function $M \to \mathbb{R}; x \mapsto h(x)$. In order to avoid possible confusion, we use in mesoscopic formulations the symbol h instead of s and call $h(x)$ an eta-function instead of entropy function. In analogy with the geometrical representation of the fundamental thermodynamic relation introduced in Section 2.1, we present the mesoscopic fundamental thermodynamic relation as a manifold (denoted now by the symbol $\mathcal{M}$), imbedded in the space (denoted now by the symbol $\mathbf{M}$) with coordinates (x, x^*, h) as the image of the mapping

$$x \hookrightarrow \left(x, \frac{\partial h}{\partial x}(x), h(x)\right) \tag{3}$$

The 1-form with which $\mathbf{M}$ is naturally equipped is $\mathrm{d}h - x^* \mathrm{d}x$.

Now we want to pass from the fundamental thermodynamic relation $h = h(x)$ in M to the fundamental thermodynamic relation $s = s(y)$ in N. First, we have to know how y is expressed in terms of x. Formally, we introduce

$$y = y(x) \tag{4}$$

Having the fundamental thermodynamic relation $h = h(x)$ and the relation (4), we can pass to the fundamental thermodynamic relation $s = s(y)$. This gives us the second answer:

***Answer* 2**: *The fundamental thermodynamic relation $s = s(y)$ in the space N is inherited from the fundamental thermodynamic relation. $h = h(x)$ in a more microscopic space M and from the relation $y = y(x)$.*

Now we explain how the passage $h(x) \to s(y)$ is made. The passage is a Legendre transformation. In order to provide an appropriate setting to formulate it, we introduce a new space $\mathbf{M}^{\mathbf{N}}$ combining the spaces **M** and **N**. Elements of $\mathbf{M}^{\mathbf{N}}$ have the coordinates (x,y^*,x^*,y,φ). The 1-form with which $\mathbf{M}^{\mathbf{N}}$ is naturally equipped is $\mathrm{d}\varphi - x^*\mathrm{d}x - y\ \mathrm{d}y^*$. The fundamental thermodynamic relation in $\mathbf{M}^{\mathbf{N}}$ that combines the fundamental thermodynamic relation $h = h(x)$ in M and the way $y \in N$ is expressed in terms of $x \in M$ (see (4)) takes now the form

$$\varphi = \varphi(x, y^*) = -h(x) + \langle y^*, y(x)\rangle \tag{5}$$

where $\langle y^*,y(x)\rangle = e^*e(x) + n^*n(x)$. The Gibbs–Legendre manifold (denoted by the symbol $\mathcal{M}^{\mathcal{N}}$) representing it is a manifold imbedded in the space $\mathbf{M}^{\mathbf{N}}$ by the mapping

$$(x,y^*) \hookrightarrow \left(x, y^*, \frac{\partial\varphi}{\partial x}(x,y^*),\ \frac{\partial\varphi}{\partial y^*}(x,y^*),\ \varphi(x,y^*)\right) \tag{6}$$

Let $\mathcal{M}^{\mathcal{N}}|_{x^*=0}$ be the intersection of $\mathcal{M}^{\mathcal{N}}$ with the plane $x^*=0$. We note that its restriction to the plane x is a manifold of the states that we denote $x_{\mathrm{eth}}(y^*)$ and call equilibrium states. These are the states for which φ reaches its extremum if considered as a function of x. We shall denote the manifold of equilibrium states by the symbol M_{eth}. Restriction of $\mathcal{M}^{\mathcal{N}}|_{x^*=0}$ to the plane y is the manifold representing y expressed in terms of x (i.e. the function (4)), and its restriction to the plane (y^*,φ) is the Gibbs–Legendre manifold $\mathcal{N}^*$ representing the dual form $s^* = s^*(y^*)$ of the fundamental thermodynamic relation $s = s(y)$ in N that is implied by the fundamental thermodynamic relation $h = h(x)$ in M. This completes our presentation of the passage $h(x) \to s(y)$.

The setting of contact geometry that we have used in the presentation following Hermann (1984) is very useful at least for three reasons: (i) It puts the calculations involved in thermodynamics on a firm ground. The formulation presented above remains in fact the same as the original Gibbs formulation of thermodynamics except that it naturally incorporates the "Maximum entropy principle" and the Legendre transformations; (ii) It unifies the formulations of equilibrium theories on all levels of description; and (iii) It prepares the setting for investigating the multiscale time evolution (discussed in Sections 3 and 4).

Answer 2 given above invites, of course, another question: Where do the fundamental thermodynamic relation $h = h(x)$ and the relation $y = y(x)$ come from? An attempt to answer this question makes us to climb more and more microscopic levels. The higher we stay on the ladder the more detailed physics enters our discussion of $h = h(x)$ and $y = y(x)$. Moreover, we also note that the higher we are on the ladder, the more of the physics enters into $y = y(x)$ and less into $h = h(x)$. Indeed, on the most macroscopic level, i.e., on the level of classical equilibrium thermodynamics sketched in Section 2.1, we have $s = s(y)$ and $y = y$. All the physics enters the fundamental thermodynamic relation $s = s(y)$, and the relation $y = y$ is, of course, completely universal. On the other hand, on the most microscopic level on which states are characterized by positions and velocities of all ($\sim 10^{23}$) microscopic particles (see more in Section 2.2.3) the fundamental thermodynamic relation $h = h(x)$ is completely universal (it is the Gibbs entropy expressed in terms of the distribution function of all the particles) and all physics (i.e., all the interactions among particles) enters the relation $y = y(x)$.

The geometrical setting for the Legendre transformation $h(x) \rightarrow s(y)$ that has been introduced above is illustrated below on a few examples. A particularly simple illustration (but still containing all the structure) is developed in Section 3.1.1. The other examples presented below in Sections 2.2.1–2.2.5 deal mostly with well-known and well-studied physical systems. The geometrical setting is demonstrated to provide a unified framework for their investigation on all scales.

Before starting to develop the physical illustrations we shall briefly turn to an illustration which does not contain all the structure but it does allow us to make a graphical representation of a part of the geometry described above.

In Figure 1 we illustrate the Gibbs and Gibbs–Legendre manifolds. We take the space M to be one dimensional (i.e., $x \in \mathbb{R}$) and $h(x) = -x \ln x$.

In Figures 2 we illustrate the manifold $\mathcal{M}^{\mathcal{N}}$ and in Figure 3 the manifold $\mathcal{M}^{\mathcal{N}}|_{x^* = 0}$. We take both M and N as one dimensional, $y(x) = x$, and $\varphi(x, y^*) = x \ln x + y^* x$.

2.2.1 Example: equilibrium kinetic theory (ideal gas)

In this illustration we choose

$$x = n(\boldsymbol{r}, \boldsymbol{v}) \tag{7}$$

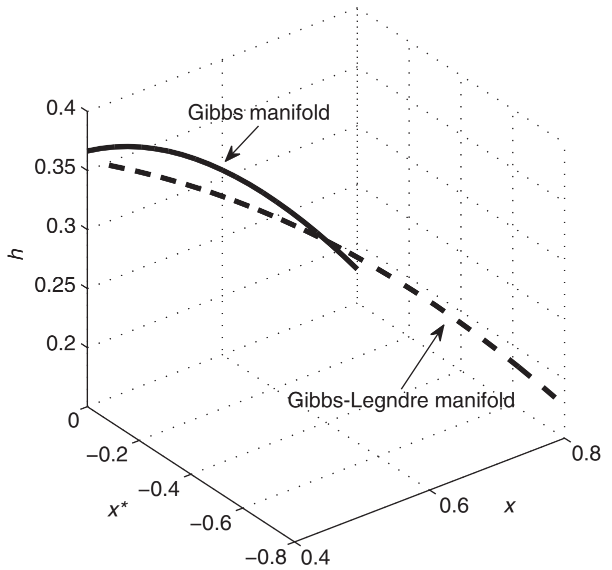

Figure 1 Gibbs and Gibbs–Legendre manifolds for $\varphi(x, y^*) = x \ln\, x + y^* x$.

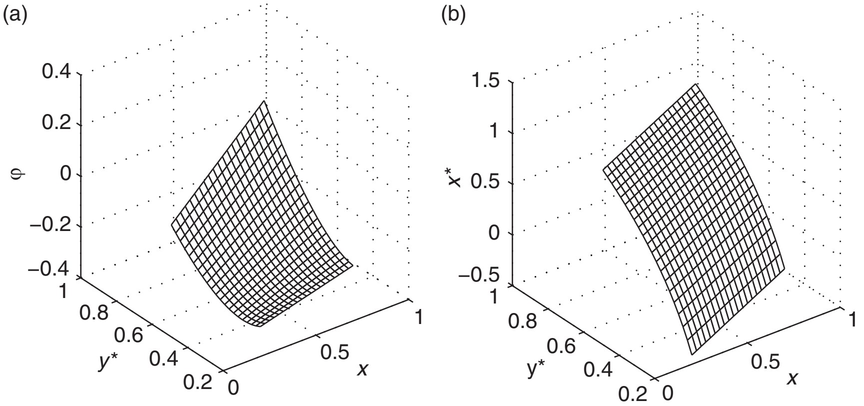

Figure 2 Manifold $\mathcal{M}^N$ for $\varphi(x, y^*) = x \ln\, x + y^* x$.

and y is given in (1). By ($\boldsymbol{r}$, $\boldsymbol{v}$) we denote the position coordinate and momentum of a particle, $n(\boldsymbol{r}, \boldsymbol{v})$ is a one-particle distribution function. The projection (4) is given by

$$
\begin{aligned}
n &= \frac{1}{V} \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{v}\, n(\boldsymbol{r}, \boldsymbol{v}) \\
e &= \frac{1}{V} \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{v}\, \frac{\boldsymbol{v}^2}{2m} n(\boldsymbol{r}, \boldsymbol{v})
\end{aligned}
\tag{8}
$$

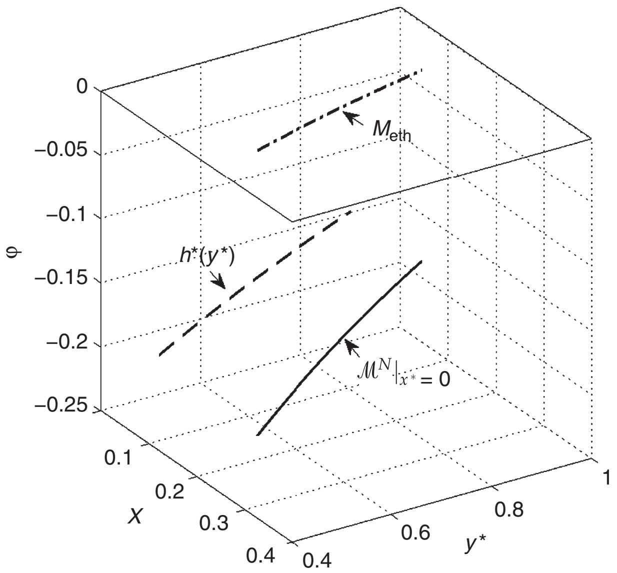

Figure 3 Manifolds $\mathcal{M}^N|_{x^*=0}$, M_{eth}, and the conjugate Gibbs manifold $h^*{=}h^*(y^*)$ for $\varphi(x,y^*) = x\ \ln\ x + y^*x$.

where V is the volume of the fixed region in the position space in which the system under consideration is confined, m is the mass of one particle. The first line in (8) is simply the chosen normalization of the distribution function $n(\boldsymbol{r}, \boldsymbol{v})$; the second line means that the only energy in the gas that we investigate is the kinetic energy of the particles. The particles do not interact among each other. The system under consideration is thus an ideal gas.

Next, we turn to the eta-function $h(x)$. Following Boltzmann, we choose

$$h(n) = -\frac{1}{V}k_{\text{B}}\int \mathrm{d}\boldsymbol{r}\int \mathrm{d}\boldsymbol{v}\ n(\boldsymbol{r},\boldsymbol{v})\ln n(\boldsymbol{r},\boldsymbol{v}) \tag{9}$$

where k_{B} is the Boltzmann constant.

Now, we proceed to make the Legendre transformation leading from $h(n(\boldsymbol{r},\boldsymbol{v}))$ to $s(e,n)$. The thermodynamic potential (5) becomes

$$\begin{aligned}\varphi(n,e^*,n^*) = {}& k_{\text{B}}\frac{1}{V}\int \mathrm{d}\boldsymbol{r}\int \mathrm{d}\boldsymbol{v}\ n(\boldsymbol{r},\boldsymbol{v})\ln n(\boldsymbol{r},\boldsymbol{v}) \\ & + \frac{1}{T}\frac{1}{V}\int \mathrm{d}\boldsymbol{r}\int \mathrm{d}\boldsymbol{v}\frac{\boldsymbol{v}^2}{2m}n(\boldsymbol{r},\boldsymbol{v}) - \frac{\mu}{T}\frac{1}{V}\int \mathrm{d}\boldsymbol{r}\int \mathrm{d}\boldsymbol{v}\ n(\boldsymbol{r},\boldsymbol{v})\end{aligned} \tag{10}$$

where we put $e^*=1/T$ and $n^*=-\mu/T$. The equation $\varphi_n=0$ becomes

$$\frac{1}{V}\left[k_B \ln n(\boldsymbol{r},\boldsymbol{v}) + k_B + \frac{1}{T}\frac{\boldsymbol{v}^2}{2m} - \frac{\mu}{T}\right] = 0 \tag{11}$$

Its solutions, i.e., equilibrium states, are

$$n_{\text{eth}}(\boldsymbol{r},\boldsymbol{v}) = \exp\left(\frac{\mu}{k_B T} - 1\right)\exp\left(-\frac{\boldsymbol{v}^2}{2mk_B T}\right) \tag{12}$$

This is the well-known Maxwell distribution function. If we now evaluate the thermodynamic potential (10) at the equilibrium states (12) we obtain

$$\begin{aligned} s^*\left(\frac{1}{T},\frac{\mu}{T}\right) &= -\frac{P}{k_B T} = -\frac{1}{V}\int d\boldsymbol{r}\int d\boldsymbol{v}\, n_{\text{eth}}(\boldsymbol{r},\boldsymbol{v}) \\ &= \exp\left(\frac{\mu}{k_B T} - 1\right)\left(\frac{m}{2\pi k_B T}\right)^{-3/2} \end{aligned} \tag{13}$$

that is the dual form $s^*=s^*\left(\frac{1}{T}, \frac{\mu}{T}\right)$ of the fundamental thermodynamic relation $s=s(e,n)$. In order to obtain $s=s(e,n)$ itself, we make another Legendre transformation. We introduce $\varphi(y^*,y) = -s^*(y^*) + \langle y, y^*\rangle$, solve $\varphi_{y^*} = 0$, and insert the solutions to $\varphi(y^*,y)$. In this way we arrive at

$$s(e,n) = \text{const.}\, n + Rn \ln \left[\left(\frac{e}{n}\right)^{3/2}\left(\frac{1}{n}\right)\right] \tag{14}$$

where $R = k_B N_{\text{Av}}$, N_{Av} is the Avogadro number. The $P-V-T$ relation $P=nRT$ implied by the fundamental thermodynamic relation (14) is already seen directly in the second equality in (13) (note that $nN_{A\boldsymbol{v}} = \frac{1}{V}\int d\boldsymbol{r}\int d\boldsymbol{v}\, n_{\text{eth}}(\boldsymbol{r},\boldsymbol{v})$).

2.2.2 Example: equilibrium kinetic theory (van der Waals gas)

In this example we keep the same state variables (7) as in the previous example but change the projection (8). The new relation $y=y(x)$ is

$$\begin{aligned} n &= \frac{1}{V}\int d\boldsymbol{r}\int d\boldsymbol{v}\, n(\boldsymbol{r},\boldsymbol{v}) \\ e &= \frac{1}{V}\int d\boldsymbol{r}\int d\boldsymbol{v}\frac{\boldsymbol{v}^2}{2m} n(\boldsymbol{r},\boldsymbol{v}) + \frac{1}{V}\omega_{\text{long}}(\varrho) \end{aligned} \tag{15}$$

where

$$\omega_{\text{long}}(\varrho) = \frac{1}{2}\int d\boldsymbol{r}_1\int d\boldsymbol{r}_2 \varepsilon(|\boldsymbol{r}_1 - \boldsymbol{r}_2|)\varrho(\boldsymbol{r}_1)\varrho(\boldsymbol{r}_2) \tag{16}$$

is a contribution to the energy due to the long-range interactions among the particles; $\varepsilon(|\boldsymbol{r}_1 - \boldsymbol{r}_2|)$ is the potential generating attractive interaction between two particles at the points with coordinates $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. The subscript "*long*" denotes "long range." By the symbol $\varrho(\boldsymbol{r})$ we denote

$$\varrho(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{v}\, n(\boldsymbol{r}, \boldsymbol{v}) \tag{17}$$

The short-range (hard-core type) interactions will be expressed in the following modification of the eta-function:

$$h(n) = -\frac{1}{V} k_{\mathrm{B}} \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{v}\, n(\boldsymbol{r}, \boldsymbol{v}) \ln n\, (\boldsymbol{r}, \boldsymbol{v}) - \frac{1}{V} k_{\mathrm{B}} \omega_{\mathrm{short}}(\varrho) \tag{18}$$

where $\omega_{\mathrm{short}}(\varrho)$ remains at this point unspecified.

The thermodynamic potential $\varphi(n, e^*, n^*)$ becomes now

$$\begin{aligned}\varphi(n, e^*, n^*) = {} & k_{\mathrm{B}} \frac{1}{V} \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{v}\, n(\boldsymbol{r}, \boldsymbol{v}) \ln\, n(\boldsymbol{r}, \boldsymbol{v}) + \frac{1}{V} k_{\mathrm{B}} \omega_{\mathrm{short}}(\varrho) \\ & + \frac{1}{T} \frac{1}{V} \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{v} \frac{\boldsymbol{v}^2}{2m} n(\boldsymbol{r}, \boldsymbol{v}) + \frac{1}{T} \frac{1}{V} \omega_{\mathrm{long}}(\varrho) \\ & - \frac{\mu}{T} \frac{1}{V} \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{v}\, n(\boldsymbol{r}, \boldsymbol{v})\end{aligned} \tag{19}$$

The equation $\varphi_n = 0$ implies

$$\frac{1}{V} \left[k_{\mathrm{B}} \ln n(\boldsymbol{r}, \boldsymbol{v}) + k_{\mathrm{B}} + \frac{1}{T} \frac{\boldsymbol{v}^2}{2m} + k_{\mathrm{B}} \left(\omega_{\mathrm{short}} \right)_{\varrho(\boldsymbol{r})} + \frac{1}{T} \left(\omega_{\mathrm{long}} \right)_{\varrho(\boldsymbol{r})} - \frac{\mu}{T} \right] = 0 \tag{20}$$

Its solutions are

$$n_{\mathrm{eth}}(\boldsymbol{r}, \boldsymbol{v}) = \left(\frac{m}{2\pi k_{\mathrm{B}} T} \right)^{3/2} \varrho_{\mathrm{eth}}(\boldsymbol{r}) \exp \left(-\frac{\boldsymbol{v}^2}{2m k_{\mathrm{B}} T} \right) \tag{21}$$

where the number density $\varrho_{\mathrm{eth}}(\boldsymbol{r})$ is a solution of

$$\ln \varrho(\boldsymbol{r}) + \left(\omega_{\mathrm{short}} \right)_{\varrho(\boldsymbol{r})} + \frac{1}{k_{\mathrm{B}} T} \left(\omega_{\mathrm{long}} \right)_{\varrho(\boldsymbol{r})} + \ln \left(\frac{m}{2\pi k_{\mathrm{B}} T} \right)^{3/2} + 1 - \frac{\mu}{k_{\mathrm{B}} T} = 0 \tag{22}$$

To complete the Legendre transformation we evaluate (19) at (21) and arrive at

$$\begin{aligned}\frac{PV}{k_{\mathrm{B}} T} = {} & \int \mathrm{d}\boldsymbol{r}\, \varrho_{\mathrm{eth}}(\boldsymbol{r}) - \left(\omega_{\mathrm{short}}(\varrho_{\mathrm{eth}}) - \int \mathrm{d}\boldsymbol{r}\, \varrho_{\mathrm{eth}}(\boldsymbol{r}) \left[\left(\omega_{\mathrm{short}} \right)_{\varrho(\boldsymbol{r})} \right]_{\varrho(\boldsymbol{r}) = \varrho_{\mathrm{eth}}(\boldsymbol{r})} \right) \\ & - \frac{1}{k_{\mathrm{B}} T} \left(\omega_{\mathrm{long}}(\varrho_{\mathrm{eth}}) - \int \mathrm{d}\boldsymbol{r}\, \varrho_{\mathrm{eth}}(\boldsymbol{r}) \left[\left(\omega_{\mathrm{long}} \right)_{\varrho(\boldsymbol{r})} \right]_{\varrho(\boldsymbol{r}) = \varrho_{\mathrm{eth}}(\boldsymbol{r})} \right)\end{aligned} \tag{23}$$

In order to make the fundamental thermodynamic relation (23) explicit we have to solve Equation (22). We now proceed to do it. We begin by looking for a solution in the form

$$\varrho_{\text{eth}}(\boldsymbol{r}) = \varrho_{\text{eth}} = \text{const.} = n \tag{24}$$

We note that if we insert this solution into (23) we obtain the well known van der Waals fundamental thermodynamic relation $s(e,n) = \text{const.}\, n + Rn \ln\left[\left(\frac{e}{n} + an\right)^{3/2}\left(\frac{1}{n} - b\right)\right]$ provided $\omega_{\text{short}}(\varrho)$ and $\omega_{\text{long}}(\varrho)$ are chosen as follows:

$$\begin{aligned} \frac{1}{V}\omega_{\text{long}} &= -an^2 \\ \frac{1}{V}\omega_{\text{short}} &= -n\ln(1-bn) \end{aligned} \tag{25}$$

where $a > 0$ and $b > 0$ are the two parameters appearing in the famous van der Waals P–V–T relation $P = \frac{nRT}{1-bn} - an^2$. We note that for $a = 0$ and $b = 0$ both ω_{long} and ω_{short} disappear and the projection (15) becomes the same as (8), which then means that the van der Waals fundamental thermodynamic relation reduces to the fundamental thermodynamic relation (14) of the ideal gas.

In this example we can also illustrate how the violation of the convexity of the thermodynamic potential ϕ (i.e., existence of multiple solutions of (22), in particular then solutions that are not independent of $\boldsymbol{r}$) is physically interpreted as an appearance of two or more phases.

2.2.3 Example: Gibbs equilibrium statistical mechanics

In this example we take the most microscopic viewpoint of macroscopic systems. We regard them as being composed of $n_{\text{p}} \sim 10^{23}$ number of particles. Gibbs (1902) has realized that the state variable of classical mechanics, namely

$$x = (\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n, \boldsymbol{v}_1, \boldsymbol{v}_2, \ldots, \boldsymbol{v}_{n_{\text{p}}}) \tag{26}$$

where ($\boldsymbol{r}_i$, v_i) are the position coordinate and momenta of i-th particle is not a good choice of state variables if one wants to investigate thermodynamics. With $(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n, \boldsymbol{v}_1, \boldsymbol{v}_2, \ldots, \boldsymbol{v}_{n_{\text{p}}})$ we cannot express the eta-function. In the search for an alternative state variables, we may recall that a standard tool used in mathematics to investigate a set $D \subset \mathbb{R}^{6n_p}$ is to investigate the set of functions $D \to \mathbb{R}$. This suggests to replace ($\boldsymbol{r}_1$, $\boldsymbol{r}_2$,…, $\boldsymbol{r}_n$, v_1, v_2,…, $\boldsymbol{v}_{n_{\text{p}}}$) by functions $f : (\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n, \boldsymbol{v}_1, \boldsymbol{v}_2, \ldots, \boldsymbol{v}_{n_{\text{p}}}) \mapsto \mathbb{R}$. This is indeed the state variable suggested by Gibbs

$$x = f(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n, \boldsymbol{v}_1, \boldsymbol{v}_2, \ldots, \boldsymbol{v}_{n_{\text{p}}}) \tag{27}$$

In fact, Gibbs (following Maxwell) has proposed (27) on the basis of another type of consideration. The function $f(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n, \boldsymbol{v}_1, \boldsymbol{v}_2, \ldots, \boldsymbol{v}_{n_\mathrm{p}})$ is physically interpreted as a distribution function. This means that the functions f have some particular properties (e.g., $f(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n, \boldsymbol{v}_1, \boldsymbol{v}_2, \ldots, \boldsymbol{v}_{n_\mathrm{p}})$ is always positive) and that, from the physical point of view, we are starting to see macroscopic systems as statistical ensembles of macroscopic systems. From this interpretation comes then the name (coined by Maxwell) "statistical mechanics." However useful is the statistical viewpoint, it is important to realize that it is not the only viewpoint that one can adopt in statistical mechanics (of course, we are obliged to keep the well established name "statistical mechanics" even if we choose not to see anything "statistic" in it).

In the illustration discussed in this section we shall consider the number of particles n_p as well as the volume V in which the macroscopic system under consideration is confined as fixed. We constrain thus f by

$$\int \mathrm{d}1 \int \mathrm{d}2 \ldots \int \mathrm{d}n_\mathrm{p} f_{(V, n_\mathrm{p})}(1, 2, \ldots, n_\mathrm{p}) = 1 \tag{28}$$

and the projection (4) becomes

$$e = \frac{1}{V} \int \mathrm{d}1 \int \mathrm{d}2 \ldots \int \mathrm{d}n_\mathrm{p} e_{n_\mathrm{p}}(1, 2, \ldots, n_\mathrm{p}) f_{(V, n_\mathrm{p})}(1, 2, \ldots, n_\mathrm{p}) \tag{29}$$

where

$$e_{n_\mathrm{p}}(1, 2, \ldots, n_\mathrm{p}) = \sum_{i=1}^{n_\mathrm{p}} \left(\frac{\boldsymbol{v}_i^2}{2m} + \varepsilon(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_{n_\mathrm{p}}) \right) \tag{30}$$

The subscript (V, n_p) indicates the constraints $V = \mathrm{const}$, and $n_\mathrm{p} = \mathrm{const}$. We are also using the abbreviated notation $1 = (\boldsymbol{r}_1, \boldsymbol{v}_1), 2 = (\boldsymbol{r}_2, \boldsymbol{v}_2), \ldots, n_\mathrm{p} = (\boldsymbol{r}_{n_\mathrm{p}}, \boldsymbol{v}_{n_\mathrm{p}})$, m is the mass of one particle (all particles are assumed to be identical), and $\varepsilon(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_{n_\mathrm{p}})$ is the interaction potential among the particles. The constraint (28) is the normalization (if we are interpreting $f_{(V, n_\mathrm{p})}$ as a distribution function), the first term in (29) is the kinetic energy and the second the potential energy.

Next, we turn to the eta-function $h(f(V, n_p))$. Gibbs proposed

$$h(f_{(V, n_\mathrm{p})}) = -k_\mathrm{B} \frac{1}{V} \int \mathrm{d}1 \int \mathrm{d}2 \ldots \int \mathrm{d}n_\mathrm{p} f_{(V, n_\mathrm{p})}(1, 2, \ldots, n_\mathrm{p}) \ln f_{(V, n_\mathrm{p})}(1, 2, \ldots, n_\mathrm{p}) \tag{31}$$

In the setting (27), (28), (29), and (31) that we have just presented, the individual features of the macroscopic system under consideration are expressed solely in (29). Everything else is universal; it remains the same for all systems. This is of course consistent with classical mechanics where all information about the individual features of a system is expressed in the energy.

The rest is now routine. The thermodynamic potential is

$$\varphi\Big(f_{(V,n_\mathrm{p})}, e^*\Big) = k_\mathrm{B}\frac{1}{V}\int \mathrm{d}1\int \mathrm{d}2\ldots\int \mathrm{d}n_\mathrm{p} f_{(V,n_\mathrm{p})}(1,2,\ldots,n_\mathrm{p})\ln f_{(V,n_\mathrm{p})}(1,2,\ldots,n_\mathrm{p}) + e^*\frac{1}{V}\int \mathrm{d}1\int \mathrm{d}2\ldots\int \mathrm{d}n_\mathrm{p} f_{(V,n_p)}(1,2,\ldots,n_\mathrm{p})e_{n_\mathrm{p}}(1,2,\ldots,n_\mathrm{p}) \tag{32}$$

The equation $\varphi f_{(V,n_\mathrm{p})} = 0$ thus becomes

$$\Big(f_{(V,n_\mathrm{p})}\Big)_\mathrm{eth}(1,2,\ldots,n_\mathrm{p}) = \leftarrow\frac{\exp\left(-\dfrac{e^*}{k_\mathrm{B}}\displaystyle\sum_{i=1}^{n_\mathrm{p}}\left(\frac{\boldsymbol{v}_i^2}{2m} + \varepsilon(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_{n_\mathrm{p}})\right)\right)}{Z_{(n_\mathrm{p},V)}(e^*)} \tag{33}$$

where $Z_{(n_\mathrm{p},V)}(e^*)$, called a partition function, is given by

$$Z_{(n_\mathrm{p},V)}(e^*) = \int \mathrm{d}1\int \mathrm{d}2\ldots\int \mathrm{d}n_\mathrm{p}\exp\left(-\frac{e^*}{k_\mathrm{B}}e_{n_\mathrm{p}}(1,2,\ldots,n_\mathrm{p})\right) \tag{34}$$

Consequently

$$h^*(e^*,n_\mathrm{p},V) = \varphi\Big(\Big(f_{(V,n_\mathrm{p})\leftarrow}\Big)_\mathrm{eth}, n_\mathrm{p}, e^*\Big) = -k_\mathrm{B}\frac{1}{V}\ln Z_{(n_\mathrm{p},V)}(e^*) \tag{35}$$

is the fundamental relation of classical equilibrium thermodynamics implied by (27), (28), (29), and (31).

The above realization of the abstract mesoscopic equilibrium thermodynamics is called a *Canonical-Ensemble Statistical Mechanics*. We shall now briefly present also another realization, called a *Microcanonical-Ensemble Statistical Mechanics* since it offers a useful physical interpretation of entropy.

In addition to keeping the volume V and the number n_p of particles fixed, we shall also keep fixed the energy (29). This means that only the subspace of the $6n_\mathrm{p}$-dimensional phase space corresponding to a fixed energy e constitutes the space M. Its elements are

$$f_{(V,n_\mathrm{p},e)}(1,2,\ldots,n_\mathrm{p}) = \int \mathrm{d}1\int \mathrm{d}2\ldots\int \mathrm{d}n_\mathrm{p}\delta(e - e_{n_\mathrm{p}}(1,2,\ldots,n_\mathrm{p}))f_{(V,n_\mathrm{p})}(1,2,\ldots,n_\mathrm{p}) \tag{36}$$

The eta-function is the same as (31) except that $f(V, n_\mathrm{p})$ is replaced by $f(V, n_\mathrm{p}, e)$.

We can now proceed to the Legendre transformation. The potential generating it is now

$$\varphi\Big(f_{(V,n_p,e)}\Big) = k_{\mathrm{B}}\frac{1}{V}\int \mathrm{d}1\int \mathrm{d}2\ldots\int \mathrm{d}n_{\mathrm{p}}f_{(V,n_{\mathrm{p}},e)}(1,2,\ldots,n_{\mathrm{p}})\ln\, f_{(V,n_{\mathrm{p}},e)}(1,2,\ldots,n_{\mathrm{p}}) \tag{37}$$

Solution to the equation $\varphi_{f_{(V,n_{\mathrm{p}},e)}} = 0$ is

$$\Big(f_{(V,n_{\mathrm{p}},e)}\Big)_{\mathrm{eth}}(1,2,\ldots,n_{\mathrm{p}}) = \frac{1}{Z_{(V,n_{\mathrm{p}},e)}} \tag{38}$$

where

$$Z_{(V,n_{\mathrm{p}},e)} = \int \mathrm{d}1\int \mathrm{d}2\int \mathrm{d}n_{\mathrm{p}}\delta(e - e_{n_{\mathrm{p}}}(1,2,\ldots,n_{\mathrm{p}})) \tag{39}$$

is a uniform distribution on the energy shell in the $6n_{\mathrm{p}}$-dimensional phase space. Finally, we obtain

$$h^{*}(V,n_{\mathrm{p}},e) = -k_{\mathrm{B}}\frac{1}{V}\ln Z_{(V,n_{\mathrm{p}},e)} \tag{40}$$

We note that the classical equilibrium entropy (i.e., the eta-function evaluated at equilibrium states) acquires in the context of the Microcanonical Ensemble an interesting physical interpretation. The entropy becomes a logarithm of the volume of the phase space that is available to macroscopic systems having the fixed volume, fixed number of particles and fixed energy. If there is only one microscopic state that corresponds to a given macroscopic state, we can put the available phase space volume equal to one and the entropy becomes thus zero. The one-to-one relation between microscopic and macroscopic thermodynamic equilibrium states is thus realized only at zero temperature.

2.2.4 Example: multicomponent isothermal systems

Let the system under consideration be composed of k' components. Let the mixture moreover be kept under constant temperature T. We thus replace (by making an appropriate Legendre transformation) the state variable e by the temperature T and then, since $T = \mathrm{const.}$, we shall, in order to simplify the notation, completely omit it. Consequently, we have in this illustration:

$$x = \boldsymbol{n}' = (n'_1, n'_2, \ldots, n'_{k'}) \tag{41}$$

The system under consideration is at equilibrium. Let us suddenly switch on new interactions among the components. The components start to react chemically. They start to transform one into another. This new type of interactions brings the system initially out of equilibrium but eventually the system will reach a new equilibrium, called a chemical equilibrium. What is the fundamental thermodynamic relation of the system involving chemically reacting components at new chemical equilibrium?

First, we need to identify the state variables y describing the chemical equilibrium. Following the notation of Gorban and Karlin (2003), the conservation laws in chemical reactions introduce k linearly independent vectors $\boldsymbol{b}_1$, $\boldsymbol{b}_2$,..., $\boldsymbol{b}_k$. The state variables describing the system at the chemical equilibrium are

$$y = \boldsymbol{n} = (n_1, n_2, \ldots, n_k) \tag{42}$$

where

$$n_j = \langle \boldsymbol{b}_j, \boldsymbol{n}' \rangle; \quad j == 1, 2, \ldots, k \tag{43}$$

the relation (43) serves in this particular example the role of the projection (4).

Let us assume now that we know the eta-function $h = h(x)$. We have thus everything that we need to follow the general theory and derive the fundamental thermodynamic relation at the chemical equilibrium (we introduce $\varphi(\boldsymbol{n}', \boldsymbol{n}^*) = -h(\boldsymbol{n}') + \langle n^*, \boldsymbol{n}(\boldsymbol{n}') \rangle$, identify $\boldsymbol{n}'_{\text{eth}}$ that are solutions to $\varphi \boldsymbol{n}' = 0$, and evaluate φ at $n'^{\leftarrow}_{\text{eth}}$).

The time evolution bringing the system from $\boldsymbol{n}'^{\leftarrow}$to the chemical equilibrium described by $\boldsymbol{n}$ will be discussed in Section 3.1.3. Here we shall only recall the standard notation for chemical reactions. Let the species be denoted by the symbols $\mathbb{A}_1, \mathbb{A}_2, \ldots, \mathbb{A}_{k'}$. The chemical reactions are

$$\alpha_1^{(j)} \mathbb{A}_1 + \cdots + \alpha_{k'}^{(j)} \mathbb{A}_{k'} \rightleftarrows \beta_1^{(j)} \mathbb{A}_1 + \ldots + \beta_{\kappa'}^{(j)} \mathbb{A}_{k'} \tag{44}$$

where j enumerates reaction steps. The quantities defined by

$$\gamma_i^{(j)} = \beta_i^{(j)} - \alpha_i^{(j)}; \quad j == 1, 2, \ldots, J; \; i = =1, 2, \ldots, k' \tag{45}$$

are called stoichiometric coefficients.

As a particular example we take a two-step, four-component reaction with one catalyst $\mathbb{A}_2$: discussed in Gorban and Karlin (2003):

$$\mathbb{A}_1 + \mathbb{A}_2 \rightleftarrows \mathbb{A}_3 \rightleftarrows \mathbb{A}_2 + \mathbb{A}_4 \tag{46}$$

In this example we thus have $k' = 4$ in (41) and $k = 2$ in (42) with $\boldsymbol{n} = (\langle \boldsymbol{b}_1, \boldsymbol{n}' \rangle, \langle \boldsymbol{b}_2, \boldsymbol{n}' \rangle)$; $\boldsymbol{b}_1 = (1, 0, 1, 1)$; $\boldsymbol{b}_2 = (0, 1, 1, 0)$

2.2.5 Example: multicomponent nonisothermal systems

In this example we consider the same situation as in the previous example except that the temperature is left unregulated. The state variables x are thus

$$x = (e', \boldsymbol{n}') \tag{47}$$

The state variables describing chemical equilibrium are

$$y = (e, \boldsymbol{n}) \tag{48}$$

The projection $y = y(x)$ becomes

$$\begin{aligned} n_j &= \langle \boldsymbol{b}_j, \boldsymbol{n}' \rangle; \quad j = 1, 2, \ldots, k \\ e &= e' + \sum_{j=1}^{k'} \epsilon'_j \left(1 - \sum_{l=1}^{k} b_{lj} \right) n'_j \end{aligned} \tag{49}$$

where the first line is the same as in (43), b_{lj} is the j-th component of the vector $\boldsymbol{b}_l$. The second line is implied by the conservation of energy between the state before switching on the chemical reactions and at the state of chemical equilibrium, ϵ_j is the energy of formation of one mole per unit volume of the species i, where $i = 1, 2, \ldots, k'$.

3. MULTISCALE NONEQUILIBRIUM THERMODYNAMICS

The most fundamental experimental observation on which equilibrium thermodynamics is based on is the observation that all externally unforced macroscopic systems (with some exceptions, namely glasses, that we shall mention later in Section 4) can be prepared in such a way that their behavior shows some universal features. Subsequent investigation of these features leads then to the formulation of equilibrium thermodynamics. The preparation process consists of letting the macroscopic systems evolve sufficiently long time without external influences. The states reached when the preparation process is completed are called equilibrium states. The approach to equilibrium states is thus a primary experience; the behavior at equilibrium states is the secondary experience. An investigation of the secondary experience leads to equilibrium thermodynamics. We may expect that an investigation of the primary experience (i.e., an investigation of the approach to equilibrium) will possibly contribute in an important way to equilibrium thermodynamics. Indeed, we shall argue below that the question asked at the beginning of Section 2 can be answered as follows:

Answer 3: *The fundamental thermodynamic relation $h = h(x)$ and the relation $y = y(x)$ in the space M emerge in an investigation of the time evolution of x representing the approach to equilibrium.*

Let $x_{\mathrm{eth}} \in M$ denote the state variable corresponding to the equilibrium state. We shall now investigate the time evolution bringing $x \in M$ to x_{eth} as $t \to \infty$. Roughly speaking, we look for a time evolution for which $y(x)$ are constants of motion, x_{eth} are the fixed points, and $h(x)$ the Lyapunov function associated naturally with the approach to the fixed points. In addition, the time evolution has to be somewhat compatible with the multiscale equilibrium thermodynamics discussed in Section 2. In fact it is this last requirement with which we begin. We shall argue as follows: We have seen in Section 2.2 that the passage from a mesoscopic equilibrium theory to the classical equilibrium theory is made by a Legendre transformation taking the mesoscopic Gibbs–Legendre manifold $\mathcal{M}^{\mathcal{N}}$ to the classical Gibbs–Legendre manifold $\mathcal{N}^*$ that is a submanifold of $\mathcal{M}^{\mathcal{N}}|_{x^*=0}$ Now, *we extend the mesoscopic equilibrium theory to a mesoscopic nonequilibrium theory by requiring that the passage$\mathcal{M}^{\mathcal{N}} \to \mathcal{M}^{\mathcal{N}}|_{x^*=0}$ is made by mesoscopic time evolution taking place in the space* M^{N} *and preserving the 1-form with which the space* M^{N} *is naturally equipped* (see Section 2.2.2). We shall call such time evolution a Legendre time evolution since Legendre transformations preserve the 1-form, and consequently, the time evolution in which the 1-form is preserved can be seen as a continuous sequence of Legendre transformations. In the rest of this section we shall identify the Legendre time evolution,

By applying well-known results of differential geometry (see, e.g., Appendix 4 in Arnold (1989)) to the space $\mathbf{M}^{\mathbf{N}}$ we arrive at the following equations governing the Legendre time evolution:

$$\begin{aligned}
\dot{x} &= \Psi_{x^*} \\
\dot{x}^* &= -\Psi_x + x^*\Psi_\varphi \\
\dot{y}^* &= \Psi_y \\
\dot{y} &= -\Psi_{y^*} + y\Psi_\varphi \\
\dot{\varphi} &= -\Psi + \langle x^*, \Psi_{x^*} \rangle + \langle y, \Psi_y \rangle
\end{aligned} \tag{50}$$

where Ψ is a real-valued function (called a contact Hamiltonian) of $(x, y^*, x^*, y, \varphi)\epsilon M^N$ such that $\Psi|_{M^N} = 0$. The symbol <, > denotes the inner product. We shall use hereafter the shorthand notation: $\Psi_x = \leftarrow \frac{\partial \Psi}{\partial x}$, ….

Our problem now is to find the contact Hamiltonian Ψ for which the time evolution generated by (50) has the following properties: [Ψ 1]: the Gibbs–Legendre manifold M^N is invariant, i.e., the time evolution that starts on $\mathcal{M}^{\mathcal{N}}$ remains there in all times, and $[\Psi\, 2]$ the time evolution generated by (50) carries $\mathcal{M}^{\mathcal{N}}$ into $\mathcal{M}^{\mathcal{N}}|_{x^*=0}$ as $t \to \infty$

It is easy to verify that

$$\Psi(x, x^*, y^*) = -\boldsymbol{\mathcal{H}}(x, x^*, y^*) + \leftarrow \frac{1}{e^*} \mathcal{E}\big(\mathrm{x}, \mathrm{x}^*, \mathrm{y}^*\big) \tag{51}$$

where $\boldsymbol{\mathcal{H}}(x, x^*, y^*) = \Xi(x^*) - \Xi(\varphi_x)$ and $\mathcal{E}\big(\mathrm{x}, \mathrm{x}^*, \mathrm{y}^*\big) = \langle \mathrm{x}^*, L\varphi_x \rangle$ with L and Ξ appearing in (55) is such contact Hamiltonian provided the operator

$$\begin{aligned} &L \ \textit{is skew symmetric} \\ &\textit{and degenerate in the sense that } Lh_x = 0 \textit{ and } Ln_x = 0, \end{aligned} \tag{52}$$

the dissipation potential

$$\begin{aligned} &\Xi \ \textit{is degenerate in the sense that} \\ &\langle e_x, \Xi_{x^*}|_{x^*=h_x} \rangle = \langle h_x, \Xi_{x^*}|_{(x^*=e_x)} \rangle = 0 \\ &\langle n_x, \Xi_{x^*}|_{x^*=h_x} \rangle = \langle h_x, \Xi_{x^*}|_{(x^*=n_x)} \rangle = 0 \end{aligned} \tag{53}$$

and the inequality

$$\langle h_x, \Xi_{x^*}|_{x^*=h_x} \rangle > 0 \tag{54}$$

holds.

In many applications, the operator L is, besides being skew symmetric, also a Poisson operator, which means that $\langle A_x, LB_x \rangle$ is a Poisson bracket denoted hereafter by the symbol $\{A, B\}$; A and B are real-valued functions (sufficiently regular) of x. We recall that the Poisson bracket, in addition to satisfying the skew symmetry $\{A, B\} = -\{B, A\}$, satisfies also the Jacobi identity $\{A, \{B, C\}\} + \{B, \{C, A\}\} + \{C, \{A, B\}\} = 0$.

If the time evolution Equations (50) with the contact Hamiltonian (51) are restricted to the invariant manifold M^N then they become

$$\frac{\mathrm{d}x}{\mathrm{d}t} = L\frac{\partial e}{\partial x} + \leftarrow \frac{\partial \Xi}{\partial\left(\dfrac{\partial h}{\partial x}\right)} \tag{55}$$

Indeed, $\mathcal{E}|_{\mathcal{M}^{\mathcal{N}}} = 0$ due to the skew symmetry of L (skew-symmetric multiplication of two identical terms gives always zero) and $\boldsymbol{\mathcal{H}}|_{\mathcal{M}^{\mathcal{N}}} = 0$ as a result of subtraction of two identical terms. The first line in (50) evaluated on $\mathcal{M}^{\mathcal{N}}$ is clearly identical to (55). The second line evaluated on $\mathcal{M}^{\mathcal{N}}$ is (55) multiplied by φ_{xx}. The third and the fourth lines evaluated on $\mathcal{M}^{\mathcal{N}}$ become $\dot{y}^* = 0$; $\dot{y} = 0$. The fifth line evaluated on $\mathcal{M}^{\mathcal{N}}$ becomes $\dot{\phi} = \langle \varphi_x, \Psi_{\varphi_x} \rangle > 0$. The inequality sign is a consequence of the requirements put on the dissipation potential Ξ.

Solutions to (55) have the following properties:

$$\frac{\mathrm{d}e}{\mathrm{d}t} = 0; \quad \frac{\mathrm{d}n}{\mathrm{d}t} = 0; \quad \frac{\mathrm{d}h}{\mathrm{d}t} > 0 \tag{56}$$

which then implies that $\frac{\mathrm{d}\varphi}{\mathrm{d}t} \leq 0$. If the thermodynamic potential φ is a convex function of x, it can serve thus as a Lyapunov function for the approach $x \to x_{\mathrm{eq}}$ as $t \to \infty$.

Summing up, we have arrived at the mesoscopic time evolution Equation (55) by extending the geometrical structure of equilibrium thermodynamics to the time evolution. A few observations are now in order:

1. In order to prove that (55) is the only possible equation generating the Legendre time evolution we would have to prove that (51) is the only possible contact Hamiltonian. While we cannot prove its uniqueness, we cannot also find other possible contact Hamiltonians satisfying the properties [Ψ 1] and [Ψ 2] introduced above in this section.
2. We note that the Jacobi identity for the bracket $\{A, B\} = (A_x, LB_x)$ is not needed for the manifold $\mathcal{M}^{\mathcal{N}}$ to be invariant and for (50) evaluated on it to become equivalent to (55). The skew symmetry of L suffices to guarantee both these properties. If however we begin with the time evolution generated by (50) and define the manifold $\mathcal{M}^{\mathcal{N}}$ as the manifold on which (51) equals zero then the Jacobi identity is the integrability condition for $\mathcal{M}^{\mathcal{N}}$ (see Courant (1989)).
3. There is also another way the mesoscopic time evolution Equation (55) can be introduced. We collect a list of well-established (i.e., well tested with experimental observations) time evolution equations on many different levels of description and try to identify their common features. This is indeed the way the time evolution Equation (55) has been first introduced. The Hamiltonian structure of the nondissipative part has been discovered first in the context of hydrodynamics by Clebsch (1895). Equations of the type (55) have started to appear in Dzyaloshinskii and Volovick (1980) and later in

Grmela (1984), Kaufman (1984), Beris and Edwards (1994), and Morrison (1984). In the form (55) and with the name GENERIC (an acronym for general equation for nonequilibrium reversible–irreversible coupling), the abstract time evolution Equation (55) has appeared first in Grmela and Ottinger (1997) and Ottinger and Grmela (1998). GENERIC has been then further developed in Grmela (2001, 2002, 2004, and 2010) and in a different direction in Ottinger (1998, 2005). There is now a large list of new and very useful time evolution equations of complex fluids that have been introduced first as particular realizations of (55) (some of them are listed in Section 3.1.6).

4. It has been noted in Grmela (2002) that the total eta-function produced in the course of the approach to equilibrium governed by the GENERIC Equation (55) reaches its extremum. The proof of this statement proceeds as follows: First, we note that with the choice (51) the second term on the right-hand side of the second equation in (50) equals zero. Next, we introduced a function

$$\mathcal{I} = \int \mathrm{d}t \left[\Psi(x, x^*, y^*) - \langle x^* \dot{x} \rangle \right] \tag{57}$$

and note that the Euler–Lagrange equations corresponding to the variations with respect to x^* and x are the same as the first two equations in (50). Indeed, $\frac{\partial \mathcal{I}}{\partial x^*} = 0$ is the first equation and $-\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{\partial \mathcal{I}}{\partial \dot{x}}\right) + \frac{\partial \mathcal{I}}{\partial x} = 0$ is the second equation in (50). Moreover, we note that on the Gibbs–Legendre manifold (i.e., $x^* = \varphi_x$), the function $\mathcal{I} = -\int \mathrm{d}t\, \varphi_x \dot{x} = -\int \mathrm{d}t\, \dot{\varphi} = \int \mathrm{d}t\, h(x)$, which is the eta-function produced in the course of the approach to the equilibrium state x_{eth}. This concludes the proof.

3.1 Single scale realizations

We recall a terminology used routinely in mathematics. Let us have an abstract mathematical object $\mathcal{G}; g \epsilon \mathcal{G}$ (e.g., $\mathcal{G}$ is a group). We say that $\mathcal{G}_{\mathrm{real}}$; $\mathcal{G}_{\mathrm{real}} \epsilon \mathcal{G}_{\mathrm{real}}$ is a particular realization (or representation) of $\mathcal{G}$ if the elements g_{real} of $\mathcal{G}_{\mathrm{real}}$ assume a concrete identity (e.g., they are linear transformations in the space $\mathbb{R}^{\mathrm{n}}$) but the structure (e.g., the group structure if $\mathcal{G}$ is a group) of $\mathcal{G}$ and $\mathcal{G}_{\mathrm{real}}$ remain the same. Analogically, we say that a particular realization of the abstract Equation (55) is the time evolution Equation (55) in which all the building blocks have been specified. The building blocks are state variables $x \epsilon M$, their Hamiltonian kinematics L, dissipation potential Ξ, the eta-function $h(x)$, the energy $e(x)$, and the number of moles $n(x)$. The point of departure of every construction of a particular realization of (55) is a physical insight that arises from a combination of an experience collected in experimental observations and a hypothesis of the physical mechanisms involved. The insight is then expressed in the building blocks. We shall now present some examples. In this subsection we shall consider single-level realizations. Multilevel realizations are illustrated in the next subsection.

3.1.1 Example: a simple illustration

The main purpose of this example is to provide a very simple but still physically meaningful illustration of the Legendre time evolution introduced above. The physical system that we have in mind is a polymeric fluid. We regard it as Simha and Somcynski (1969) do in their equilibrium theory but extend their analysis to the time evolution. As the state variables we choose

$$x = (q, p, \epsilon, \nu) \tag{58}$$

and the projection $y = y(x)$

$$\begin{aligned} e &= \epsilon \\ n &= \nu \end{aligned} \tag{59}$$

The quantity q has the physical interpretation of the free volume. It is the state variable used in the Simha–Somcynski equilibrium theory of polymeric fluids (Simha and Somcynski, 1969). The new variable p that we adopt has the meaning of the velocity (or momentum) associated with q.

The polymeric fluid that we investigate with the state variables (58) is thus static (i.e., without any macroscopic flow) and spatially homogeneous. The only time evolution that takes place in it is the evolution of the internal structure characterized by two scalars q, p.

The physical insight involved in the Simha–Somcynski theory and an additional insight that we need to extend it to the time evolution will now be expressed in the building blocks of (55). We shall construct a particular realization of (55). We begin with the state variables. They have already been specified in (58).

Now we proceed to specify the kinematics of (58). In order that the eta-function h (that remain unspecified at this point) and the number of moles n be preserved in the nondissipative time evolution (i.e., the time evolution governed by the first term on the right-hand side of (55)), the matrix L has to be such that $Lh_x = 0$ and $Ln_x = 0$. This degeneracy can be discussed more easily if we pass from the state variables x to a new set of state variables $\xi = (q, p, h, v)$. Using the terminology of equilibrium thermodynamics (see Callen, 1960), x are the state variables in the entropy representation and ξ in the energy representation. The passage $x \leftrightarrow \xi$ is assumed to be one-to-one since the fundamental thermodynamic relation $h(x)$ is assumed to satisfy $h_e > 0$. Since h_ε has the physical interpretation of the inverse of temperature, this requirement means that we require the temperature to be always positive. The matrix L expressing kinematics of ξ is chosen to be $L = \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$. This matrix manifestly satisfies the degeneracy requirement (note that $h_\xi = (0, 0, 1, 0)^{\mathrm{T}}$ and $n_\xi = (0, 0, 1, 0)^{\mathrm{T}}$; $()^{\mathrm{T}}$ denotes the transpose operation). If this L is transformed (by using the one-to-one transformation $x \leftrightarrow \xi$) into the state variables x it takes the form $L = \begin{pmatrix} 0 & 1 & -\frac{h_p}{h_\epsilon} & 0 \\ -1 & 0 & \frac{h_q}{h_\epsilon} & 0 \\ \frac{h_q}{h_\epsilon} & -\frac{h_p}{h_\epsilon} & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}$. We are using hereafter the notation $h_p = \partial h/\partial p$; .... We directly verify that $Lh_x = Ln_x = 0$. The kinematics of q and p is chosen to be the same as if q is the position coordinate and p the momentum associated with it. In other words, whatever is the physical interpretation of q (e.g., free volume in the Simha–Somcynski theory), p is the momentum associated with it.

The thermodynamic force X that generates the dissipation will be assumed to be a standard friction force. This means that $X = h_{\mathrm{p}}$. For the sake of simplicity, we shall limit ourselves only to small forces and introduce the quadratic dissipation potential $\Xi = \frac{1}{2}\Lambda X^2$, where $\lambda > 0$ is a kinetic coefficient. [We can easily consider also non-quadratic potentials as, for example, $\Xi = \Lambda(\exp X + \exp(-X) - 2)$].

The energy $e(x)$ appearing in (55) is chosen to be $e(x) = \epsilon$(see (59)) and $h(x)$ can be, for example, the fundamental thermodynamic relation arising in the Simha–Somcynski theory supplemented by a new term proportional to p^2 representing the contribution of the internal structure (characterized by (q,p)) to the kinetic energy. In this illustration we leave the function $h(x)$ unspecified. The thermodynamic potential φ becomes in this case $\phi(x, y^*) = -h(q, p, \epsilon, \nu) + e^* \epsilon + n^* \nu$ and the contact Hamiltonian (51)

$$\Psi(q, p, \epsilon, \nu, q^*, p^*, \epsilon^*, \nu^*, e^*, n^*) = \frac{1}{h_\epsilon}\left(-p^* h_q - q^* h_p\right) + \Lambda\left(h_p^2 - (p^*)^2\right) \qquad (60)$$

Consequently Equations (50) look as follows:

$$
\begin{aligned}
&\dot{q} = -\frac{h_p}{h_\epsilon}\\
&\dot{p} = \frac{h_q}{h_\epsilon} - \Lambda p^*\\
&\dot{\epsilon} = 0\\
&\dot{\nu} = 0\\
&\dot{\epsilon} = 0\\
&\dot{\nu} = 0\\
&\dot{q}^{\,*} = -\Lambda h_p h_{pq} - \left(\frac{1}{h_\epsilon}\left(p^* h_q - q^* h_p\right)\right)_q\\
&\dot{p}^{\,*} = -\Lambda h_p h_{pp} - \left(\frac{1}{h_\epsilon}\left(p^* h_q - q^* h_p\right)\right)_q\\
&\dot{\epsilon}^{\,*} = -\Lambda h_p h_{p\epsilon} - \left(\frac{1}{h_\epsilon}\left(p^* h_q - q^* h_p\right)\right)_\epsilon\\
&\dot{\nu}^{\,*} = -\Lambda h_p h_{p\nu} - \left(\frac{1}{h_\epsilon}\left(p^* h_q - q^* h_p\right)\right)_\nu\\
&\dot{e}^{\,*} = 0\\
&\dot{n}^{\,*} = 0\\
&\dot{e} = 0\\
&\dot{n} = 0\\
&\dot{\varphi} = \frac{1}{2}\Lambda\left((p^*)^2 - h_p^2\right) - \frac{1}{h_\epsilon}\left(p^* g_q - q^* h_p\right) - q^*\frac{h_p}{h_\epsilon} + p^*\frac{h_q}{h_\epsilon} - \Lambda (p^*)^2
\end{aligned}
\tag{61}
$$

If this time evolution is restricted to the invariant Gibbs–Legendre manifold $\mathcal{M}^{\mathcal{N}}$[recall that on this manifold $x^* = \varphi_x(x, x^*, y^*)$ and $\varphi = \varphi(x, x^*, y^*)$], we obtain

$$
\dot{q} = -\frac{h_p}{h_\epsilon}; \quad \dot{p} = \frac{h_q}{h_\epsilon} + 2\Lambda h_p; \quad \dot{\epsilon} = 0, \quad \dot{v} = 0; \quad \dot{\varphi} = -\Lambda (h_p)^2 \tag{62}
$$

Equations (62) represent indeed a particular realization of GENERIC (55) in which our insight into the physics that is behind the model discussed in this illustration is expressed. It is easy to verify that solutions to (62) have the following properties: $\frac{\mathrm{d}e}{\mathrm{d}t} = 0$; $\frac{\mathrm{d}n}{\mathrm{d}t} = 0$; $\frac{\mathrm{d}h}{\mathrm{d}t} > 0$; $x \to x_{\mathrm{eth}}$ *as* $t \to \infty$, where x_{eth} is the equilibrium state at which the thermodynamic potential $\varphi(x, y^*)$ reaches its minimum.

3.1.2 Example: chemically reacting isothermal systems

The physical systems considered in this example are the same as in Example 2.2.4. We also choose the same state variables (41). What is new now is that we shall follow explicitly the time evolution initiated by switching on the chemical reactions. The final state reached as $t \to \infty$ will be the equilibrium state (chemical equilibrium state) characterized by the state variables (42) discussed in Section 2.2.4.

The mass action law corresponding to the reaction (44) leads to the following time evolution equations:

$$\begin{aligned}
\frac{\mathrm{d}n_1}{\mathrm{d}t} &= -\gamma_1^{(1)}\mathcal{J}^{(1)} - \gamma_1^{(2)}\mathcal{J}^{(2)} - \cdots - \gamma_1^{(J)}\mathcal{J}^{(J)} \\
\frac{\mathrm{d}n_2}{\mathrm{d}t} &= -\gamma_2^{(1)}\mathcal{J}^{(1)} - \gamma_2^{(2)}\mathcal{J}^{(2)} - \cdots - \gamma_2^{(J)}\mathcal{J}^{(J)} \\
&\vdots \\
\frac{\mathrm{d}n_{k'}}{\mathrm{d}t} &= -\gamma_{k'}^{(1)}\mathcal{J}^{(1)} - \gamma_{k'}^{(2)}\mathcal{J}^{(2)} - \cdots - \nu_{k'}^{(J)}\mathcal{J}^{(J)}
\end{aligned} \tag{63}$$

where $(\mathcal{J}^{(1)}, \ldots, \mathcal{J}^{(J)})$ are the fluxes given by

$$\mathcal{J}^{(j)} = \overleftarrow{k}^{(j)} n_1^{\beta_1^{(j)}} n_2^{\beta_2^{(j)}} \ldots n_{k'}^{\beta_{k'}^{(j)}} - \overrightarrow{k}^{(j)} n_1^{\alpha_1^{(j)}} n_2^{\alpha_2^{(j)}} n_{k'}^{\alpha_{k'}^{(j)}} \tag{64}$$

$\overleftarrow{k}^{(j)}, \overrightarrow{k}^{(j)}$ are the rate coefficients of the backward and the forward j-th reaction step, respectively.

An obvious disadvantage of this formulation of the time evolution is that we do not see in it any connection with the equilibrium analysis that we have done in Section 2.2.1. In order to establish such connection we now reformulate (63) as a particular realization of (55).

The state variables are (41). The time evolution (63) does not involve any nondissipative part and consequently the operator L, in which the Hamiltonian kinematics of (41) is expressed, is absent (i.e., $L \equiv 0$). Time evolution will be discussed in Section 3.1.3. We now continue to specify the dissipation potential Ξ. Following the classical nonequilibrium thermodynamics, we introduce first the so-called thermodynamic forces $(X^{(1)}, \ldots, X^{(J)})$driving the chemically reacting system to the chemical equilibrium. As argued in nonequilibrium thermodynamics, they are linear functions of $\left(\overset{*}{n}_1, \ldots, \overset{*}{n}_{k'}\right)$ (we recall that $\overset{*}{n} = \varphi_{n_i}$; $i = 1, 2, \ldots, k'$ on the Gibbs–Legendre manifold) with the coefficients

$$\gamma_j^{(i)} = \frac{\partial X^{(i)}}{\partial \overset{*}{n}_j}; \quad i = 1, 2, \ldots, J;\ j = 1, 2, \ldots, k' \tag{65}$$

that are the stoichiometric coefficients defined in (45). We note that the thermodynamic forces $X^{(j)}$; $j = 1, 2, \ldots, J$ indeed disappear at the chemical equilibrium.

The next problem is to find the dissipation potential that is a function of the thermodynamic forces, and $-\frac{\partial \Xi}{\partial \overset{*}{n}_j}$ is identical with the right-hand side of *i*-th equation in (63). Since the thermodynamic forces involve $\left(\overset{*}{n}_1, \ldots, \overset{*}{n}_{k'}\right)$ and (63) does not, we see that we have to begin with the specification of the thermodynamic potential $\varphi(x)$ so that we can express the conjugate variables $\left(\overset{*}{n}_1, \ldots, \overset{*}{n}_{k'}\right)$ in terms of the state variables (41). We choose it

$$\varphi(x) = \sum_{j=1}^{k'} (n_j \ln n_j + Q_j n_j) \tag{66}$$

where $Q_1, \ldots, Q_{k'\leftarrow}$are parameters.

Now we proceed to the specification of the dissipation potential $X^{(i)}$. First, we note that $-\frac{\partial \Xi}{\partial \overset{*}{n}_j} = -\Sigma_{i=1}^{J} \frac{\partial \Xi}{\partial X^{(i)}} \frac{\partial X^{(i)}}{\partial \overset{*}{n}_j}$, which, in view of (65), implies that the dissipation potential Ξ that we look for has to satisfy

$$\mathcal{J}^{(l)} = \frac{\partial \Xi}{\partial X^{(l)}} \tag{67}$$

The most obvious candidate with which we satisfy the properties (53) is

$$\Xi = \sum_{j=1}^{J} W_j(x) \left(X^{(j)}\right)^2 \tag{68}$$

provided $W_j(x) > 0$; $j = =1, \ldots, J$. But with this dissipation potential we have $\mathcal{J}^{(l)} = 2W_j(x)X^{(i)}$ that are not the mass action law fluxes (64). The expression $2W_j(x)X^{(i)}$ is however related to (64). When we appropriately relate the rate coefficients $\overset{\leftarrow(j)}{k}$ and $\overset{\rightarrow(j)}{k}$ to W_j we see that $2W_j(x)X^{(i)}$ is the flux (64) linearized about the state of chemical equilibrium. With the potential (68) in (55) we are thus describing the time evolution in a small neighborhood of equilibrium.

The following question now arises: What is the dissipation potential Ξ that implies the mass action law fluxes? In other words, we look for Ξ that (i) satisfies (53), (ii) satisfies (67) with the fluxes given in (64), and (iii) in a small neighborhood of the equilibrium it reduces to (68). The answer is the following:

$$\Xi = \sum_{l=1}^{J} W^{(l)}(x) \left(e^{\frac{1}{2} X^{(l)}} + e^{-\frac{1}{2} X^{(l)\leftarrow}} - 2 \right) \tag{69}$$

If we insert this dissipation potential into the right-hand side of (67) and use (66) then indeed we get the flux (64) with

$$\overset{\leftarrow}{k}^{(j)} = \frac{1}{2} W^{(j)} \mathrm{e}^{\frac{1}{2}\left((Q_1+1)\gamma_1^{(j)}+(Q_2+1)\gamma_2^{(j)}+\cdots+(Q_K+1)\gamma_K^{(j)}\right)} \times \left(n_1^{\beta_1^{(j)}} n_2^{\beta_2^{(j)}} \cdots n_{k'}^{\beta_{k'}^{(j)}} n_1^{\alpha_1^{(j)}} n_2^{\alpha_2^{(j)}} \cdots n_{k'}^{\alpha_{k'}^{(j)}}\right)^{\frac{1}{2}} \tag{70}$$

and

$$\frac{\overset{\leftarrow}{k}^{(j)}}{\vec{k}^{(j)}} = \mathrm{e}^{\left((Q_1+1)\gamma_1^{(j)}+(Q_2+1)\gamma_2^{(j)}+\cdots+(Q_K+1)\gamma_K^{(j)}\right)} \tag{71}$$

We also immediately see that (69) turns into (68) if we neglect the terms $\sim X^m$; $m \geq 3$ and also that (53) holds. We recall that in order that the inequality (54) holds we need a function Ξ with the following properties: $\Xi = 0$ at 0, Ξ reaches its minimum at 0, and Ξ is convex in a neighborhood of 0. All these three properties clearly hold for Ξ given in (69).

We have just demonstrated that the multiscale nonequilibrium thermodynamics includes the mass action law of chemical kinetics as a particular case. The form (69) of the dissipation potential has been, at least implicitly, introduced already by Marcelin and de Donder (de Donder et al., 1936; Feinberg, 1972; Bykov et al., 1977; Gorban and Karlin, 2003, 2005). In the case when the thermodynamic potential does not have the specific form (66), the fluxes (67) are not exactly the same as the fluxes (64) given by the mass action law. Marcelin and de Donder have suggested that for the modified free energy the fluxes (67) should replace the fluxes given by the mass action law.

3.1.3 Example: kinetic theory of chemically reacting systems

We take in this example a more microscopic viewpoint of chemically reacting systems. In order to be able to take into account more details, we change the state variables (41). The number of moles n_i; $i = 1, 2, \ldots, k'$ are replaced by distribution functions. We begin with the case $k' = 1$, i.e., with a one-component system and choose the kinetic theory state variables (7), i.e., the number of moles n becomes the one-particle distribution function $n(\boldsymbol{r},\boldsymbol{v})$.

First, we turn our attention to the Hamiltonian kinematics of the distribution function (7). Hamilton's equations governing the time evolution of one particle with the position coordinate $\boldsymbol{r}$ and momentum $\boldsymbol{v}$ are

$$\begin{pmatrix} \dot{\boldsymbol{r}} \\ \dot{\boldsymbol{v}} \end{pmatrix} = L^{\mathrm{mech}} \begin{pmatrix} e_{\boldsymbol{r}} \\ e_{|\boldsymbol{v}} \end{pmatrix} \tag{72}$$

where $e^{\mathrm{mech}}(\boldsymbol{r},\boldsymbol{v})$ is the energy and $L^{\mathrm{mech}} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$. The (canonical) Poisson bracket $\{a,b\}$ expressing the particle Hamiltonian kinematics is thus

$$\{a,b\}^{\mathrm{mech}} = (a_{\boldsymbol{r}}, a_{\boldsymbol{v}})L\begin{pmatrix} b_{\boldsymbol{r}} \\ b_{\boldsymbol{v}} \end{pmatrix} = a_{\boldsymbol{r}}b_{\boldsymbol{v}} - b_{\boldsymbol{r}}a_{\boldsymbol{v}} \tag{73}$$

where a and b are sufficiently regular real-valued functions of $(\boldsymbol{r},\boldsymbol{v})$.

Instead of $(\boldsymbol{r},\boldsymbol{v})$ we now take the distribution function $n(\boldsymbol{r},\boldsymbol{v})$ as the state variable. The time evolution of $n(\boldsymbol{r},\boldsymbol{v})$ is governed by the Liouville equation corresponding to (72). Can the Liouville equation be cast into the form

$$\frac{\partial n}{\partial t} = Le_n \tag{74}$$

The answer is yes. This can indeed be done with

$$\{A,B\}^{\mathrm{Liouville}} = \int d\boldsymbol{r}\int d\boldsymbol{v}\; n(\boldsymbol{r},\boldsymbol{v})\{A_{n(\boldsymbol{r},\boldsymbol{v})}, B_{n(\boldsymbol{r},\boldsymbol{v})}\}^{\mathrm{mech}} \tag{75}$$

and

$$e(n) - \frac{1}{V}\int d\boldsymbol{r}\int d\boldsymbol{v}\; n(\boldsymbol{r},\boldsymbol{v})e^{\mathrm{mech}}(\boldsymbol{r},\boldsymbol{v}) \tag{76}$$

It is easy to verify that time evolution (74) is the Liouville equation corresponding to the particle time evolution governed by (72).

Since the verification is made in essentially the same way also for all other Poisson bracket formulations that will be discussed below, we shall write down the details. The easiest way to pass from the Poisson bracket (75) to the time evolution (72) is by noting that (74) can also be written as $\frac{dA}{dt} = \{A,e\}$ holds for all $A(n)$. This equation, if written explicitly, becomes

$$\begin{aligned} &\int d\boldsymbol{r}\int d\boldsymbol{v}\; A_{n(\boldsymbol{r},\boldsymbol{v})}\frac{\partial n(\boldsymbol{r},\boldsymbol{v})}{\partial t} \\ =&\int d\boldsymbol{r}\int d\boldsymbol{v}\; A_{n(\boldsymbol{r},\boldsymbol{v})}\left[-\frac{\partial}{\partial \boldsymbol{r}}\left(n(\boldsymbol{r},\boldsymbol{v})e^{\mathrm{mech}}_{\boldsymbol{v}}\right) + \frac{\partial}{\partial \boldsymbol{v}}\left(n(\boldsymbol{r},\boldsymbol{v})e^{\mathrm{mech}}_{\boldsymbol{r}}\right)\right] \end{aligned}$$

In the calculation needed to arrive at the right-hand side we have used integrations by part and boundary conditions that make to disappear the integrals over the boundaries that arise in the calculations. This equation can hold for all $A(n)$ only if

$$\frac{\partial n(\boldsymbol{r},\boldsymbol{v})}{\partial t} = -\frac{\partial}{\partial \boldsymbol{r}}\left(n(\boldsymbol{r},\boldsymbol{v})e_{\boldsymbol{v}}^{\mathrm{mech}}\right) + \frac{\partial}{\partial \boldsymbol{v}}\left(n(\boldsymbol{r},\boldsymbol{v})e_{\boldsymbol{v}}^{\mathrm{mech}}\right)$$

which is indeed the Liouville equation corresponding to (72).

Both the Poisson bracket (75) and the energy (76) are averages of the mechanical Poisson bracket (73) and the mechanical energy. While this observation helps to understand the physical interpretation of the formulation (74), it does not constitute the proof that (75) is indeed a Poisson bracket (i.e., in particular that it satisfies the Jacobi identity). Such proof can be made by a direct verification of the Jacobi identity. An alternative proof is based on a general association of Poisson brackets with Lie algebras (e.g., Marsden et al., 1983). This way of seeing the Poisson bracket is physically very meaningful since the Lie group involved is the group representing the kinematics. In the case of $n(\boldsymbol{r},\boldsymbol{v})$, the Lie group implying the bracket (75) is the group of canonical transformations of $(\boldsymbol{r},\boldsymbol{v})$. As for the degeneracy of the bracket (75), we easily verify that a function $C = \int d\boldsymbol{r}\int d\boldsymbol{v}F(n)$, where $F : n(\boldsymbol{r},\boldsymbol{v}) \to \mathbb{R}$ is a sufficiently regular function is a Casimir function. That is, $\{A, C\}^{\mathrm{Liouville}} = 0$ for all A. Thus, in particular, $\{A, h\}^{\mathrm{Liouville}} = 0$ for h given in (9).

Having established the nondissipative time evolution of $n(\boldsymbol{r},\boldsymbol{v})$, we now turn to the dissipative part. Following the insight of Boltzmann, we shall regard collisions as a source of the emergence of the time irreversibility and the dissipation. The act of collision (we restrict ourselves only to collisions of two particles) is, of course, a part of the time-reversible motion (graphically represented by trajectories) of the particles. The trajectory of a colliding particle remains smooth and time reversible. The changes of the trajectory are however more pronounced. Following Boltzmann, we exaggerate the singular nature of the act of collision, make it into a real singularity, and give it a role of forgetting (except the information needed to conserve the momentum and the energy) everything that went on with the colliding particles before the collision. Having this picture in mind, we can treat collisions as chemical reactions with the momentum $\boldsymbol{v}$ playing the role of the label of species. We consider the particles with a different momentum as belonging to a different species. In the following discussion we shall consider the particles to be points, which then means that the position coordinate $\boldsymbol{r}$ is not affected by collisions. In the discussion of collisions we can thus omit the position coordinate $\boldsymbol{r}$ altogether. This brings us to the setting discussed in Section 3.1.2 with $n_1, n_2, \ldots, n_{k'\leftarrow}$ replaced by $n(\boldsymbol{v})$. The chemical reaction representing the collision is

$$\mathbb{V} + \mathbb{V}_1 \rightleftarrows \mathbb{V}' + \mathbb{V}_1' \tag{77}$$

where $\mathbb{V}$ denotes the species with the label $\boldsymbol{v}$, $\mathbb{V}_1$ with the label $\boldsymbol{v}_1$, $\mathbb{V}'$ with the label $\boldsymbol{v}'$, and $\mathbb{V}_1'$ with the label $\boldsymbol{v}_1'$. Following Section 3.1.2, we introduce the thermodynamic force (chemical affinity)

$$X = -n^*(\boldsymbol{v}) - n^*(\boldsymbol{v}_1) + n^*(\boldsymbol{v}') + n^*(\boldsymbol{v}_1') \tag{78}$$

and the dissipation potential

$$\Xi = \int d\boldsymbol{v} \int d\boldsymbol{v}_1 \int d\boldsymbol{v}' \int d\boldsymbol{v}_1' \, W(n; \boldsymbol{v}, \boldsymbol{v}_1, \boldsymbol{v}', \boldsymbol{v}_1')\left(e^{\frac{1}{2}X} + e^{-\frac{1}{2}X} - 2\right) \tag{79}$$

where $W \geq 0$, symmetric with respect to the interchange of $\boldsymbol{v} \leftrightarrows \boldsymbol{v}_1$ and the interchange of $(\boldsymbol{v}, \boldsymbol{v}_1) + (\boldsymbol{v}', \boldsymbol{v}_1')$. Moreover, $W \neq 0$ if and only if

$$\boldsymbol{v} + \boldsymbol{v}_1 = \boldsymbol{v}' + \boldsymbol{v}_1' \tag{80}$$

and

$$\boldsymbol{v}^2 + (\boldsymbol{v}_1)^2 = (\boldsymbol{v}')^2 + (\boldsymbol{v}_1')^2 \tag{81}$$

The dissipative time evolution of $n(\boldsymbol{r},\boldsymbol{v})$ is thus governed by

$$\begin{aligned}\left(\frac{\partial n}{\partial t}\right)_{\text{dissip}} = & \int d\boldsymbol{v}_1 \int d\boldsymbol{v}' \int d\boldsymbol{v}_1' \, W^{\text{Boltzmann}}(n;\ \boldsymbol{v},\ \boldsymbol{v}_1, \boldsymbol{v}', \boldsymbol{v}_1') \\ & \times (n(\boldsymbol{r},\boldsymbol{v}')n(\boldsymbol{r}, \boldsymbol{v}_1') - n(\boldsymbol{r},\boldsymbol{v})n(\boldsymbol{r}, \boldsymbol{v}_1))\end{aligned} \tag{82}$$

where

$$W^{\text{Boltzmann}} = \frac{1}{2} W(n; \boldsymbol{v}, \boldsymbol{v}_1, \boldsymbol{v}', \boldsymbol{v}_1')(n(\boldsymbol{r}, \boldsymbol{v})n(\boldsymbol{r}, \boldsymbol{v}_1)n(\boldsymbol{r}, \boldsymbol{v}')n(\boldsymbol{r}, \boldsymbol{v}_1'))^{-\frac{1}{2}} \tag{83}$$

provided $h(n)$ is chosen to be (9). The right-hand side of (82) is indeed the famous Boltzmann collision term in the Boltzmann equation. If we choose the energy (76) to be $e(n) - \frac{1}{V} \int d\boldsymbol{r} \int d\boldsymbol{v} \, \frac{\boldsymbol{v}^2}{2m}$ and the eta-function (9) then the time evolution of $n(\boldsymbol{r},\boldsymbol{v})$ is governed by the Boltzmann equation

$$\begin{aligned}\frac{\partial n(\boldsymbol{r}, \boldsymbol{v})}{\partial t} = & -\frac{\boldsymbol{v}_j}{m} \frac{\partial n(\boldsymbol{r}, \boldsymbol{v})}{\partial \boldsymbol{r}_j} + \int d\boldsymbol{v}_1 \int d\boldsymbol{v}' \int d\boldsymbol{v}_1' \, W^{\text{Boltzmann}}(n; \boldsymbol{v}, \boldsymbol{v}_1, \boldsymbol{v}', \boldsymbol{v}_1') \\ & \times (n(\boldsymbol{r}, \boldsymbol{v}')n(\boldsymbol{r}, \boldsymbol{v}_1') - n(\boldsymbol{r}, \boldsymbol{v})n(\boldsymbol{r}, \boldsymbol{v}_1))\end{aligned} \tag{84}$$

In the rest of this section we shall briefly describe a few variations on the theme of the Boltzmann equation (presented above as a particular realization of (55)) that are or could be of interest to chemical engineers.

3.1.3.1 Multicomponent systems with binary chemical reactions. The setting discussed above can be extended in an obvious way to multicomponent gases and also to multicomponent gases involving binary chemical reactions.

3.1.3.2 Spatially nonlocal collisions. The collisions discussed above are all local, i.e., they take place at one point and the position coordinates of the incoming and the outcoming particles remain unchanged. This is the consequence of considering the particles as points. Following Enskog, we can extend the collision transformation $(\boldsymbol{v}, \boldsymbol{v}_1) \rightarrow (\boldsymbol{v}', \boldsymbol{v}_1')\leftarrow$to $(\boldsymbol{v}, \boldsymbol{r}, \boldsymbol{v}_1, \boldsymbol{r}_1) \rightarrow (\boldsymbol{v}', \boldsymbol{r}'\boldsymbol{v}_1', \boldsymbol{r}_1')$. By doing it we change the Boltzmann kinetic equation into the Enskog kinetic equation or, depending on the choice of the nonlocal collision transformation, into an Enskog-like kinetic equation. This type of modification of the time evolution provides a dynamical setting for the equilibrium theory discussed in Section 2.2.2 (see Grmela, 1971)

3.1.3.3 Exchange-of-identity collisions. Instead of the collision $(\boldsymbol{v}, \boldsymbol{v}_1) \rightarrow (\boldsymbol{v}', \boldsymbol{v}_1')$ we can try a particularly weak collision consisting only of the exchange of identities of the colliding particles, i.e., $\boldsymbol{v}' = \boldsymbol{v}_1$ and $\boldsymbol{v}_1' = \boldsymbol{v}$. This type of collision makes the Boltzmann collision term to disappear. However, in the context of two point kinetic theory (i.e., $n(\boldsymbol{r},\boldsymbol{v})$ is replaced by $n(\boldsymbol{r}_1, \boldsymbol{v}_1, \boldsymbol{r}_2, \boldsymbol{v}_2)$) the corresponding collision term is nontrivial. It drives the gas to states at which $n(\boldsymbol{r}_1, \boldsymbol{v}_1, \boldsymbol{r}_2, \boldsymbol{v}_2) = n(\boldsymbol{r}_1, \boldsymbol{v}_1)n(\boldsymbol{r}_2, \boldsymbol{v}_2)$.

3.1.3.4 Inelastic collisions. If the particles composing the gas have an internal structure, in particular an internal energy ε, we replace $n(\boldsymbol{r},\boldsymbol{v})$ by $n(\boldsymbol{r},\boldsymbol{v},\varepsilon)$ and replace the elastic collisions $(\boldsymbol{v}, \boldsymbol{v}_1) \rightarrow (\boldsymbol{v}', \boldsymbol{v}_1')$ for which (80) and (81) hold with inelastic collisions $(\boldsymbol{v}, \epsilon, \boldsymbol{v}_1, \epsilon_1) \rightarrow (\boldsymbol{v}', \epsilon', \boldsymbol{v}_1', \epsilon_1')$ for which (80) still holds but (81) is replaced by $\boldsymbol{v}^2 + (\boldsymbol{v}_1)^2 + \epsilon + \epsilon_1 = (\boldsymbol{v}')^2 + (\boldsymbol{v}_1')^2 + \epsilon' + \epsilon_1'$. In this way we arrive at a modified version of the kinetic theory that is suitable for discussing the time evolution of granular gases.

3.1.4 Example: fluid mechanics

At least in the traditional domains of chemical engineering and in the traditional core of instructions that chemical engineers receive during their education, fluid mechanics (transport phenomena) has played a key role. Also one of the principal motivations for creating nonequilibrium thermodynamics was an attempt to make fluid mechanics manifestly compatible with equilibrium thermodynamics. Even the noncanonical Hamiltonian structures that play such an important role in the multiscale nonequilibrium thermodynamics presented in Section 3 have been first discovered by Clebsch (1895) for the Euler equation. We shall therefore recall below how fluid mechanics arises as a particular realization of (55).

The state variables (called hydrodynamic fields) chosen in fluid mechanics are

$$x = (\rho(\boldsymbol{r}),e(\boldsymbol{r}),\boldsymbol{u}(\boldsymbol{r})) \tag{85}$$

where $\rho(\boldsymbol{r})$ is the field of mass per unit volume, $e(\boldsymbol{r})$ the field of the total energy per unit volume, $\boldsymbol{u}(\boldsymbol{r})$ the field of momentum also per unit volume, and $\boldsymbol{r}$ denotes the position vector. Except for the field of momentum, the state variables (85) are the same as those used in classical equilibrium thermodynamics (1) but they are let to depend on the position coordinate $\boldsymbol{r}$. Consequently, the projection (4) is given by

$$\begin{aligned} e &= \frac{1}{V}\int \mathrm{d}\boldsymbol{r}\; e(\boldsymbol{r}) \\ n &= \frac{1}{VM_{\mathrm{mol}}}\int \mathrm{d}\boldsymbol{r}\; \rho(\boldsymbol{r}) \end{aligned} \tag{86}$$

where M_{mol} is the molecular weight and V is, as in the previous examples, the volume of the region of the space confining the fluid under consideration.

The eta-function

$$h = h(\rho, e, \boldsymbol{u}) \tag{87}$$

will be left in the discussion below unspecified. We only recall that the choice of the most used eta-function is based on the following argument. We regard the fluid as being locally at equilibrium. This means that we choose $h(\rho,e,\boldsymbol{u};\boldsymbol{r})$ to be the function $s(e,n)$ with e replaced by the internal energy $e(\boldsymbol{r}) - \frac{\boldsymbol{u}^2(\boldsymbol{r})}{2\rho(\boldsymbol{r})}$ and n replaced by $\frac{\rho(\boldsymbol{r})}{M_{\mathrm{mol}}}$, Examples of spatially nonlocal eta-functions (needed, e.g., when dealing with fluids involving large spatial inhomogeneities as, e.g., fluids in the vicinity of gas–liquid phase transitions) can be found in Grmela (2008).

The next step in the construction of the particular realization of (55) is the specification of the kinematics of (85) (i.e., specification of the operator L). The necessity to satisfy the degeneracy requirement (52) suggests to begin the search for the operator L by passing to new state variables

$$\hat{x} = (\rho(\boldsymbol{r}), h(\boldsymbol{r}), \boldsymbol{u}(\boldsymbol{r})) \tag{88}$$

We have already used the same strategy in Section 3.1.1. The transformation $x \to \hat{x}$ is one-to-one because h_e, having the physical interpretation of the inverse of the temperature, is always positive. We need now to find L expressing kinematics of (88). The physical insight on which we shall base our search is the following: The motion of a fluid is seen as a continuous sequence of transformations $\mathbb{R}^3 \to \mathbb{R}^3$. These transformations form a Lie group and the field $\boldsymbol{u}(\boldsymbol{r})$ is an element of the dual of the Lie algebra corresponding to the group. The general relation (see, e.g., Marsden et al. (1983)) between the Lie group structure and the Poisson bracket in the dual of its Lie algebra (that we have already used in kinetic theory—see (75)) implies $\{A,B\} = \int \mathrm{d}\boldsymbol{r}\, u_i\left(\partial_j(A_{u_i})B_{u_j} - \partial_j(B_{u_i})A_{u_j}\right)$. The two remaining scalar fields $\rho(\boldsymbol{r})$ and $h(\boldsymbol{r})$ in (88) are assumed to be passively advected (in other words, Lie dragged) by the flow generated by $\boldsymbol{u}(\boldsymbol{r})$. Consequently, the Poisson bracket expressing kinematics of (88) is given by

$$\begin{aligned}\{A,B\} = \int \mathrm{d}\boldsymbol{r}\Big[&u_i\left(\partial_j(A_{u_i})B_{u_j} - \partial_j(B_{u_i})A_{u_j}\right)\\ &+\rho\left(\partial_j(A_\rho)B_{u_j} - \partial_j(B_\rho)A_{u_j}\right)\\ &+h\left(\partial_j(A_h)B_{u_j} - \partial_j(B_h)A_{u_j}\right)\Big]\end{aligned} \tag{89}$$

It is easy to verify that the degeneracy requirements (52) are indeed satisfied.

By applying the one-to-one transformation $\hat{x} \leftrightarrow x$ on (89) we obtain a new Poisson bracket $\left(H = \int \mathrm{d}\boldsymbol{r}\, h(x)\right)$

$$\begin{aligned}\{A,B\} = \int \mathrm{d}\boldsymbol{r}\Big[&u_i\Big(\partial_j\left(A_{u_i} - A_e\frac{h_{u_i}}{h_e}\right)\left(B_{u_j} - B_e\frac{h_{u_j}}{h_e}\right)\\ &-\partial_j\left(B_{u_i} - B_e\frac{h_{u_i}}{h_e}\right)\left(A_{u_j} - A_e\frac{h_{u_j}}{h_e}\right)\\ &+\rho\Big(\partial_j\left(A_\rho - A_e\frac{h_\rho}{h_e}\right)\left(B_{u_j} - B_e\frac{h_{u_j}}{h_e}\right)\\ &-\partial_j\left(B_\rho - B_e\frac{h_\rho}{h_e}\right)\left(A_{u_j} - A_e\frac{h_{u_j}}{h_e}\right)\\ &+h\left(\partial_j\left(A_e\frac{1}{h_e}\right)\left(B_{u_j} - B_e\frac{h_{u_j}}{h_e}\right) - \partial_j\left(B_e\frac{1}{h_e}\right)\left(A_{u_j} - A_e\frac{h_{u_j}}{h_e}\right)\right)\end{aligned} \tag{90}$$

expressing kinematics of x (see (85)).

We turn our attention now to the dissipative part of the time evolution. We shall discuss it with the state variables (85). Following Navier, Stokes, and Fourier, the thermodynamic forces driving the fluid to equilibrium are

$$X_i^{(\mathrm{F})}(e^*) = \partial_i e^* \tag{91}$$

$$X_{ij}^{(NS)}(\boldsymbol{u}^*, e^*) = \overset{1}{\underset{2}{\longleftarrow}}\left(\partial_j\left(\frac{u_i^*}{e^*}\right) + \partial_i\left(\frac{u_j^*}{e^*}\right)\right) \tag{92}$$

$$X^{(NSvol)}(\boldsymbol{u}^*, e^*) = \partial_j\left(\frac{u_j^*}{e^*}\right) \tag{93}$$

where $\partial_i = \frac{\partial}{\partial r_i}$. The force (91) generates the Fourier heat flow, the force (92) the Navier Stokes friction, and (93) the Navier–Stokes friction in the volume deformation. From these three thermodynamic forces we now construct a dissipation potential Ξ. If we limit ourselves to small thermodynamic forces (recall that the thermodynamic forces disappear at equilibrium) then we can choose the following quadratic potential:

$$\Xi = \int d\boldsymbol{r}\left[\frac{1}{2}\lambda X_i^{(\mathrm{F})} X_i^{(\mathrm{F})} + \frac{1}{2}\eta X_{ij}^{(\mathrm{NS})} X_{ij}^{(\mathrm{NS})} + \frac{1}{2}\eta_{\mathrm{vol}} X^{(\mathrm{NS\ vol})} X^{(\mathrm{NS\ vol})}\right] \tag{94}$$

where the three coefficients $\lambda > 0$, $\eta > 0$, and $\eta_{\mathrm{vol}} > 0$ are material parameters (or material functions) in which the individual features of the fluids under consideration are expressed; λ is called a coefficient of heat conduction, η a coefficient of viscosity, and η_{vol} a coefficient of volume viscosity.

We can now write explicitly (55)

$$\begin{aligned}
\frac{\partial \rho}{\partial t} &= -\partial_j(\rho v_j) \\
\frac{\partial u_i}{\partial t} &= -\partial_j(u_i v_j) - \partial_i p - \partial_j \sigma_{ij}^{(\mathrm{NS})} \\
\frac{\partial e}{\partial t} &= -\partial_j(e v_j) - \partial_j(p v_j) - \partial_j\left(v_j \sigma_{ij}^{(\mathrm{NS})}\right) - \partial_j q_j^{(\mathrm{F})} \\
\dot{h} &= \int d\boldsymbol{r}\left[X_i^{(\mathrm{F})} \Xi_{X_i^{(\mathrm{F})}} + X_{ij}^{(\mathrm{NS})} \Xi_{X_{ij}^{(\mathrm{NS})}} + X^{(\mathrm{NS\ vol})} \Xi_{X^{(\mathrm{NS\ vol})}}\right]
\end{aligned} \tag{95}$$

where $\tau = \frac{1}{h_e}$ is the local hydrodynamic temperature, $\boldsymbol{v} = -\tau h_{\mathbf{u}}$ is the fluid velocity.

$$\sigma_{ij}^{(\mathrm{NS})} = \tau\, \Xi_{\partial_j v_j} \tag{96}$$

is the Navier–Stokes extra stress tensor

$$q_i^{(\mathrm{F})\leftarrow} = \partial_i \Xi_{h_e} \tag{97}$$

is the Fourier heat flow, and

$$p = -e - \rho\tau h_\rho + h\tau + u_j v_j \tag{98}$$

the local hydrodynamic pressure. Equations (95) are indeed the familiar Navier–Stokes–Fourier equations.

The computations involved in the passage from (94) and (89) to the time evolution equations are straightforward. Here we shall only indicate the calculations. We note, as we already did in Section 3.1.3 (see the text following Equation (76)), that the equation $\dot{x} = L\varphi_x$ can also be written as $\dot{A} = \{A, \Phi\}$ required to hold for all sufficiently regular functions $A(x)$. This formulation provides a systematic method for passing from the bracket to the time evolution equation. We shall illustrate it below on the example of the bracket (89), but the method can obviously be used for any bracket. We proceed as follows: (i) we replace in (89) B by φ, (ii) we write (if necessary using integration by parts) $\{A, \varphi\}$ as $\int d\boldsymbol{r}\left[A_\rho(\cdot) + A_\eta(\cdot\cdot) + A_u(\cdot\cdot\cdot)\right]$. The equation $\dot{x} = L\varphi_x$ is then $\partial_t\rho = (\cdot)$; $\partial_t\eta = (\cdot\cdot)$; $\partial_t u = (\cdot\cdot\cdot)$.

3.1.5 Example: particle dynamics

In this example we shall comment about the time evolution corresponding to the Gibbs equilibrium statistical mechanics (see Section 2.2.2). We shall use the same notation as the one used in Section 2.2.2.

The macroscopic system under consideration is regarded as being composed of $n_\mathrm{p} \sim 10^{23}$ particles. The state variables describing it are (26). Their time evolution is governed by (72) extended in an obvious way from one to n_p particles. If we pass from (26) to the state variable (27), the time evolution (72) transforms into the Liouville equation corresponding to (72), i.e., to Equation (74) with n replaced by (27) and the Poisson bracket that extends (75) in an obvious way to n_p particles (i.e., $\{A,\ B\} = \Sigma_{i=1}^{n_p} \int d1 \ldots \int dn_\mathrm{p} f\left(1, \ldots, n_\mathrm{p}\right) \left[\frac{\partial A_f}{\partial \boldsymbol{r}_i} \ \frac{\partial B_f}{\partial \boldsymbol{v}_i} - \frac{\partial B_f}{\partial \boldsymbol{r}_i} \ \frac{\partial A_f}{\partial \boldsymbol{v}_i}\right]$).

But this is only the starting point. In order to see the approach to $\mathcal{L}_\mathrm{eth}$ (in other words in order to provide an appropriate dissipative part to the Liouville equation), we have to enter the process of solving the Liouville equation. Roughly speaking, the process is a pattern recognition in the phase portrait that corresponds to the Liouville equation (i.e., a pattern recognition in the set of all trajectories generated by the Liouville equation with a family of $e_p(1, \ldots,\ n_p)$). The pattern recognition process may involve, for example, an investigation of various ergodic and/or chaotic type properties of the particle trajectories. An alternative and a very interesting strategy to proceed in the pattern recognition consists of transforming first the Liouville equation governing the time evolution of (27) into a hierarchy of coupled equations governing the time evolution of $x = \left(f_1(1), f_2(1,\ 2), \ldots, f_{n_p}(1,\ 2,\ \ldots,\ n_p)\right)$, where $f_{n_i}(1,\ \ldots,\ n_i)$; $n_i\ < n_p$ are reduced distribution functions, and then entering the process of reductions that we shall discuss in some detail in Section 4 below. The famous BBGKY hierarchy is an example of the hierarchy of equations governing the time evolution of $\left(f_1(1), f_2(1,\ 2), \ldots, f_{n_p}(1,\ 2,\ \ldots,\ n_p)\right)$. Another hierarchy of this type has been introduced in Grmela (2001). In the particular case of $n_p = 1$ (i.e., the state variable is the one-particle distribution function), the Boltzmann collision term discussed in Section 3.1.3 is an example of the dissipative term that, if attached to the Liouville part, provides a time evolution equation describing the approach to L_{eth}. The pattern recognition process is in this case a separation of particle trajectories into collisionless and collision parts and treating them in a different way.

The term "coarse-graining" is often used to denote the process leading to reduced descriptions. Indeed, one possible strategy that can be applied to recognize patterns is to coarse grain. However, because the coarse-graining is only one among the many ways to proceed in the pattern recognition process, because it is important to emphasize the complexity involved in the reduction process (by invoking our innate ability to recognize patterns in everyday life), and because the coarse-graining is obviously very coordinate dependent and as such very nongeometrical in its nature, it is always preferable to visualize the micro → macro passage as a "pattern recognition in the phase portrait" rather than a "coarse-graining."

3.1.6 Examples: complex fluids

Complex fluids are the fluids for which the classical fluid mechanics discussed in Section 3.1.4 is found to be inadequate. This is because the internal structure in them evolves on the same time scale as the hydrodynamic fields (85). The role of state variables in the extended fluid mechanics that is suitable for complex fluids play the hydrodynamic fields supplemented with additional fields or distribution functions that are chosen to characterize the internal structure. In general, a different internal structure requires a different choice of the additional fields. The necessity to deal with the time evolution of complex fluids was the main motivation for developing the framework of dynamics and thermodynamics discussed in this review. There is now a large amount of papers in which the framework is used to investigate complex fluids. In this review we shall list only a few among them. The list below is limited to recent papers and to the papers in which I was involved.

A simple fluid like, e.g., water, that is in the vicinity of the point of phase transition becomes a complex fluid. Large spatial inhomogeneities and long range pair correlations become the internal structure whose time evolution cannot be ignored. An extension of the setting of Section 3.1.4 to this type of fluids is discussed in Grmela (2008). We can see this extended fluid mechanics also as an attempt to provide the time evolution corresponding to the equilibrium theory discussed in Section 2.2.2.

Suspensions of various types are all complex fluids. We list a few examples: suspensions of macromolecules (polymeric fluids) (Eslami and Grmela, 2008), suspensions of nanoparticles in polymeric fluids (Eslami et al., 2007, 2009), suspensions of membranes (immiscible blends and biological fluids) (Gu and Grmela, 2008, 2008a, 2009; Gu et al., 2008), and suspensions of rigid spherical particles (Zmijevski et al., 2005, 2007)

Interesting examples of complex fluids are superfluids. The time evolution of these fluids is dominated by the nondissipative part. The framework (55) is thus particularly well suited to deal with this type of the time evolution (Holm et al., 1987; Grmela, 2008a))

3.2 Combination of scales

In this subsection we shall construct two independent realizations of (55) on two independent levels and then we combine them.

3.2.1 Example: direct molecular simulations

In chemical engineering as well as in physics and in science in general, direct molecular simulations became very popular. The enormous computing power that is now routinely available allows to make a direct passage from molecules to macroscopic properties. The idea is simple. We calculate trajectories of all the molecules composing the macroscopic system and then extract from them the macroscopic properties of our interest. When trying to follow this path, we meet however some difficulties. Leaving aside the technical challenges in calculations (the problem of solving numerically a very large system of ordinary differential equations), there are three important issues that have to be addressed: (Problem 1) The actual number of molecules in macroscopic systems is $\sim 10^{23}$ but computers can deal at most with $\sim 10^6$. (Problem 2) The macroscopic systems of interest are often subjected to external forces that are defined and have a clear meaning only on some mesoscopic and macroscopic levels of description. For example, the macroscopic system that we regard in direct molecular simulations as composed of, say, 10^6 particles can be subjected to a temperature gradient. How do the particles feel such force? (Problem 3) The results coming out of computers are trajectories of the particles. How shall we extract from this information the information that we can compare with results of mesoscopic or macroscopic measurements (e.g., the measurements done in fluid mechanics)? We shall now use the setting developed above in this chapter to address these three problems.

We begin with the first problem (Problem 1). Let n_p be the number of particles whose trajectories are actually followed in computers. Since $n_p \sim 10^6 << 10^{23}$, we shall choose to describe states of the particles by the n_p-particle phase space distribution function rather than by points in the $6n_\mathrm{p}$-dimensional phase space with coordinates $\left(\boldsymbol{r}_1, \boldsymbol{v}_1, \ldots, \boldsymbol{r}_{n_\mathrm{p}}, \boldsymbol{v}_{n_\mathrm{p}}\right)$ as it is done in particle mechanics. Next, we shall proceed as follows: First, we construct the time evolution equation (the n_p-particle kinetic equation) and establish the passage from the n_p-particle distribution functions to quantities measured in macroscopic measurements. Second, we solve the kinetic equation by regarding it (approximately) as a Liouville equation corresponding to time evolution equations of n_p particles whose trajectories we then find with the assistance of computers. Following this route, the equations used in the simulations (a system of $6n_\mathrm{p}$ or more ordinary differential equations) are not constructed directly from Newton's mechanics of n_p particles but indirectly by writing down first a kinetic equation and only then arriving at the time evolution equations of particles as a result of choosing a particular method of solving the kinetic equation. In the text below, we shall address mainly the first step (i.e., formulation of the kinetic equation and its coupling with other scales). The second step (passage from the kinetic equations to particle equations) will only be indicated.

We proceed now to the problems (Problem 2) and (Problem 3). At least two levels of description are involved in direct molecular simulations. The first one is the level of the n_p-particle kinetic theory and the second is the level of fluid mechanics on which the external forces and the final results that we seek are formulated. We shall use the multiscale formulation developed above and combine the two levels. The two levels that we consider in this section are

$\mathcal{L}_1$–classical fluid mechanics
with the state variables x_1 given in (85) or (87) whose kinematics is expressed in the bracket (89) and

$\mathcal{L}_2$–n_p-particle kinetic theory
with the state variables

$$x_2 = f_{n_\mathrm{p}}\left(\boldsymbol{r}_1, \boldsymbol{v}_1, \cdots, \boldsymbol{r}_{n_\mathrm{p}}, \boldsymbol{v}_{n_\mathrm{p}}\right) \tag{99}$$

whose kinematics is expressed in the Poisson bracket

$$\{A, B\} = \int d\boldsymbol{r}_1 \int d\boldsymbol{v}_1 \cdots \int d\boldsymbol{r}_{n_\mathrm{p}} \int d\boldsymbol{v}_{n_\mathrm{p}} \; f_{n_\mathrm{p}} \sum_{i=1}^{n_\mathrm{p}} \left[\frac{\partial A_{f_{n_\mathrm{p}}}}{\partial \boldsymbol{r}_i} \frac{\partial B_{f_{n_\mathrm{p}}}}{\partial \boldsymbol{v}_i} - \frac{\partial B_{f_{n_\mathrm{p}}}}{\partial \boldsymbol{r}_i} \frac{\partial A_{f_{n_\mathrm{p}}}}{\partial \boldsymbol{v}_i} \right] \tag{100}$$

which is based on the same physics as the bracket (75) except that one particle is replaced by n particles.

From the above two levels we construct now a third level as their combination:

$\mathcal{L}_{1\&2}$–classical fluid mechanics and n_p-particle kinetic theory

The level $\mathcal{L}_{1\&2}$ is a simple superposition of the two levels $\mathcal{L}_1$ and $\mathcal{L}_2$. This means that the state variables on the levels $\mathcal{L}_{1\&2}$ are

$$x_3 = (x_1,\ x_2) \tag{101}$$

with the kinematics given by the sum of the brackets (89) and (100).

Next, we introduce new coordinates on the level $\mathcal{L}_{1\&2}$. The coordinates $(x_1,\ x_2)$are replaced by

$$x = \left(\tilde{\eta}(\boldsymbol{r}),\ \tilde{\rho}(\boldsymbol{r}),\ \tilde{\boldsymbol{u}}(\boldsymbol{r}),\ \widetilde{f_{n_p}}\left(\boldsymbol{r}_1,\ \boldsymbol{v}_1, \ldots,\ \boldsymbol{r}_{n_\mathrm{p}}, \boldsymbol{v}_{n_\mathrm{p}}\right)\right) \tag{102}$$

that are related to $(x_1,\ x_2)$ by

$$\begin{aligned}
\tilde{\eta}(\boldsymbol{r}) &= \eta(\boldsymbol{r}) - k_B\int \mathrm{d}\boldsymbol{r}_1\int \mathrm{d}\boldsymbol{v}_1\ldots\int \mathrm{d}\boldsymbol{r}_{n_\mathrm{p}}\int \mathrm{d}\boldsymbol{v}_{n_\mathrm{p}}\sum_{i=1}^{n}\delta(\boldsymbol{r}_i-\boldsymbol{r})f_{n_\mathrm{p}}\ln f_{n_\mathrm{p}}\\
\tilde{\rho}(\boldsymbol{r}) &= \rho(\boldsymbol{r}) + \int \mathrm{d}\boldsymbol{r}_1\int \mathrm{d}\boldsymbol{v}_1\ldots\int \mathrm{d}\boldsymbol{r}_{n_\mathrm{p}}\int \mathrm{d}\boldsymbol{v}_{n_\mathrm{p}}\sum_{i=1}^{n}\delta(\boldsymbol{r}_i-\boldsymbol{r})f_{n_\mathrm{p}}\\
\tilde{u}(\boldsymbol{r}) &= \boldsymbol{u}(\boldsymbol{r}) + \int \mathrm{d}\boldsymbol{r}_1\int \mathrm{d}\boldsymbol{v}_1\ldots\int \mathrm{d}\boldsymbol{r}_{n_\mathrm{p}}\int \mathrm{d}\boldsymbol{v}_{n_\mathrm{p}}\sum_{i=1}^{n}\boldsymbol{v}_i\delta(\boldsymbol{r}_i-\boldsymbol{r})f_{n_\mathrm{p}}\\
\widetilde{f_{n_p}}\left(\boldsymbol{r}_1,\ \boldsymbol{v}_1,\ldots,\ \boldsymbol{r}_{n_\mathrm{p}},\ \boldsymbol{v}_{n_\mathrm{p}}\right) &= f_{n_\mathrm{p}}\left(\boldsymbol{r}_1,\ \boldsymbol{v}_1,\ldots,\ \boldsymbol{r}_{n_\mathrm{p}},\ \boldsymbol{v}_{n_\mathrm{p}}\right)
\end{aligned} \tag{103}$$

We note that the transformation $(x_1,\ x_2) \rightarrow x$ defined in (103) is one-to-one. We interpret physically $\tilde{\eta},\ \tilde{\rho},\ \tilde{\boldsymbol{u}}$ as overall (i.e., large-scale) hydrodynamic fields on which there are superposed "$\mathcal{L}_2$-fluctuations" (i.e., small-scale quantities) characterized by the n_p-particle distribution function $\widetilde{f_{n_p}}$.

We apply now the one-to-one transformation (103) on the bracket expressing kinematics of $(x_1,\ x_2)$ (i.e., on the sum of the brackets (89) and (100)). To prepare the calculations we note that

$$\begin{aligned}
A_{\eta(\boldsymbol{r})} &= A_{\tilde{\eta}(\boldsymbol{r})}\\
A_{\rho(\boldsymbol{r})} &= A_{\tilde{\rho}(\boldsymbol{r})}\\
A_{\boldsymbol{u}(\boldsymbol{r})} &= A_{\tilde{\boldsymbol{u}}(\boldsymbol{r})}\\
A_{f_{n_\mathrm{p}}\left(\boldsymbol{r}_1,\boldsymbol{v}_1,\ldots,\boldsymbol{r}_{n_\mathrm{p}},\boldsymbol{v}_{n_\mathrm{p}}\right)} &= A_{\tilde{f_{np}}}\left(\boldsymbol{r}_1,\boldsymbol{v}_1,\ldots,\boldsymbol{r}_{n_\mathrm{p}},\boldsymbol{v}_{n_\mathrm{p}}\right)\\
&\quad -k_\mathrm{B}\sum_{i=1}^{n_\mathrm{p}}\left[1+\ln f_{n_\mathrm{p}}\right]\left(\boldsymbol{r}_1,\boldsymbol{v}_1,\ldots,\boldsymbol{r}_{n_\mathrm{p}},\boldsymbol{v}_{n_\mathrm{p}}\right)A_{\tilde{\eta}}\ (\boldsymbol{r}_i)\\
&\quad +\sum_{i=1}^{n_\mathrm{p}}A_{\tilde{\rho}(\boldsymbol{r}_i)} + \sum_{i=1}^{n_\mathrm{p}}\boldsymbol{v}_i A_{\tilde{\boldsymbol{u}}(\boldsymbol{r}_i)}
\end{aligned} \tag{104}$$

Using (104) in the brackets (89) and (100), whose sum is the bracket expressing the kinematics of (x_1, x_2), we arrive, after somewhat lengthy but completely straightforward calculations, to (we are omitting hereafter the tilde)

$$
\begin{aligned}
\{A,B\} = {} & \{A,B\}^{(\mathrm{hyd})} + \{A,B\}^{(KTn_\mathrm{p})} + \int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{v}_1 \ldots \int \mathrm{d}\boldsymbol{r}_{n_\mathrm{p}} \int \mathrm{d}\boldsymbol{v}_{n_\mathrm{p}} \\
& \Bigg[f_{n_\mathrm{p}} \sum_{i=1}^{n_\mathrm{p}} \left(\frac{\partial}{\partial \boldsymbol{r}_i} \left(A_{f_{n_\mathrm{p}}} \right) B_{\boldsymbol{u}(\boldsymbol{r}_i)} - \frac{\partial}{\partial \boldsymbol{r}_i} \left(B_{f_\mathrm{n}} \right) A_{\boldsymbol{u}(\boldsymbol{r}_i)} \right) \\
& + f_{n_\mathrm{p}} \sum_{i=1}^{n_\mathrm{p}} \left(\frac{\partial}{\partial \boldsymbol{r}_i} \left(A_{\rho(\boldsymbol{r}_i)} \right)\!\leftarrow\! \frac{\partial}{\partial \boldsymbol{v}_i} \left(B_{f_{n_\mathrm{p}}} \right) - \frac{\partial}{\partial \boldsymbol{r}_i} \left(B_{\rho(\boldsymbol{r}_i)} \right) \frac{\partial}{\partial \boldsymbol{v}_i} \left(A_{f_{n_\mathrm{p}}} \right) \right) \\
& + f_{n_\mathrm{p}} \sum_{i=1}^{n_\mathrm{p}} \left(\boldsymbol{v}_i \frac{\partial}{\partial \boldsymbol{r}_i} \left(A_{\boldsymbol{u}(\boldsymbol{r}_i)} \right)\!\leftarrow\! \frac{\partial}{\partial \boldsymbol{v}_i} \left(B_{f_{n_\mathrm{p}}} \right) - \boldsymbol{v}_i \frac{\partial}{\partial \boldsymbol{r}_i} \left(B_{\boldsymbol{u}(\boldsymbol{r}_i)} \right)\!\leftarrow\! \frac{\partial}{\partial \boldsymbol{v}_i} \left(A_{f_{n_\mathrm{p}}} \right) \right) \\
& - k_\mathrm{B} f_{n_\mathrm{p}} \ln f_{n_\mathrm{p}} \sum_{i=1}^{n_\mathrm{p}} \left(\frac{\partial}{\partial \boldsymbol{r}_i} \left(A_{\eta(\boldsymbol{r}_i)} \right)\!\leftarrow\! \frac{\partial}{\partial \boldsymbol{v}_i} \left(B_{f_{n_\mathrm{p}}} \right) - \frac{\partial}{\partial \boldsymbol{r}_i} \left(B_{\eta(\boldsymbol{r}_i)} \right)\!\leftarrow\! \frac{\partial}{\partial \boldsymbol{v}_i} \left(A_{f_{n_\mathrm{p}}} \right) \right) \Bigg]
\end{aligned}
\tag{105}
$$

where $\{A,B\}^{(\mathrm{hyd})}$ is the Poisson bracket (89) expressing kinematics in classical hydrodynamics and $\{A,B\}^{(KTn_\mathrm{p})}$ is the Poisson bracket (100) expressing kinematics in the n_p-particle kinetic theory.

The nondissipative time evolution equations $\dot{x} = \frac{1}{e^*} L \varphi_x$ (see (55)) corresponding to (105) are the following:

$$
\begin{aligned}
\partial_t \rho = {} & -\frac{\partial}{\partial \boldsymbol{r}} \left(\rho \varphi \boldsymbol{u}(\boldsymbol{r}) \right) \\
& - \frac{\partial}{\partial \boldsymbol{r}} \left(\sum_{i_r} \int \boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{v}_1 \ldots \int \mathrm{d}\boldsymbol{r}_{n_\mathrm{p}} \int \mathrm{d}\boldsymbol{v}_{n_\mathrm{p}} \delta(\boldsymbol{r} - \boldsymbol{r}_i) f_n \frac{\partial \varphi_{f_{n_\mathrm{p}}}}{\partial \boldsymbol{v}_i} \right) \\
\partial_t \eta = {} & - \frac{\partial}{\partial \boldsymbol{r}} \left(\rho \varphi \boldsymbol{u}(\boldsymbol{r}) \right) \leftarrow \\
& + k_B \frac{\partial}{\partial \boldsymbol{r}} \left(\sum_{i_r} \int \boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{v}_1 \ldots \int \mathrm{d}\boldsymbol{r}_{n_\mathrm{p}} \int \mathrm{d}\boldsymbol{v}_{n_\mathrm{p}} \delta(\boldsymbol{r} - \boldsymbol{r}_i) f_{n_\mathrm{p}} \ln f_{n_\mathrm{p}} \frac{\partial \varphi_{f_{n_\mathrm{p}}}}{\partial \boldsymbol{v}_i} \right) \\
\partial_t \boldsymbol{u} = {} & - \frac{\partial}{\partial \boldsymbol{r}} \left(\boldsymbol{u} \varphi_{\boldsymbol{u}(\boldsymbol{r})} \right) - \frac{\partial p(\boldsymbol{r})}{\partial \boldsymbol{r}} - \frac{\partial \sigma(\boldsymbol{r})}{\partial \boldsymbol{r}} \\
\partial_t f_{n_\mathrm{p}} = {} & \sum_{i=1}^{n_\mathrm{p}} \Bigg[-\frac{\partial}{\partial \boldsymbol{r}_i} \left(f_{n_\mathrm{p}} \frac{\partial \varphi_{f_{n_\mathrm{p}}}}{\partial \boldsymbol{v}_i} \right) - \frac{\partial}{\partial \boldsymbol{v}_i} \left(f_{n_\mathrm{p}} \frac{\partial \varphi_{f_{n_\mathrm{p}}}}{\partial \boldsymbol{r}_i} \right) \\
& - \frac{\partial}{\partial \boldsymbol{r}_i} \left(f_{n_\mathrm{p}} \varphi_{\boldsymbol{u}(\boldsymbol{r}_i)} \right) + \frac{\partial}{\partial \boldsymbol{v}_i} \left(f_{n_\mathrm{p}} \boldsymbol{v}_i \frac{\partial \varphi_{\boldsymbol{u}(\boldsymbol{r}_i)}}{\partial \boldsymbol{r}_i} \right) \\
& + \frac{\partial}{\partial \boldsymbol{v}_i} \left(f_{n_\mathrm{p}} \frac{\partial \varphi_{\rho(\boldsymbol{r}_i)}}{\partial \boldsymbol{r}_i} \right) - \frac{\partial}{\partial \boldsymbol{v}_i} \left(k_\mathrm{B} f_{n_\mathrm{p}} \ln f_{n_\mathrm{p}} \frac{\partial \varphi_{\eta(\boldsymbol{r}_i)}}{\partial \boldsymbol{r}_i} \right) \Bigg]
\end{aligned}
\tag{106}
$$

where $p(\boldsymbol{r})$ is the hydrostatic pressure given by

$$\begin{aligned} p(\boldsymbol{r}) = -\phi(\boldsymbol{r}) + \rho(\boldsymbol{r})\varphi_{\rho(\boldsymbol{r})} + \eta(\boldsymbol{r})\varphi_{\eta(\boldsymbol{r})} + \boldsymbol{u}(\boldsymbol{r})\varphi_{u(\boldsymbol{r})} \\ + \sum_{i_r} \int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{v}_1 \ldots \int \mathrm{d}\boldsymbol{r}_{n_\mathrm{p}} \int \mathrm{d}\boldsymbol{v}_{n_\mathrm{p}}\, f_{n_\mathrm{p}} \delta(\boldsymbol{r} - \boldsymbol{r}_i)\varphi_{f_{n_\mathrm{p}}} \end{aligned} \tag{107}$$

and

$$\begin{aligned} \sigma(\boldsymbol{r}) = -\sum_{i_r} \int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{v}_1 \ldots \int \mathrm{d}\boldsymbol{r}_{n_\mathrm{p}} \int \mathrm{d}\boldsymbol{v}_{n_\mathrm{p}} f_{n_\mathrm{p}} \delta(\boldsymbol{r} - \boldsymbol{r}_i)\boldsymbol{v}_i \frac{\partial \varphi_{f_{n_\mathrm{p}}}}{\partial \boldsymbol{v}_i} \\ + \sum_{i_r} \sum_{j_r} \int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{v}_1 \ldots \int \mathrm{d}\boldsymbol{r}_{n_\mathrm{p}} \int \mathrm{d}\boldsymbol{v}_{n_\mathrm{p}} f_{n_\mathrm{p}} \delta(\boldsymbol{r} - \boldsymbol{r}_i)(\boldsymbol{r}_i - \boldsymbol{r}_j) \frac{\partial \varphi_{f_{n_\mathrm{p}}}}{\partial(\boldsymbol{r}_i - \boldsymbol{r}_j)} \end{aligned} \tag{108}$$

By Σ_{i_r} we denote sum over the particles that are in a neighborhood of the point with the coordinate $\boldsymbol{r}$.

The next steps are the following: Step 1: Passage to the entropy representation and specification of the dissipative thermodynamic forces and the dissipative potential Ξ. Step 2: Specification of the thermodynamic potential ϕ. Step 3: Recasting of the equation governing the time evolution of the n_p-particle distribution function f_{n_p} into a Liouville equation corresponding to the time evolution of n_p particles (or $n_\mathrm{p}'^{\leftarrow}$quasi-particles, $n_\mathrm{p}' > n_\mathrm{p}$ —see the point 4 below) that then represent the governing equations of direct molecular simulations.

We shall leave to interested readers to make these three steps (see also Grmela (1993) where a similar approach is taken but only for isothermal fluids). We end this section with a few observations about Equations (106).

1. We note that the n_p-particle kinetic equation in (106) implies that

$$\dot{\boldsymbol{r}}_i = \leftarrow \frac{\partial \varphi_{f_{n_\mathrm{p}}}}{\partial \boldsymbol{v}_i} + \varphi_{u(\boldsymbol{r})} \tag{109}$$

   if φ involves the kinetic energy $\int \mathrm{d}\boldsymbol{r} u^2/2\rho + \int \mathrm{d}\boldsymbol{r}_1 \int \mathrm{d}\boldsymbol{v}_1 \cdots \int \mathrm{d}\boldsymbol{r}_{n_\mathrm{p}} \int \mathrm{d}\boldsymbol{v}_{n_\mathrm{p}} f_{n_\mathrm{p}} \sum_{i=1}^{n_\mathrm{p}} \boldsymbol{v}_i^2/2m$ then (109) shows that the velocities $(v_1,\ldots, \boldsymbol{v}_{n_\mathrm{p}})$ are the peculiar velocities (i.e., the velocities modulo the overall velocity) of the simulated particles.
2. If we omit the last two terms in the kinetic equation (involving gradients of ρ and η) then (106) implies

$$\dot{\boldsymbol{v}}_i = -\frac{\partial \varphi_{f_{n_\mathrm{p}}}}{\partial \boldsymbol{r}_i} - \boldsymbol{v}_i \frac{\partial \varphi_u}{\partial \boldsymbol{r}} \tag{110}$$

The first term on the right-hand side of (110) is the gradient of the particle potential energy and the second term the force induced by the imposed gradient of the overall flow.

3. We note that the second term in (108) is the familiar Kirkwood expression for the stress tensor in terms of the n-particle distribution function.
4. The kinetic equation (the last equation in (106)) is, in general, a nonlinear equation and as such it cannot be seen as being exactly equivalent to a Liouville equation corresponding to ordinary differential equations representing the time evolution of n_{p} particles. The nonlinearity of the kinetic equation becomes apparent in particular in terms of involving the entropy (or alternatively the temperature). In order to proceed with recasting the n_{p}-particle kinetic equation into a set of $6n_{\mathrm{p}}$ ordinary differential equations governing the time evolution of the n_{p} particles, we have to make an approximation which, in general, will bring into the picture other particles (called quasiparticles or also "ghost" particles) representing collective features. Such features are described by the distribution function but are not described by the position coordinate and momenta of the n_{p} particles. They can however be brought (but only approximately) into the formulation as the time evolution of some kind of quasiparticles. How to make this type of approximation and keep at the same time the GENERIC structure (55) remains an open problem.

4. MULTISCALE NONEQUILIBRIUM THERMODYNAMICS OF DRIVEN SYSTEMS

The time evolution that has been investigated in Section 3 is the time evolution seen experimentally in externally unforced macroscopic systems approaching, as $t \to \infty$, equilibrium states at which their behavior is seen experimentally to be well described by classical equilibrium thermodynamics. In other words, in Section 3, we have investigated the time evolution

$$\mathcal{L}_{\mathrm{meso}\ 1} \to \mathcal{L}_{\mathrm{eth}} \tag{111}$$

where $\mathcal{L}_{\mathrm{meso}\ 1}$ is a symbol denoting a mesoscopic level (e.g., the level of kinetic theory) on which $x_1 \epsilon M_1$ serves as a state variable and $\mathcal{L}_{\mathrm{eth}}$ denotes the level of classical equilibrium thermodynamics (discussed in Section 2) on which $y \in N$ serves as a state variable. We recall the main features of (111) that are all displayed in (50) and in the associated with it Gibbs Legendre manifold $\mathcal{M}_1^{\mathcal{N}}$:

$$(I) \tag{112}$$

The thermodynamic potential $\varphi(x_1, y^*) = -h(x_1) + <y^*, y(x_1)>$; $h(x_1)$ *is the eta-function;* $y(x_1)$ *is the projection* $M_1 \to N$ *of* x_1 *on y. The potential* φ *plays the role of the Lyapunov function associated with the approach (111).*

$$(II) \tag{113}$$

The Invariant manifold $M_{\mathrm{eth}} \subset M_1$ *composed of equilibrium states* $(x_1)_{\mathrm{eth}}(y^*) \in M_1$*. This manifold is invariant with respect to the time evolution taking place on* M_1*, and its elements are states on which the thermodynamic potential* $\varphi(x_1, y^*)$ *reaches its minimum if considered as a function of* $x_1 \epsilon M_1$.

$$(III) \tag{114}$$

No time evolution takes place on M_{eth}.

$$(IV) \tag{115}$$

The fundamental thermodynamic relation $\varphi^*(y^*) = \varphi((x_1)_{\mathrm{eth}}(y^*), y^*))$

We recall that both the manifold M_{eth} and the fundamental thermodynamic relations φ^* are displayed on the manifold $\mathcal{M}^{\mathcal{N}}|_{x^*=0}$ (see the text following (6)).

Experimental observations of the time evolution of externally unforced macroscopic systems on the level $\mathcal{L}_{\mathrm{meso}\ 1}$ show that the level $\mathcal{L}_{\mathrm{eth}}$ of classical equilibrium thermodynamics is not the only level offering a simplified description of appropriately prepared macroscopic systems. For example, if $\mathcal{L}_{\mathrm{meso}\ 1}$ is the level of kinetic theory (Sections 2.2.1, starting point. In order to see the approach 2.2.2, and 3.1.3) then, besides the level, also the level of fluid mechanics (we shall denote it here $\mathcal{L}_{\mathrm{eth}}$) emerges in experimental observations as a possible simplified description of the experimentally observed time evolution. The preparation process is the same as the preparation process for $\mathcal{L}_{\mathrm{eth}}$ (i.e., the system is left sufficiently long time isolated) except that we do not have to wait till the approach to equilibrium is completed. If the level of fluid mechanics indeed emerges as a possible reduced description, we have then the following four types of the time evolution leading from a mesoscopic to a more macroscopic level of description: (i) $\mathcal{M}_{\mathrm{slow}}$, (ii) $\mathcal{L}_{\mathrm{meso}\ 2} \to \mathcal{L}_{\mathrm{eth}}$, (iii) $\mathcal{L}_{\mathrm{meso}\ 1} \to \mathcal{L}_{\mathrm{meso}\ 2}$, and (iv) $\mathcal{L}_{\mathrm{meso}\ 1} \to \mathcal{L}_{\mathrm{meso}\ 2} \to \mathcal{L}_{\mathrm{eth}}$. The first two are the same as (111). We now turn our attention to the third one, that is,

$$\mathcal{L}_{\mathrm{meso}\ 1} \to \mathcal{L}_{\mathrm{meso}\ 2} \tag{116}$$

We shall call the time evolution involved in (116) a *fast time evolution* and the time evolution taking place on $\mathcal{L}_{\mathrm{meso}\ 2}$ a *slow time evolution*. We can use this terminology also for $\mathcal{L}_{\text{meso }1} \rightarrow \mathcal{L}_{\text{eth}}$. The slow time evolution is in this case indeed very slow. It is no (or we can also say still) time evolution.

Before starting to discuss (116), we make an observation. The fast time evolution (116) is also observed in driven systems that cannot be described on the level $\mathcal{L}_{\text{eth}}$. For example, let us consider the Rayleigh–Bénard system (i.e., a horizontal layer of a fluid heated from below). It is well established experimentally that this externally driven system does not reach thermodynamic equilibrium states but its behavior is well described on the level of fluid mechanics (by Boussinesq equations). This means that if we describe it on a more microscopic level, say the level of kinetic theory, then we shall observe the approach to the level of fluid mechanics. Consequently, the comments that we shall make below about (116) apply also to driven systems and to other types of systems that are prevented from reaching thermodynamical equilibrium states (as, e.g., glasses where internal constraints prevent the approach to $\mathcal{L}_{\text{eth}}$).

We propose that the fast time evolution (116) is governed by the same equations as those governing the time evolution involved in $\mathcal{L}_{\text{meso }1} \rightarrow \mathcal{L}_{\text{meso }2}$ (discussed in Section 3) with only a few necessary modifications.

$$(I) \tag{117}$$

The thermodynamic potential $\varphi(x_1, \overset{*}{x_2}) = -h(x_1) + \langle \overset{*}{x_2}, x_2(x_1)\rangle$; $h(x_1)$ *is the eta-function,* $x_2 = x_2(x_1)$ *is the projection* $M_1 \rightarrow M_2$ *of* x_1 *on* x_2. *The potential* ϕ *plays the role of the Lyapunov function associated with the approach* $\mathcal{L}_{\text{meso }1} \rightarrow \mathcal{L}_{\text{meso }2}$.

$$(II) \tag{118}$$

The quasi-invariant manifold $M_{\text{slow}} \subset M_1$ *composed of slow states* $(x_1)_{\text{slow}}(\overset{*}{x_2}) \epsilon M_1$. *This manifold is quasi-invariant with respect to the time evolution taking place on* M_1, *and its elements are states on which the thermodynamic potential* $\varphi(x_1, \overset{*}{x_2})$ *reaches its minimum if considered as a function of* $x_1 \epsilon M_1$.

As we have already pointed out in Section 3, our primary knowledge of macroscopic systems comes from observing their time evolution. To provide the space M with time evolution means to provide it with a vector field. We can thus visualize M equipped with a vector field as M filled with arrows providing the orders to move. The manifold M_{eth} is the manifold of fixed points, i.e., the points to which there is no arrow attached. It is much more difficult to recognize M_{slow} than to recognize M_{eth}. Roughly speaking, in order to recognize M_{slow}, we look for a manifold (a submanifold of M_1, imagine it as a surface imbedded in M) on which the arrows filling the space M_1 will appear to be attached in such a way that they are as much as possible tangent to the surface (if they are exactly tangent then the surface is exactly invariant with respect to the time evolution) and relatively small (guaranteeing that the time evolution taking place on M_{slow} will be slow). We have to emphasize that the whole picture of M filled with arrows is coordinate dependent. It changes by changing the way the elements $x \in M$ are represented (i.e., by making one-to-one nonlinear transformations of x). The recognition of an appropriate M_{slow} is thus a sort of pattern recognition process involving a play with different views (in different coordinate systems) of M. In addition, in order to be able to see more clearly the pattern and the extent of the invariance of M_{slow}, the passing from arrows to trajectories or at least to pieces of trajectories (i.e., the governing equations have to be solved or at least partially solved) has to be made. The manifold M_{slow} emerging in the process is not anymore an invariant manifold as M_{eth} but a quasi-invariant manifold. It is difficult to give a precise definition of a "quasi-invariant manifold". Examples (some of which are presented below) provide the best way to explain this important concept.

$$(III) \tag{119}$$

Slow time evolution takes place on M_{slow}.

While there is, of course, no interest in the slow time evolution in the discussion of $\mathcal{L}_{\mathrm{meso}\ 1} \to \mathcal{L}_{\mathrm{eth}}$, since the slow time evolution is in this case no time evolution, this point is the main focus of the investigation of reduced descriptions (see, e.g., Gorban and Karlin, 2005; Yablonskii et al., 1991). The lack of interest in the point (III) (see (114)) in the context of $\mathcal{L}_{\mathrm{meso}\ 1} \to \mathcal{L}_{\mathrm{eth}}$ then also means the lack of interest in the manifold M_{eth}, i.e., in the point (II) (see (113)).

$$(IV) \tag{120}$$

The slow fundamental thermodynamic relation

The main difference between $\overset{*}{\varphi}_{\mathrm{slow}}(\overset{*}{x}_2) = \varphi((x_1)_{\mathrm{slow}}(\overset{*}{x}_2), \overset{*}{x}_2))$ and $\mathcal{L}_{\mathrm{meso}\ 1} \to \mathcal{L}_{\mathrm{meso}\ 2}$ is that the focus in the investigation of $\mathcal{L}_{\mathrm{meso}\ 1} \to \mathcal{L}_{\mathrm{eth}}$ is put on the points (III) and (II) (see (119),(118)) while the focus in the investigation of $\mathcal{L}_{\mathrm{meso}\ 1} \to \mathcal{L}_{\mathrm{meso}\ 2}$ is put on the points (I) and (IV) (see (112),(115)). The most important message that we want to convey in this section is that *attention should be paid also to the points (I) and (IV) in the investigation of the reduction* $\mathcal{L}_{\mathrm{meso}\ 1} \to \mathcal{L}_{\mathrm{eth}}$. Even if the slow time evolution is certainly the main output of the investigation of $\mathcal{L}_{\mathrm{meso}\ 1} \to \mathcal{L}_{\mathrm{meso}\ 2}$, the fast time evolution complementing the slow time evolution provides an additional useful information. It provides the fundamental thermodynamic relation in the space in which the slow time evolution takes place. We shall call it a "*slow fundamental thermodynamic relation*." The slow dynamics and the slow fundamental thermodynamic relation are two features of the reduced description inherited from the more microscopic space $\mathcal{L}_{\text{meso }1} \to \mathcal{L}_{\text{meso }2}$. If seen only on the reduced level $M_{\text{meso }1}$, these two features are independent of each other. Since $\mathcal{L}_{\text{meso }2}$ applies also to driven systems, the slow fundamental thermodynamic relation introduces thermodynamics into the investigation of driven systems (Grmela, 1993a)

We shall not enter here into the general formulation in the context of contact geometry. Instead, we shall only work out two examples.

4.1 Example: a simple illustration

We take the level $\mathcal{L}_{\text{meso }1}$ to be the level discussed in Section 3.1.1 (we shall now use $x_1 \epsilon M_1$ instead of $x \epsilon M$ to denote the state variables) and the level $\mathcal{L}_{\text{meso }2}$ on which

$$x_2 = (q, \epsilon, \nu) \tag{121}$$

serve as state variables and

$$\begin{aligned} \dot{q} &= \Lambda_2 h_q \\ \dot{\epsilon} &= 0 \\ \dot{\nu} &= 0 \end{aligned} \tag{122}$$

govern their time evolution; $\Lambda(\epsilon,\nu) > 0$ is a material parameter. The physical system that we can think of being represented by (121) and (122) is a glass. The state variable q is a kind of free volume. Due to internal constraints, the material parameter $\Lambda_2(\epsilon,\nu)$ becomes very small for some (ϵ,ν) which then means that the approach to equilibrium (i.e., to the state at which $h_q = 0$) is prevented and the system "freezes" in a state out of equilibrium.

The projection $x_1 \to x_2$ is given by:

$$(q, p, \epsilon, \nu) \mapsto (q, \epsilon, \nu) \tag{123}$$

As for the eta-function $h(q, p, \epsilon, \nu)$, we choose it to be

$$h(q, p, \epsilon, \nu) = h(q, \epsilon, \nu) - \frac{1}{2} a p^2, \tag{124}$$

where $h(p, \epsilon, \nu)$ is the eta-function on the level $\mathcal{L}_2$, and $a > 0$ is a material parameter. The time evolution Equations (62) thus become

$$\begin{aligned}\dot{q} &= \frac{ap}{h_\epsilon}\\ \dot{p} &= \frac{h_q}{h_\epsilon} - \Lambda ap\\ \dot{\epsilon} &= 0\\ \dot{\nu} &= 0\end{aligned} \tag{125}$$

In order to identify the manifold $M_{\text{slow}} \subset M_1$ we assume that λ in (125) is large and that p has already reached its stationary value determined by equating the right-hand side of the second equation in (125) to zero. We note that if we interpret p as a momentum corresponding to q then the above assumption has the physical meaning of applying a large friction force and neglecting inertia. As a consequence of the assumption we obtain

$$M_{\text{slow}} = \left\{ (q, p, \epsilon, \nu) \epsilon M_1 \,|\, p = \leftarrow \frac{1}{\Lambda a} \frac{h_q}{h_\epsilon} \right\} \tag{126}$$

The slow time evolution on M_1 (i.e., the time evolution on M_1 restricted to M_{slow}) is governed by

$$\begin{aligned}\dot{q} &= \frac{1}{\Lambda (h_\epsilon)^2} h_q\\ \dot{\epsilon} &= 0\\ \dot{\nu} &= 0\end{aligned} \tag{127}$$

If we compare (127) with (122), we see that the reduction process brought us the following relation between the material parameters λ introduced on the level $\mathcal{L}_{\text{meso }1}$ and λ_2 introduced on the level $\mathcal{L}_{\text{meso }2}$:

$$\Lambda_2 = \frac{1}{\Lambda (h_\epsilon)^2} \tag{128}$$

Everything that we have done so far in this example is completely standard. The next step in which we identify the slow fundamental thermodynamic relation in the state space M_2 (i.e., we illustrate the point (IV) (see (120))) is new. Having found the slow manifold M_{slow} in an analysis of the time evolution in M_1, we now find it from a thermodynamic potential. We look for the thermodynamic potential $\varphi(q, p, \epsilon, \nu, q^*, \epsilon^*, \nu^*)$ so that the manifold M_{slow} arises as a solution to

$$\varphi_\epsilon = 0, \quad \varphi_\nu = 0, \quad \varphi_q = 0, \quad \varphi_p = 0 \tag{129}$$

We look for φ in the form

$$\varphi(e, q, p; q^*, e^*) = -h(\epsilon, \nu, q, p) + e^* \epsilon + n^* \nu + q^* q + p^* (q^*, e^*, n^*) p \tag{130}$$

where $p^* = p^*(q^*, e^*, n^*)$ is a function to be specified. We easily verify that with

$$p^* = -\frac{q^*}{\Lambda e^*} \tag{131}$$

solutions to (129) is the slow manifold M_{slow}.

Finally, the fast time evolution (i.e., the time evolution governing the approach to the slow time evolution on M_{slow} governed by (122), (128)) is governed by

$$\dot{p} = -\Lambda \varphi_p \tag{132}$$

and the slow fundamental thermodynamic relation (i.e., φ evaluated on the slow manifold M_{slow}) becomes

$$h^*_{\text{slow}}(e^*, n^*, q^*) = h^*(e^*, n^*, q^*) - \frac{1}{2a\Lambda^2}\left(\frac{q^*}{e^*}\right)^2 \tag{133}$$

which $h^*(e^*, n^*, q^*)$ is the dual form of the eta-function $h(e, n, q)$.

4.2 Example: Chapman–Enskog reduction of kinetic theory to fluid mechanics

In this illustration we take the level L_1 to be the level of kinetic theory (see Section 3.1.3), the level L_2 the level of fluid mechanics (see Section 3.1.4), and the projection $x_2 = x_2(x_1)$ is given by

$$\begin{aligned} \rho(\boldsymbol{r}) &= \int \mathrm{d}\boldsymbol{v}\, m\, n(\boldsymbol{r}, \boldsymbol{v}) \\ u(\boldsymbol{r}) &= \int \mathrm{d}\boldsymbol{v}\, \boldsymbol{v}\, n(\boldsymbol{r}, \boldsymbol{v}) \\ e(\boldsymbol{r}) &= \int \mathrm{d}\boldsymbol{v} \frac{\boldsymbol{v}^2}{2m} n(\boldsymbol{r}, \boldsymbol{v}) \end{aligned} \tag{134}$$

Reduction of kinetic theory to fluid mechanics is historically the first example of a successful reduction of a mesoscopic dynamical theory to a more macroscopic dynamical theory. The method (called the Chapman–Enskog method) that was invented by Chapman and Enskog for this particular reduction remains still a principal inspiration for all other types of reduction (see, e.g.,. Gorban and Karlin, 2003, 2005), Yablonskii et al., 1991). In this example we briefly recall the geometrical viewpoint of the Chapman–Enskog method. We shall also illustrate the point (IV) (see (120)). This illustration is a new result in the Chapman–Enskog reduction.

The setting for our discussion is the space M_1 equipped with the vector field $(v.f.)_1$ and the mapping $pr_{1\to 2}: M_1 \to M_2$. Our problem is to equip the space M_2 with a vector field $(v.f.)_2$ that is inherited from the vector field $(v.f.)_1$ in M_1. The elements x_1 of M_1 are the distribution functions (7); the elements x_2 of M_2 are the hydrodynamic fields (85).

We shall organize the Chapman–Enskog reduction into four steps: (*Step 1*) Initial suggestion $M_{\mathrm{slow}}^{(0)} \subset M_1$ for the slow manifold $M_{\mathrm{slow}} \subset M_1$ is made. It is a manifold that has a one-to-one relation with the space M_2. We can regard it as an imbedding of M_2 in M_1. (*Step 2*) The vector field $(v.f.)_1$ is projected on $M_{\mathrm{slow}}^{(0)}$ (i.e., $(v.f.)_1^{(0)}$ denoting the vector field $(v.f.)_1$ attached to a point of $M_{\mathrm{slow}}^{(0)}$, is projected on the tangent plane of $M_{\mathrm{slow}}^{(0)}$ at that point). The projected vector field is denoted by the symbol $(v.f.)_1^{M_{\mathrm{slow}}^{(0)}}$. (*Step 3*) The slow manifold $M_{\mathrm{slow}}^{(0)}$ is deformed into $M_{\mathrm{slow}}^{(1)}$ in such a way that the difference between $(v.f.)_1^{(1)}$ attached to a point of $M_{\mathrm{slow}}^{(1)}$ and its projection $(v.f.)_1^{M_{\mathrm{slow}}^{(1)}}$ becomes smaller (as small as possible) than for the slow manifold $M_{\mathrm{slow}}^{(0)}$. (*Step 4*) The slow fundamental thermodynamic relations associated with the slow manifolds $M_{\mathrm{slow}}^{(0)}$ and $M_{\mathrm{slow}}^{(1)}$ are identified.

Step 1

The dominant term in the Boltzmann Equation (84) is assumed to be the collision term, i.e., the second term on the right-hand side of (84). This then implies that, as $t \to \infty$, solutions to Equation (82), denoted $n^{(0)}(\boldsymbol{r}, \boldsymbol{v}; \rho, \boldsymbol{u}, e)$ represent a good approximation to the asymptotic solution to (84). Consequently, we choose

$$M_{\mathrm{slow}}^{(0)} = \left\{ n(\boldsymbol{r}, \boldsymbol{v}) \epsilon M_1 | n(\boldsymbol{r}, \boldsymbol{v}) = n^{(0)}(\boldsymbol{r}, \boldsymbol{v}; \rho, \boldsymbol{u}, e) \right\} \tag{135}$$

Equivalently, $M_{\mathrm{slow}}^{(0)} = \{ n(\boldsymbol{r}, \boldsymbol{v}) \epsilon M_1 | X = 0 \}$, where X is the thermodynamic force given in (79). The elements of $M_{\mathrm{slow}}^{(0)}$ are the local Maxwell distribution functions. They are denoted hereafter by the symbol $n^{(0)}(\boldsymbol{r}, \boldsymbol{v}; \rho, \boldsymbol{u}, e)$.

Step 2

The vector fields $(\boldsymbol{v}.f.)_1$ $(\boldsymbol{v}.f.)_1^{(0)}$ $(\boldsymbol{v}.f.)_1^{M_{\mathrm{slow}}^{(0)}}$ and $(\boldsymbol{v}.f.)_2^{(0)}$ are given by

$$
\begin{aligned}
&(\boldsymbol{v}.f.)_1 \text{ is given by the right hand side of (84)}\\
&(v.f.)_1^{(0)} = \left[-\frac{1}{m} v_i \frac{\partial n}{\partial \boldsymbol{r}_i}\right]_{n=n^{(0)}}\\
&(v.f.)_2^{(0)} = \left(\left((v.f.)_2^{(0)}\right)^{(\rho)}, \left((v.f.)_2^{(0)}\right)^{(u)}, \left((v.f.)_2^{(0)}\right)^{(e)}\right)\\
&\qquad\qquad = \left(-\int \mathrm{d}\boldsymbol{v}\left[v_j \frac{\partial n}{\partial r_j}\right]_{n=n^{(0)}}, -\int \mathrm{d}\boldsymbol{v}\left[\boldsymbol{v} v_j \frac{\partial n}{\partial r_j}\right]_{n=n^{(0)}}, -\int \mathrm{d}\boldsymbol{v}\left[\frac{\boldsymbol{v}^2}{2m} v_j \frac{\partial n}{\partial r_j}\right]_{n=n^{(0)}}\right)\\
&(v.f.)_1^{M_{\text{slow}}^{(0)}} = \left(\frac{\partial n^{(0)}}{\partial \rho(\boldsymbol{r})}\left((v.f.)_2^{(0)}\right)^{(\rho)}, \frac{\partial n^{(0)}}{\partial \boldsymbol{u}(\boldsymbol{r})}\left((v.f.)_2^{(0)}\right)^{(u)}, \quad \frac{\partial n^{(0)}}{\partial e(\boldsymbol{r})}\left((v.f.)_2^{(0)}\right)^{(e)}\right)
\end{aligned}
\tag{136}
$$

The vector field $(v.f.)_2^{(0)}$ is the pull back of $(v.f.)_1^{M_{\text{slow}}^{(0)}}$ by the mapping $(e(\boldsymbol{r}), \rho(\boldsymbol{r}), \boldsymbol{u}(\boldsymbol{r})) \to n^{(0)}(\boldsymbol{r}, \boldsymbol{v}; \rho, \boldsymbol{u}, e)$.

It is easy to verify that the slow time evolution on M_2 corresponding to the choice (135) of the slow manifold (i.e., the time evolution governed by the vector field $(v.f.)_2^{(0)}$) is the Euler time evolution (see (95) with $\lambda = 0$; $\eta = 0$; $\eta_{\text{vol}} = 0$).

Step 3

If the vector field $(v.f.)_1^{(0)}$ (i.e., the vector field $(v.f.)_1$ evaluated on the slow manifold $M_{\text{slow}}^{(0)}$ is identical to the vector field $(v.f.)_1^{M_{\text{slow}}^{(0)}}$ then the slow manifold $M_{\text{slow}}^{(0)}$ is invariant (i.e., any trajectory that starts on it remains on it). However, $(v.f.)_1^{M_{\text{slow}}^{(0)}} \neq (v.f.)_1^{M_{\text{slow}}^{(0)}}$ and consequently $(v.f.)_1^{(0)}$ sticks out of the slow manifold $M_{\text{slow}}^{(0)}$ and $M_{\text{slow}}^{(0)}$ is thus not invariant. Following Chapman and Enskog we shall now deform the slow manifold $M_{\text{slow}}^{(0)}$ into $M_{\text{slow}}^{(1)}$ with the objective to make $M_{\text{slow}}^{(1)}$ "more invariant" than $M_{\text{slow}}^{(0)}$ (i.e., the vector field $(v.f.)_1$ evaluated on the deformed manifold will stick less out of it than $(v.f.)_1$ evaluated on $M_{\text{slow}}^{(0)}$ sticks out of $M_{\text{slow}}^{(0)}$. The deformation is made by passing from $n^{(0)}(\boldsymbol{r},\ \boldsymbol{v};\ \rho,\ \boldsymbol{u},\ e)ton^{(1)}(\boldsymbol{r},\ \boldsymbol{v};\ \rho,\ \boldsymbol{u},\ e)$ that is a solution to

$$
\begin{aligned}
(v.f.)_1^{M_{\text{slow}}^{(0)}} - (v.f.)_1^{(0)} = \ &\int \mathrm{d}\boldsymbol{v}_1 \int \mathrm{d}\boldsymbol{v}' \int \mathrm{d}\boldsymbol{v}_1'\ W^{\text{Boltzmann}}(n;\ \boldsymbol{v}, \boldsymbol{v}_1,\ \boldsymbol{v}',\ \boldsymbol{v}_1')\\
&\times\left(n^{(1)}(\boldsymbol{r},\ \boldsymbol{v}')n^{(1)}(\boldsymbol{r},\ \boldsymbol{v}_1') - n^{(1)}(\boldsymbol{r},\ \boldsymbol{v})n^{(1)}(\boldsymbol{r},\ \boldsymbol{v}_1)\right)
\end{aligned}
\tag{137}
$$

The new slow manifold will be

$$
M_{\text{slow}}^{(1)} = \left\{n(\boldsymbol{r},\ \boldsymbol{v})\epsilon M_1 | n(\boldsymbol{r},\ \boldsymbol{v}) = n^{(1)}(\boldsymbol{r},\ \boldsymbol{v}; \rho,\ \boldsymbol{u},\ e)\right\}
\tag{138}
$$

How shall we solve Equation (137)? Again, following Chapman and Enskog, we assume that the deformation from $n^{(0)}(\boldsymbol{r},\ \boldsymbol{v};\ \rho,\ \boldsymbol{u},\ e)$ to $n^{(1)}(\boldsymbol{r},\ \boldsymbol{v};\ \rho,\ \boldsymbol{u},\ e)$ is small. We thus introduce $n^{(1)}(\boldsymbol{r},\ \boldsymbol{v}';\ \rho,\ \boldsymbol{u},\ e) = n^{(0)}(\boldsymbol{r},\ \boldsymbol{v}';\ \rho,\ \boldsymbol{u},\ e)\left(1+\nu^{(1)}(\boldsymbol{r},\ \boldsymbol{v};\ \rho,\ \boldsymbol{u},\ e)\right)$, consider $\nu^{(1)}(\boldsymbol{r},\ \boldsymbol{v};\ \rho,\ \boldsymbol{u},\ e)$ as small, and replace (137) by its linearized version

$$\begin{aligned}(v.f.)_1^{M^{(0)}_{\text{slow}}} - (v.f.)_1^{(0)} = &\int d\boldsymbol{v}_1 \int d\boldsymbol{v}' \int d\boldsymbol{v}'_1\, W^{\text{Boltzmann}}\,(n;\ \boldsymbol{v},\ \boldsymbol{v}_1,\ \boldsymbol{v}',\ \boldsymbol{v}'_1)\\ &\times n^{(0)}(\boldsymbol{r},\ \boldsymbol{v}';\ \rho,\ \boldsymbol{u},\ e)n^{(0)}(\boldsymbol{r},\ \boldsymbol{v}'_1;\ \rho,\ \boldsymbol{u},\ e)\\ &\times \left(\nu^{(1)}(\boldsymbol{r},\ \boldsymbol{v}',\ \rho,\ \boldsymbol{u},\ e) + \nu^{(1)}(\boldsymbol{r},\ \boldsymbol{v}'_1,\ \rho,\ \boldsymbol{u},\ e)\right.\\ &\left. -\nu^{(1)}(\boldsymbol{r},\ \boldsymbol{v},\ \rho,\ \boldsymbol{u},\ e) - \nu^{(1)}(\boldsymbol{r},\ \boldsymbol{v}_1,\ \rho,\ \boldsymbol{u},\ e)\right)\end{aligned} \tag{139}$$

This is a linear integral equation for the unknown function $\nu^{(1)}(\boldsymbol{r},\ \boldsymbol{v};\ \rho,\ \boldsymbol{u},\ e)$. To find its solution is a technical problem that we shall ignore here and consider hereafter $\nu^{(1)}(\boldsymbol{r},\ \boldsymbol{v}_1,\ \rho,\ \boldsymbol{u},\ e)$ and thus $n^{(1)}(\boldsymbol{r},\ \boldsymbol{v}_1,\ \rho,\ \boldsymbol{u},\ e)$ and consequently (see (138)) the slow manifold $M^{(1)}_{\text{slow}}$ to be known.

The slow time evolution corresponding to the slow manifold $M^{(1)}_{\text{slow}}$ is governed by the vector field $(\boldsymbol{v}.f.)_1^{(1)}$ that is the same as $(\boldsymbol{v}.f.)_1^{(1)}$ introduced in (136) except that $\nu^{(0)}(\boldsymbol{r},\ \boldsymbol{v}_1,\ \rho,\ \boldsymbol{u},\ e)$ is replaced by $\nu^{(1)}(\boldsymbol{r},\ \boldsymbol{v}_1,\ \rho,\ \boldsymbol{u},\ e)$. When explicitly calculated, the slow time evolution equation turns out to be the Navier–Stokes–Fourier Equation (95) with the kinetic coefficients $\lambda,\ \eta,\ \eta_{\text{vol}}$ expressed in terms of $W^{\text{Boltzmann}}$.

With this result, the investigation of the reduction usually ends. There are, of course, many questions that remain unanswered. For example, what would be the next improvement in the search for the slow manifold (i.e., what is the manifold $M^{(2)}_{\text{slow}}$)? How shall we address the fact that we have succeeded to relate two theories belonging to two different levels of description but with the domains of applicability that hardly have a common intersection? Indeed, the domain of applicability of fluid mechanics, regarded as an autonomous theory, are fluids (e.g., water) and the domain of applicability of the Boltzmann kinetic theory are gases (e.g., air). We shall not discuss here these questions but proceed to illustrate the point (IV) (see (120)) of the reduction process. The observations made in the rest of this section are new.

Step 4

We shall make the fourth step. We shall make it first for the slow manifold $M^{(0)}_{\text{slow}}$and then for its deformation $M^{(1)}_{\text{slow}}$.

The slow manifold $M^{(0)}_{\text{slow}}$

Let the slow manifold be $M^{(0)}_{\text{slow}}$ (see 135) and the slow time evolution the Euler equations generated by the vector field $(v.f.)_2^{(0)}$ (see 136)). We look for the thermodynamic potential $\phi^{(0)}$ such that $M^{(0)}_{\text{slow}} = \left\{ n(\boldsymbol{r},\ \boldsymbol{v}) \epsilon M_1 \middle| \left(\varphi^{(0)}\right)_{n(\boldsymbol{r},\boldsymbol{v})} = 0 \right\}$. We easily verify that

$$\begin{aligned} \varphi^{(0)}\left(n(\boldsymbol{r},\ \boldsymbol{v}),\ \rho^*(\boldsymbol{r}),\ \boldsymbol{u}^*(\boldsymbol{r}),\ e^*(\boldsymbol{r})\right) = & -h^{(0)}(n) \\ & + \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{v}\, e^*(\boldsymbol{r}) \frac{\boldsymbol{v}^2}{2m} n(\boldsymbol{r},\ \boldsymbol{v}) \\ & + \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{v}\, \rho^*(\boldsymbol{r}) n(\boldsymbol{r},\ \boldsymbol{v}) \\ & + \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{v}\, \boldsymbol{u}^*_j(\boldsymbol{r}) \boldsymbol{v}_j n(\boldsymbol{r},\ \boldsymbol{v}) \end{aligned} \tag{140}$$

where $h^{(0)}(n)$ is the Boltzmann eta-function (9).

The thermodynamic potential evaluated on $M^{(0)}_{\text{slow}}$ (i.e., $\varphi^{(0)}|_{n \epsilon M^{(0)}_{\text{slow}}}$) becomes the fundamental thermodynamic relation of an ideal gas which differs from (13) only by the local nature of the state variables (i.e., the state variables depend on the position coordinate $\boldsymbol{r}$) and by the presence of the momentum $\boldsymbol{u}(\boldsymbol{r})$. This is the slow fundamental thermodynamic relation corresponding to the slow manifold $M^{(0)}_{\text{slow}}$.

The fast time evolution, i.e., the time evolution describing the approach the slow manifold, is governed by (82) (i.e., $M^{(0)}_{\text{slow}}$ with the dissipation potential Ξ given by (79) and with $\frac{\partial n}{\partial t} = \frac{\partial \Xi}{\partial n^*}$).

The slow manifold $n^*(\boldsymbol{r}, \boldsymbol{v}) = \frac{\partial h^{(0)}}{\partial n(\boldsymbol{r},\boldsymbol{v})}$

Now we turn to the slow manifold $M^{(1)}_{\text{slow}}$ and repeat the analysis that we have just made above for $M^{(0)}_{\text{slow}}$. We begin by looking for the thermodynamic potential $\varphi^{(1)}$ such that $M^{(1)}_{\text{slow}} = \left\{ n(\boldsymbol{r}, \boldsymbol{v}) \epsilon M_1 \middle| \left(\varphi^{(1)}\right)_{n(\boldsymbol{r},v)} = 0 \right\}$. We easily verify that

$$\begin{aligned} \varphi^{(1)}\left(n(\boldsymbol{r}, \boldsymbol{v}),\ \rho^*(\boldsymbol{r}),\ \boldsymbol{u}^*(\boldsymbol{r}),\ e^*(\boldsymbol{r})\right) = & -h^{(1)}(n;\ \rho^*,\ \boldsymbol{u}^*,\ e^*) \\ & + \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{v} e^*(\boldsymbol{r}) \frac{\boldsymbol{v}^2}{2m} n(\boldsymbol{r},\ \boldsymbol{v}) \\ & + \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{v} \rho^*(\boldsymbol{r}) n(\boldsymbol{r},\ \boldsymbol{v}) \\ & + \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{v} \boldsymbol{u}^*_j(\boldsymbol{r}) v_j n(\boldsymbol{r},\ \boldsymbol{v}) \end{aligned} \tag{141}$$

where

$$h^{(1)}\left(n, \rho^*, \boldsymbol{u}^*, e^*\right) = h^{(0)}(n) + \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{v} \nu^{(1)}\left(\boldsymbol{r}, \boldsymbol{v}; \rho^*, \boldsymbol{u}^*, e^*\right) n(\boldsymbol{r}, \boldsymbol{v}) \tag{142}$$

is such a potential provided the terms quadratic and higher order in $\nu^{(1)}$ are neglected. The slow fundamental thermodynamic relation is thus

$\varphi^{(1)}|_{n\in M^{(1)}_{\mathrm{slow}}}$. The fast time evolution, i.e., the time evolution describing the approach to the slow manifold $M^{(1)}_{\mathrm{slow}}$, is governed by $\frac{\partial n}{\partial t} = \frac{\partial \Xi}{\partial n^*}$ with the dissipation potential Ξ given by (79) and with $n^*(\boldsymbol{r}, \boldsymbol{v}) = \frac{\partial h^{(1)}}{\partial n(\boldsymbol{r}, \boldsymbol{v})}$.

5. CONCLUDING REMARKS

The titles of the first two papers (published in 1873) in which Gibbs (1984) completed the formulation of classical equilibrium thermodynamics () are: "Graphical methods in the thermodynamics of fluids" and "A method of geometrical representation of thermodynamic properties of substances by means of surfaces." This by itself clearly indicates the importance that Gibbs gave to geometry in thermodynamics and the importance that it played in his way of thinking about thermodynamics. In this review we have attempted to follow his lead. We have continued his geometrical viewpoint and extended it to multiscale formulations and to the time evolution. The resulting framework is intended to provide a basis for dealing with new challenges brought to chemical engineering by new emerging technologies (in particular then the nano- and biotechnologies). The framework embraces all scales and both equilibrium and nonequilibrium. In the illustrations developed in this review we have addressed multiscale fluid mechanics of complex fluids and multiscale chemical kinetics. Among the systems that are not included in the illustrations but that clearly need the multiscale framework for their investigation are heterogeneous systems (for a review of the research in this field that remains inside the classical nonequilibrium thermodynamics see Kjelstrup and Bedeaux (2008)). The multiscale viewpoint is essential in heterogeneous systems since the physics taking place on the boundaries and in the bulk requires typically different scales for their formulations. Other interesting lines of research that can be followed and further developed are indicated in Sections 3.1.3, 3.2.1, and 4.

Finally, we make a comment about the somewhat more-than-usual abstract character of the formalism used in this review. Any multiscale and combined equilibrium and nonequilibrium investigation has to be conducted in a setting that unifies the scales and is suitable for both statistics and dynamics. Since the formulations on every scale have been developed separately and in large extent independently of each other, the single scale formulations are typically very different one from the other (compare, e.g., the settings of fluid mechanics, kinetic theory, and classical mechanics of particles). Consequently, a setting allowing a unified formulation has to be inevitably abstract. Gibbs' success with using abstract geometrical tools in classical equilibrium thermodynamics is, of course, encouraging. Also another pioneer of chemical engineering, Leonhard Euler, encourages us to take more general viewpoints by saying: *La généralité que j'embrasse, au lieu d'éblouïr nos lumiéres, nous découvrira plutôt les véritables loix de la Nature dans tout leur èclat, et on y trouvera des raisons encore plus fortes, d'en admirer la beauté et la simplicité.*

ACKNOWLEDGMENT

The author acknowledges the financial support provided by the Natural Sciences and Engineering Research Council (NSERC) of Canada.

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