Complex fluids subjected to external influences

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Abstract

The aim of this paper is to develop a unifying framework for discussing dynamics and thermodynamics of externally driven fluids. Since the levels on which the driving force is defined and the dynamics is discussed are often different, the analysis is conducted and interpreted in the context of multilevel realizations (developed in this paper) of the unifying framework provided by generalized Hamiltonian structures. The framework is based on the experimentally established fact of the existence of reduced descriptions of both isolated and driven macroscopic systems. Thermodynamics of externally unforced as well as driven complex fluids arise from the general concept of thermodynamics introduced in the unifying framework. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

An interesting information is revealed in observations of reactions of complex fluids to external forces applied to them. In fact, most of what we know about complex fluids has been acquired in this type of observations. Among the frequently used external forces can be mentioned an imposed temperature or pressure, imposed mass and heat flows, and various forces applied on boundaries. The reactions may be observed in flow properties, stress–strain relations, light scattering, slow neutron scattering, and nuclear magnetic resonance measurements. The forces and the observations chosen in the investigation do not have to always belong to the same level. For example, a fluid can be kept under a constant temperature (an external force acting on the level of thermodynamics) while flows and stress–strain relations are observed (observations on the level of hydrodynamics).

The first question that has to be addressed in any theoretical analysis of externally forced complex fluids is how to formulate the action of forces defined on one level in the context of a dynamical theory formulated on another level. We address this question in Section 2. Taking inspiration from the Gibbs concept of ensembles we develop a setting of multilevel descriptions. In this setting the imposition of external forces takes the form of the imposition of constraints. In Section 3 we then discuss three types

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of such constraints: constraints expressing an imposition of temperature and pressure, an imposition of hydrodynamic flows, and various boundary conditions. In every case we formulate these constraints on the levels of hydrodynamics, kinetic theory, and microscopic (particulate) theories.

The analysis is conducted and interpreted in the unifying framework based on the experimentally established existence of the approach to reduced descriptions. Indeed, both isolated and driven systems are seen, after leaving them sufficiently long time without introducing new external forces, to be well described on a reduced level of description. The basic structure of the equations governing the approach is found by analyzing many examples on different levels of description, to be universal. The isolated and driven systems differ only in the state space of the reduced description and in the potentials generating the approach. These potentials, if evaluated at the states approached as the time goes to infinity, determine fundamental thermodynamic relations in the state space of the reduced description. If the fluid is isolated then the reduced state space can be chosen to be the state space of equilibrium thermodynamics and the fundamental thermodynamic relation obtained in this way is the familiar fundamental thermodynamic relation of equilibrium thermodynamics. If, on the other hand, the fluid is driven then the state space of the reduced description has to be chosen to be a state space that is more microscopic than the state space of the equilibrium thermodynamics and the resulting fundamental thermodynamic relation (in this case a relation in the state space chosen for the reduced description) represents a new thermodynamics of the driven fluid. It is worthwhile to emphasize that this viewpoint of thermodynamics of driven systems is new and very different from the viewpoints developed previously (see e.g. [1]). In the previous attempts the thermodynamics of driven systems was searched in the time evolution taking place in the reduced-description state space. We search it in a completely different time evolution, namely in the time evolution describing the approach of a more microscopic description to the reduced description. The potential needed in thermodynamics is then the potential associated with this approach. Since there is, in general, no approach involved in the time evolution in the reduced-description state space itself, there is no potential that can be associated with it, and consequently there is no thermodynamics of driven systems that can be based solely on the reduced-description time evolution. This conclusion has been also reached for example in [2].

Before starting our analysis, we shall make a comment about the type of mathematics that we shall use. As indicated above, our aim is to discuss complex macroscopic systems simultaneously on several levels of description. This then means that the concepts and the terminology that we shall use have to be such that our analysis remains meaningful on all levels of description (including for example the levels as different from the point of view of mathematical formulation as kinetic theory and classical hydrodynamics). Consequently, the concepts and the terminology that we shall use have to be sufficiently abstract and as such less familiar to many readers. It is important to realize and to accept that the nature of the subject that is under consideration in this paper makes the usage of less familiar mathematical concepts absolutely unavoidable.

2. Multilevel descriptions

Our aim in this section is to formulate action of external forces, like imposed hydrodynamic flows, in the context of kinetic and microscopic (particulate) theories. We achieve it by creating first an enlarged system in which the external forces become internal forces. The enlarged system is an isolated system that reaches, as the time goes to infinity, equilibrium states at which equilibrium thermodynamics is found

to provide an adequate description. The equations governing the time evolution of the enlarged system are constructed in such a way that their solutions are guaranteed to agree with the observed approach to equilibrium states. As the second step, we introduce in the state space of the enlarged system (denoted $\mathcal{M}$) various coordinates (fibrations) and identify the corresponding Hamiltonian kinematics (i.e. Poisson brackets). External forces are formulated as constraints in $\mathcal{M}$ equipped with appropriate coordinates. The constraints are discussed systematically in Section 3.

2.1. Grand-canonical-ensemble hierarchy

Gibbs has shown how to express the state variables of equilibrium thermodynamics on the microscopic (particulate) level. He realized that the first step that has to be made is to pass from the state space $\boldsymbol{M}$ whose elements are position coordinates, $\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n$ and momentum coordinates $\boldsymbol{v}_1, \ldots, \boldsymbol{v}_n$ (n is the number of particles composing the macroscopic system under consideration) to the infinite dimensional state space $\mathcal{M}$ whose elements are distribution functions of $(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n, \boldsymbol{v}_1, \ldots, \boldsymbol{v}_n)$. Gibbs interpreted the passage from $\boldsymbol{M}$ to $\mathcal{M}$ as the passage from considering one macroscopic system to considering an ensemble of them.

We shall establish the pattern of the discussion in the context of the grand canonical ensemble. We shall then follow this pattern in all examples discussed in this section. In order to be able to consider systems in which the number of particles is not fixed, we begin with a family of systems composed of $1, 2, 3, \ldots$ particles. The systems in the family are considered to be completely independent. We shall denote their corresponding state spaces by $\boldsymbol{M}_1, \boldsymbol{M}_2, \ldots$. Elements of $\boldsymbol{M}_1$ are $\boldsymbol{r}_1, \boldsymbol{v}_1$ (we shall use hereafter the abbreviated notation $\mathbf{1} \equiv (\boldsymbol{r}_1, \boldsymbol{v}_1), \mathbf{2} \equiv (\boldsymbol{r}_2, \boldsymbol{v}_2), \ldots$. Elements of $\boldsymbol{M}_2$ are $(\mathbf{1}, \mathbf{2}), \ldots$. Following Gibbs, we pass to the state spaces $\mathcal{M}_1, \mathcal{M}_2, \ldots$. Elements of $\mathcal{M}_1$ are distribution functions $\overline{f}_1(\mathbf{1})$, elements of $\mathcal{M}_2$ are $\overline{f}_2(\mathbf{1}, \mathbf{2}), \ldots$. We recall that due to the indistinguishability of the particles the distribution functions are symmetric with respect to the interchange of the labels of the particles. Next, we introduce

$$\mathcal{M} = \mathcal{M}_1 \times \mathcal{M}_2 \times \mathcal{M}_3 \times \cdots \tag{1}$$

(by $\times$ we denote the Cartesian product), its elements are

$$\overline{f} \equiv (\overline{f}_1, \overline{f}_2, \overline{f}_3, \ldots). \tag{2}$$

We note that the way $\mathcal{M}$ is defined in Eq. (1) provides $\mathcal{M}$ with coordinates (with a fibration). We regard $\overline{f}_1, \overline{f}_2, \ldots$ as coordinates of $\overline{f}$. The normalization of $\overline{f}$ will be discussed later in Eqs. (15) and (16).

Now, we turn our attention to the time evolution in $\mathcal{M}$. Since the system composed of $1, 2, \ldots$ particles are independent of one another, the time evolution of $\overline{f}_i, i = 1, 2, \ldots$ is governed by the Liouville equation. We shall write it in the form [3]

$$\frac{\partial \overline{f}_i}{\partial t} = \overline{L}_i (\overline{E}_i)_{\overline{f}_i}, \quad i = 1, 2, \ldots \tag{3}$$

where $\overline{E}_i$ is the energy of the system composed of i particles, $(\overline{E}_i)_{\overline{f}_i} := \partial \overline{E}_i / \partial \overline{f}_i$, where $\partial / \partial \overline{f}_i$ is the Volterra functional derivative; $\overline{L}_i$ is the operator, called Poisson bivector, transforming the covector $(\overline{E}_i)_{\overline{f}_i}$ into a vector. From the physical point of view, it expresses Hamiltonian kinematics of $\overline{f}_i$. With every

Poisson bivector $\overline{L}_i$ can be associated Poisson bracket

$$\overline{\{A, B\}}_i := \int d1 \cdots \int di\, A_{\overline{f}_i} \overline{L}_i B_{\overline{f}_i}, \tag{4}$$

where A, B are sufficiently regular real valued functions of $\overline{f}_i$, the Poisson bracket expressing the kinematics of $\overline{f}_i$ is (see [3])

$$\overline{\{A, B\}}_i = \int d1 \cdots \int di\, \overline{f}_i \sum_{k=1}^{i} \left(\frac{\partial}{\partial r_{k_\alpha}}(A_{\overline{f}_i}) \frac{\partial}{\partial v_{k_\alpha}}(B_{\overline{f}_i}) - \frac{\partial}{\partial r_{k_\alpha}}(B_{\overline{f}_i}) \frac{\partial}{\partial v_{k_\alpha}}(A_{\overline{f}_i}) \right). \tag{5}$$

We use in Eq. (5) and in the rest of this paper the summation convention over the repeated Greek indices $\alpha = 1, 2, 3$. The bracket (5) is a Poisson bracket which means that $\overline{\{A, B\}}_i = -\overline{\{B, A\}}_i$ (this is easily seen in Eq. (5)) and $\overline{\{A, \overline{\{B, C\}}_i\}}_i + \overline{\{B, \overline{\{C, A\}}_i\}}_i + \overline{\{C, \overline{\{A, B\}}_i\}}_i = 0$ (this relation, called Jacobi identity, is not easily seen in Eq. (5) but it can be verified by direct, albeit tedious, calculations; we recall that the Jacobi identity guarantees that the Poisson bracket is preserved during the time evolution (3) (i.e. $d/dt\overline{\{A, B\}}_i = \overline{\{\overline{\{A, B\}}_i, \overline{E}\}}_i$)). The time evolution in $\mathcal{M}$ is clearly governed by

$$\frac{\partial \overline{f}}{\partial t} = \overline{L}\,\overline{E}_{\overline{f}}, \tag{6}$$

where

$$\overline{E} = \sum_i \overline{E}_i(\overline{f}_i) \tag{7}$$

and

$$\overline{\{A, B\}} = \sum_i \overline{\{A, B\}}_i. \tag{8}$$

The state space $\mathcal{M}$ provides an appropriate setting for discussing macroscopic systems in which the number of particles is not fixed. We can make it even more prepared for this role by equipping it with new coordinates (with a new fibration). Following Gibbs (see also [4–8]) we introduce new distribution functions $f_1, f_2, \ldots$ related to $\overline{f}_1, \overline{f}_2, \ldots$ by

$$f_1(I) = \int d1 \overline{f}_1(1)\delta(1 - I) + \int d1 \int d2 \overline{f}_2(1, 2)(\delta(1 - I) + \delta(2 - I)) + \cdots,$$
$$f_2(I, II) = \int d1 \int d2\, \overline{f}_2(1, 2)\delta(1-I)\delta(2-II) + \int d1 \int d2 \int d3\, \overline{f}_3(1, 2, 3)(\delta(1-I)\delta(2-II)$$
$$+ \delta(1 - I)\delta(3 - II) + \delta(2 - I)\delta(3 - II)) + \cdots, \tag{9}$$
$$\vdots$$

where $I := (\boldsymbol{r}_I, \boldsymbol{v}_I), \ldots$, and δ denotes the Dirac delta function. The distribution function f_1 is now an overall one particle distribution function of the whole ensemble of the systems. The distribution function f_2 is the two particle distribution function providing a more refined (more microscopic) information about the ensemble (note in particular that $\int d2 f_2(1, 2) \neq f_1(1)$). Similarly we interpret also $f_3, \ldots$. It is worthwhile to emphasize that the distribution functions f introduced in Eq. (9) are completely standard

grand canonical distribution functions. They are defined in [5] also outside of equilibrium but their time evolution have not been investigated. We proceed to do it.

We note that the transformation (9) between $\overline{f} := (\overline{f}_1, \overline{f}_2, \dots)$ and $f := (f_1, f_2, \dots)$ is one-to-one. This then implies that the time evolution of f is governed by

$$\frac{\partial f}{\partial t} = LE_f, \tag{10}$$

where E and $\{A, B\}$ (determining L) are given in Eqs. (7) and (8), respectively, with $\overline{f}$ expressed (using the inverse of Eq. (9)) in terms of f (we shall denote it by $\overline{f}(f)$). Since the transformation (9) is one-to-one, we are certain that the bracket $\{A, B\}$ is a Poisson bracket. (We recall that a one-to-one transformation transforms a Poisson bracket into another Poisson bracket. We also recall that a subset of the one-to-one transformations are the transformations that leave unchanged the Poisson bracket, these transformations are called Poisson transformations. For example, we have seen that the Jacobi identity guarantees that the family of transformations generated by Eq. (3) are Poisson transformations. Canonical transformations are the transformations that leave unchanged the canonical Poisson bracket arising in the classical mechanics of particles. They thus form a subset of the Poisson transformations. The transformation (9) is not a Poisson transformation (and thus also not a canonical transformation), it carries a Poisson bracket $\overline{\{A, B\}}$ into another Poisson bracket $\{A, B\}$.) In view of the applications discussed later in this paper we shall write explicitly only a part of $\{A, B\}$ involving f_1 and f_n (i.e. we restrict ourselves to the functions A, B that depend only on f_1 and f_n). After straightforward calculations we obtain

$$\{A, B\} = \{A, B\}_1 + \{A, B\}_n + \{A, B\}_{1,n}, \tag{11}$$

where $\{A, B\}_1$ and $\{A, B\}_n$ are $\overline{\{A, B\}}_1$ and $\overline{\{A, B\}}_n$ in which $\overline{f}_1$ and $(\overline{f}_1, \overline{f}_n)$ are replaced by f_1 and (f_1, f_n), and

$$\{A, B\}_{1,n} = \int d1 \int dn\, f_n \sum_{i=1}^{n} \left[\left(\frac{\partial}{\partial r_{i\alpha}}(A_{f_n(1,\dots,n)}) \frac{\partial}{\partial v_{i\alpha}}(B_{f_1(i)}) - \frac{\partial}{\partial r_{i\alpha}}(B_{f_n(1,\dots,n)}) \frac{\partial}{\partial v_{i\alpha}}(A_{f_1(i)}) \right) \right.$$
$$\left. - \left(\frac{\partial}{\partial v_{i\alpha}}(A_{f_n(1,\dots,n)}) \frac{\partial}{\partial r_{i\alpha}}(B_{f_1(i)}) - \frac{\partial}{\partial v_{i\alpha}}(B_{f_n(1,\dots,n)}) \frac{\partial}{\partial r_{i\alpha}}(A_{f_1(i)}) \right) \right]. \tag{12}$$

Since in Eq. (10) the kinematics expressed by L is specified and the energy $E(f)$ remains unspecified, we regard Eq. (10) as a family of time evolution equations parameterized by $E(f)$. We emphasize that Eq. (10) is not the classical Bogoliubov–Born–Green–Kirkwood–Yvon hierarchy (BBGKY hierarchy). Eq. (10) represent the hierarchy of equations governing the time evolution of the distribution functions f that arise in the grand canonical ensemble. We shall call it a grand-canonical-ensemble hierarchy (GCE hierarchy). A part of this hierarchy will be written more explicitly below in Eq. (26). The classical BBGKY hierarchy is a hierarchy of equations governing the time evolution of the distribution functions (we shall denote them by the symbol F) arising in the canonical ensemble. The distribution functions f and F have different physical meanings (note for example that $\int d2\, F_2(1, 2) = F_1(1)$ while $\int d2\, f_2(1, 2) \neq f_1(1)$). The GCE hierarchy (10) is very different from the classical BBGKY hierarchy.

Having formulated the time evolution equations we now proceed to derive some of the properties of their solutions. First, we note that

$$\frac{dE}{dt} = 0, \tag{13}$$

$$\frac{dN}{dt} = 0, \tag{14}$$

where E, having the physical meaning of energy, is given by

$$E(f) = \sum_i \overline{E}_i(\overline{f}_i(f)) \tag{15}$$

and N, having the physical meaning of number of moles, is given by

$$N(f) = \int d1\, f_1(1). \tag{16}$$

The property (13) follows from Eq. (10) and the antisymmetry of the Poisson bracket $(dE/dt) = \{E, E\} = 0$). The property (14) follows from the degeneracy of the bracket $\{A, B\}$. The expressions (15) and (16) can be also seen as an introduction of the normalization of the distribution functions f. Other functions that provide an important information about solutions of Eq. (10) are Casimirs. A function $C(f)$ is called a Casimir (also a distinguished function) of the bracket $\{A, B\}$ if $\{A, C\} = 0$ for all A. Since Eq. (10) implies $dC/dt = \{C, E\}$, all Casimirs are preserved. It can be directly verified that the functions

$$C(f) = \sum_i F_i(\overline{f}_i(f)), \tag{17}$$

where F_i are arbitrary sufficiently regular functions $F_i : \boldsymbol{R} \to \boldsymbol{R}$, are all Casimirs of the bracket $\{A, B\}$ introduced in Eq. (8). The function $N(f)$ given in Eq. (16) is clearly of the form (17) and thus Eq. (14) is verified.

We shall include E, N (given in Eqs. (15) and (16)) into the coordinates (the fibration) of $\mathcal{M}$. We thus represent $f \in \mathcal{M}$ by

$$f = (f_1, f_2, \ldots, E, N). \tag{18}$$

The distribution functions $(f_1, f_2, \ldots)$ will be denoted by f_{fast} and (E, N) by f_{slow}. We thus write Eq. (18) also as

$$f = (f_{\text{fast}}, f_{\text{slow}}). \tag{19}$$

We are introducing in Eq. (19) a unified terminology and notation that will be used throughout this paper. The reason for using "fast" and "slow" will become clear in the subsequent section. Here we only note that the state variables that we put into the class denoted by f_{fast} change in time according to Eq. (10) while the state variables that we put into the class f_{slow} do not change in time (see Eqs. (13) and (14)). The time evolution of f_{fast} is thus clearly faster than the time evolution of f_{slow}.

We continue to investigate properties of solutions of Eq. (10). We turn now our attention to the following experimental observation. States of isolated and unconstrained (both externally and internally) macroscopic systems are seen to reach, as $t \to \infty$, equilibrium states at which their behavior is found to be adequately described by equilibrium thermodynamics. We would like to see this experimental observation in solutions of Eq. (10). How can it be done? Two paths have been suggested and explored.

On the first path introduced by Gibbs (see also [9,10]) we look at the trajectories of all particles (i.e. at solutions of the equation of which Eq. (3), with i fixed, is the Liouville equation) calculated for a family of Hamiltonians and try to extract from them a pattern registered in macroscopic observations. There are,

of course, many ways the problem of the pattern recognition can be approached. Two approaches have been explored in some detail. In the first the pattern is searched in the ergodicity-type properties [4,9], in the second (see e.g. [10]) in the comparison of nearby trajectories (calculation of Lyapunov indices). Due to the large number of trajectories ($\sim 10^{23}$) and the difficulty of the pattern recognition process, rigorous results are rare. They are often replaced by unproven albeit usually well physically motivated hypotheses.

The second path has been suggested and followed for the first time by Boltzmann [11]. The starting point on this path is a modified time evolution equation (10) in which f does not represent the complete microscopic state variables (i.e. $f \neq (f_1, f_2, \dots)$) (but f stands for a mesoscopic state variable. For example, in the original Boltzmann discussion $f \equiv f_1$. Eq. (10) is modified by adding to its right-hand side a new term that brakes the time reversal symmetry (the so called dissipation term). Due to this new term solutions of the modified equation are found to approach, as the time goes to infinity, time independent states that are then identified with the experimentally observed thermodynamic equilibrium states. The provenance of the modified time evolution equation is either an extension of the analysis followed on the first path or we regard it as an expression of the experience collected on the mesoscopic level (without making any reference to more microscopic levels).

The final destination on both paths is, of course, the same. It is classical equilibrium thermodynamics. What is remarkable is that not only the final destination but the whole final stage of the investigation is the same on both paths. We shall present it in an abstract form as a mathematical structure. We do it because we shall use it later on many different levels of description. We have to also choose a name for this structure. We shall call it simply "thermodynamics". Before presenting it we make a comment regarding the terminology. The experience shared by all physicists working in thermodynamics is that it is the terminology that is at the source of most confusions and misunderstandings. Let us begin at the point where there is no confusion. Everybody agrees on what classical equilibrium thermodynamics means and what is the meaning of all concepts introduced in it (see e.g. [11]). The difficulties begin in extensions of thermodynamics towards more microscopic descriptions and towards descriptions involving the time evolution. In all these extended theories arise concepts (like for example entropy) that eventually (for example if the time is let to go to infinity or if appropriate reductions are applied) reduce to the clearly defined concepts of classical equilibrium thermodynamics. It is not always realized and sufficiently appreciated that this common feature of all these concepts does not prevent them from having different meanings depending on the level of description and on the context in which they are introduced. Without such realization any communication is essentially hopeless. Below, we shall first introduce all these concepts in an abstract setting. In this setting their meaning is clearly defined and their physical interpretation is unambiguous. If we then realize the abstract mathematical structure in a particular physical context (a familiar example of a realization of a mathematical structure is a representation of groups) then the concepts get additional physical interpretations that are different in different realizations.

Now we proceed to formulate the abstract thermodynamics. We shall present it in four points denoted by (Th1)–(Th4).

(Th1): The state space $\mathcal{M}$ is equipped with a fibration $x \equiv (x_{\text{fast}}, x_{\text{slow}})$. By x we denote elements of $\mathcal{M}$, $x_{\text{slow}} = \Pi x, x \in \mathcal{M}$, Π is the projection on the slow state variables, $\mathcal{M}_{\text{slow}} := \Pi \mathcal{M}$, i.e. $x_{\text{slow}} \in \mathcal{M}_{\text{slow}}$. By $x_{\text{fast}}(x_{\text{slow}})$ we denote the fiber attached to x_{slow}, i.e. $x_{\text{fast}}(x_{\text{slow}}) = \{x \in \mathcal{M} | \Pi(x) = x_{\text{slow}}\} := \Pi^{-1}(x_{\text{slow}})$.

(Th2): A real valued function $S : \mathcal{M} \to \mathbf{R}$, called entropy, is introduced in $\mathcal{M}$. This function is assumed to be sufficiently regular (so that we can do calculus with it) and concave (so that the Legendre

transformation introduced below is one-to-one). The homogeneity (guaranteeing its extensivity) will not be assumed in this abstract setting.

(Th3): Legendre transformation of the entropy S introduced in (Th2) relative to the fibration introduced in (Th2) is generated by the function

$$\Phi(x; x_{\text{fast}}^*, x_{\text{slow}}^*) = -S(x) + \langle x_{\text{slow}}^*, \Pi(x)\rangle + \langle x_{\text{fast}}^*, \Pi^{-1}(x_{\text{slow}})\rangle, \tag{20}$$

where $\langle\,,\,\rangle$ denotes the pairing in $\mathcal{M}$ and x_{slow}^*, x_{fast}^* are conjugates of x_{slow} and x_{fast}, respectively. The Legendre transformation of $S(x)$ is $\Phi^*(x_{\text{fast}}^*, x_{\text{slow}}^*)$ obtained by evaluating Φ at solutions of $\partial\Phi/\partial x = 0$.

(Th4): Let Φ_{slow} be introduced by

$$\Phi|_{x_{\text{fast}}^*=0} := \Phi_{\text{slow}}(x; x_{\text{slow}}^*) = -S(x) + \langle x_{\text{slow}}^*, \Pi(x)\rangle \tag{21}$$

and solutions of

$$\frac{\partial\Phi}{\partial x} = 0 \tag{22}$$

be denoted by $x_{\text{th}}(x_{\text{slow}}^*)$ and called thermodynamic states. The manifold composed of the thermodynamic states is denoted by $\mathcal{M}_{\text{th}}$ and called a thermodynamic manifold. If Eq. (22) has only one solution then $\mathcal{M}_{\text{slow}} \hookrightarrow \mathcal{M}_{\text{th}} \subset \mathcal{M}$ is an immersion. Let moreover $\Phi^*(x_{\text{slow}}^*)$ be introduced by $\Phi_{\text{slow}}(x_{\text{th}}(x_{\text{slow}}^*); x_{\text{slow}}^*) := \Phi^*(x_{\text{slow}}^*)$. The fundamental thermodynamic relation in $\mathcal{M}_{\text{slow}}$ is given by

$$\Phi^* = \Phi^*(x_{\text{slow}}^*). \tag{23}$$

Thermodynamics presented above in the four points (Th1)–(Th4) is an abstract mathematical structure. Its realization consists of: (i) specification of the state space $\mathcal{M}$, (ii) specification of the fibration in $\mathcal{M}$ (i.e. specification of the projection Π), and (iii) specification of the entropy $S(x)$. It is in the realization where the individual features of the macroscopic system under consideration are expressed. The two paths leading from Eq. (10) to the thermodynamics (Th1)–(Th4) are also two paths to find realizations. In this paper we shall follow the second path. On this path the entropy $S(x)$ appears as a quantity closely related to the new (dissipative) term added to the right-hand side of Eq. (10) and thus as a quantity closely related to the approach of a level (let us call it Level 1) to a more macroscopic level (let us call it Level 2). In fact, we shall see that the entropy $S(x)$ generates the time evolution describing the approach of the Level 1 to the Level 2. If we change at least one level in the pair (Level 1, Level 2) we have to, of course, change in general the entropy. We shall see this in detail in Section 2.2 in the context of the pair: Level 1 = a combined level of kinetic theory and hydrodynamics and Level 2 = the level of equilibrium thermodynamics, and later in Section 3 (see in particular Example 1 in Section 3.2) in the context of several different pairs of levels.

As for the first path, we only recall briefly how on this path the realizations come about. Following Gibbs [4] we postulate the entropy:

$$S(f) = -\sum_{i=1}^{n} \int \mathrm{d}1 \cdots \int \mathrm{d}n\, \overline{f}_i(f) \ln \overline{f}_i(f), \tag{24}$$

(we put the Boltzmann constant $k = 1$). Two types of arguments are usually used to support the choice (24): the arguments developed by Gibbs (see [4,9]), and the arguments developed more recently by Jaynes (see [13–15]). In the context of the time evolution equation (10) we note that Eq. (24) is a Casimir of the

bracket $\{A, B\}$ (Eq. (24) has the form (17)) so that

$$\frac{\mathrm{d}S}{\mathrm{d}t} = 0. \tag{25}$$

We may suggest to regard Eq. (25) as an equation determining the entropy. This will not work however since Eq. (25) only says that the entropy has to be a Casimir but is unable to single out Eq. (24) among all Casimirs (17). With the state space (18), the fibration (19), and the entropy (24), the thermodynamics (Th1)–(Th4) becomes clearly (see [5–8]) the Gibbs equilibrium statistical mechanics. Another example of a realization of the thermodynamics (Th1)–(Th4) is in fact also the classical equilibrium thermodynamics. In this realization $\mathcal{M} \equiv \mathcal{M}_{\text{slow}}$, the fibration is $x_{\text{slow}} = (E, N)$, the entropy $S = S(E, N)$ is the fundamental thermodynamic relation in extensive variables, and Eq. (23) is the conjugate fundamental thermodynamic relation $P = P(T, \mu)$. Note that in this setting $E^* = T^{-1}$, $N^* = -\mu T^{-1}$, $\Phi^* = -PT^{-1}$ where T is the temperature, P is the pressure and μ chemical potential; we put the volume equal to one. Many other examples of x, x_{slow} and $S(x)$ will be introduced in Section 3. It is also worth to note that in the realization corresponding to the setting of classical equilibrium thermodynamics the fibration is universal and the individual features of the macroscopic system under consideration are expressed solely in the entropy. On the contrary, in the context of the realization corresponding to the setting of Gibbs equilibrium statistical mechanics the entropy is universal and the individual features are expressed solely in the fibration (in the energy expressed in terms of f). We shall see that in the realizations corresponding to mesoscopic settings the individual features are expressed in both the entropy and the fibration.

Before leaving this subsection we shall write explicitly the time evolution equation (10) for $(f_1(1), f_n(1, \ldots, n))$ (i.e. Eq. (10) with the Poisson bivector L specified in Eq. (12))

$$\frac{\partial f_{n(1,\ldots,n)}}{\partial t} = -\frac{\partial}{\partial r_{i\alpha}}\left(f_n \frac{\partial}{\partial v_{i\alpha}}(E_{f_n})\right) + \frac{\partial}{\partial v_{i\alpha}}\left(f_n \frac{\partial}{\partial r_{i\alpha}}(E_{f_n})\right) - \frac{\partial}{\partial r_{i\alpha}}\left(f_n \frac{\partial}{\partial v_{i\alpha}}(E_{f_1(i)})\right)$$
$$+ \frac{\partial}{\partial v_{i\alpha}}\left(f_n \frac{\partial}{\partial r_{i\alpha}}(E_{f_1(i)})\right),$$

$$\frac{\partial f_{1(1)}}{\partial t} = -\frac{\partial}{\partial r_{1\alpha}}\left(f_1 \frac{\partial}{\partial v_{1\alpha}}(E_{f_1})\right) + \frac{\partial}{\partial v_{1\alpha}}\left(f_1 \frac{\partial}{\partial r_{1\alpha}}(E_{f_1})\right)$$
$$- n\frac{\partial}{\partial r_{1\alpha}}\int \mathrm{d}2 \cdots \int \mathrm{d}n\, f_n(1, \ldots, n)\frac{\partial}{\partial v_{1\alpha}}(E_{f_n(1,\ldots,n)})$$
$$+ n\frac{\partial}{\partial v_{1\alpha}}\int \mathrm{d}2 \cdots \int \mathrm{d}n\, f_n(1, \ldots, n)\frac{\partial}{\partial r_{1\alpha}}(E_{f_n(1,\ldots,n)}). \tag{26}$$

We shall use these equations later in Section 3 (see Eq. (71)). Eq. (26) represents only a part of the GCE hierarchy (10). We can nevertheless compare Eq. (26) with the corresponding part in the classical BBGKY hierarchy and see clearly how different is the GCE hierarchy (10) from the classical BBGKY hierarchy.

2.2. Kinetic-theory-hydrodynamics-ensemble hierarchy

The new interpretation and formulation of the grand canonical ensemble, Gibbs' equilibrium statistical mechanics, and classical equilibrium thermodynamics that we have developed in the preceding subsection will be used now in a new context. We have seen that the grand canonical ensemble appeared in the

attempt to look at one macroscopic system from a family of different levels of description (the family is parametrized by the number of microscopic particles composing the macroscopic system under consideration). In this subsection we shall do the same thing with only one difference. We shall choose another family of levels of description from which we shall look at one macroscopic system. We shall choose the family composed of two levels: the level of kinetic theory and the level of hydrodynamics. We are thus introducing in this subsection a new ensemble, we shall call it a kinetic-theory-hydrodynamic ensemble (in short, KTH ensemble).

The state space on the level of kinetic theory is denoted by the symbol $\mathcal{M}_{\mathrm{kt}}$, its elements are one particle distribution functions $\overline{f}(\boldsymbol{r}, \boldsymbol{v})$. The state space on the level of hydrodynamics is denoted by the symbol $\mathcal{M}_{\mathrm{hy}}$, its elements are the hydrodynamic fields $\overline{\rho}(\boldsymbol{r}), \overline{\boldsymbol{u}}(\boldsymbol{r}), \overline{e}(\boldsymbol{r})$ representing the mass density, the momentum density and energy density, respectively. As in Eq. (1), we introduce

$$\mathcal{M} = \mathcal{M}_{\mathrm{kt}} \times \mathcal{M}_{\mathrm{hy}}, \tag{27}$$

$\mathcal{M} \ni (\overline{f}, \overline{\rho}, \overline{\boldsymbol{u}}, \overline{e})$ that provides now the setting for our kinetic-theory-hydrodynamics ensemble discussed in this subsection (similarly as Eq. (1) provides the setting for the grand canonical ensemble).

The time evolutions in $\mathcal{M}_{\mathrm{kt}}$ and $\mathcal{M}_{\mathrm{hy}}$, similarly as the time evolutions in $\mathcal{M}_1, \mathcal{M}_2, \ldots$ introduced in Section 2.1, are independent of each other. We shall look first only at the Hamiltonian part of the time evolution. In $\mathcal{M}_{\mathrm{kt}}$, the distribution function $\overline{f}$ evolves according to

$$\frac{\partial \overline{f}}{\partial t} = \overline{L}_{\mathrm{kt}}(\overline{E}_{\mathrm{kt}})_{\overline{f}}, \tag{28}$$

where $\overline{E}_{\mathrm{kt}}$ is the energy expressed in terms of $\overline{f}$ and $\overline{L}_{\mathrm{kt}}$ is the Poisson bivector given in Eq. (4) with $i = 1$. The time evolution in $\mathcal{M}_{\mathrm{hy}}$, is given by

$$\frac{\partial}{\partial t}(\overline{\rho}, \overline{\boldsymbol{u}}, \overline{s})^{\mathrm{T}} = \overline{L}_{\mathrm{hy}}((\overline{E}_{\mathrm{hy}})_{\overline{\rho}}, (\overline{E})_{\mathrm{hy}})_{\overline{\boldsymbol{u}}}, (\overline{E}_{\mathrm{hy}})_{\overline{s}})^{\mathrm{T}}, \tag{29}$$

where $(\cdots)^{\mathrm{T}}$ denotes the transpose of $(\cdots)$, $\overline{L}_{\mathrm{hy}}$ is given by [2]

$$
\begin{aligned}
\overline{\{A, B\}}_{\mathrm{hy}} &:= \int \mathrm{d}\boldsymbol{r} (A_{\overline{\rho}}, A_{\overline{\boldsymbol{u}}}, A_{\overline{s}}) \overline{L}_{\mathrm{hy}} (B_{\overline{\rho}}, B_{\overline{\boldsymbol{u}}}, B_{\overline{s}}) \\
&= \int \mathrm{d}\boldsymbol{r} \left[\overline{u}_{\gamma} \left(\frac{\partial}{\partial r_{\alpha}} (A_{\overline{u}_{\gamma}}) B_{\overline{u}_{\alpha}} - \frac{\partial}{\partial r_{\alpha}} (B_{\overline{u}_{\gamma}}) A_{\overline{u}_{\alpha}} \right) + \overline{\rho} \left(\frac{\partial}{\partial r_{\alpha}} (A_{\overline{\rho}}) B_{\overline{u}_{\alpha}} - \frac{\partial}{\partial r_{\alpha}} (B_{\overline{\rho}}) A_{\overline{u}_{\alpha}} \right) \right. \\
&\quad \left. + \overline{s} \left(\frac{\partial}{\partial r_{\alpha}} (A_{\overline{s}}) B_{\overline{u}_{\alpha}} - \frac{\partial}{\partial r_{\alpha}} (B_{\overline{s}} A_{\overline{u}_{\alpha}}) \right) \right],
\end{aligned}
\tag{30}
$$

and $\overline{E}_{\mathrm{hy}}$ is the total energy expressed in terms of $(\overline{\rho}, \overline{\boldsymbol{u}}, \overline{s})$; A, B are sufficiently regular real valued functions of $(\overline{\rho}, \overline{\boldsymbol{u}}, \overline{s})$. We use in Eqs. (29) and (30) the state variables $(\overline{\rho}, \overline{\boldsymbol{u}}, \overline{s})$ (an energy representation in the terminology of Callen [12]) instead of $(\overline{\rho}, \overline{\boldsymbol{u}}, \overline{e})$ (an entropy representation). By $\overline{s}(\boldsymbol{r})$ we denote the entropy field, its physical meaning will be explained later. We shall assume that the transformation $\overline{\rho} = \overline{\rho}, \overline{\boldsymbol{u}} = \overline{\boldsymbol{u}}, \overline{s} = \overline{s}(\overline{\rho}, \overline{\boldsymbol{u}}, \overline{e})$, is one-to-one. In general, if $x \mapsto x'$ is a one-to-one transformation, the Poisson bivector L acting on E_x and L' acting on $E'_{x'}$ are related by $L = [\partial(x)/\partial(x')]L'[(\partial(x)/\partial(x'))]^{\mathrm{T}}$. The state variables $(\overline{\rho}, \overline{\boldsymbol{u}}, \overline{s})$ are more convenient than $(\overline{\rho}, \overline{\boldsymbol{u}}, \overline{e})$ since the Poisson bracket takes in $(\overline{\rho}, \overline{\boldsymbol{u}}, \overline{s})$ a simpler form. Hereafter, we shall use freely both energy and entropy representations depending on which one appears to be more convenient.

Since the time evolutions in $\mathcal{M}_{kt}$ and in $\mathcal{M}_{hy}$, are independent, the time evolution in $\mathcal{M}$ is governed by

$$\frac{\partial}{\partial t}(\overline{f}, \overline{\rho}, \overline{\boldsymbol{u}}, \overline{s})^{\mathrm{T}} = \overline{L}(E_{\overline{f}}, E_{\overline{\rho}}, E_{\overline{\boldsymbol{u}}}, E_{\overline{s}})^{\mathrm{T}}, \tag{31}$$

where $\overline{E} = \overline{E}_{kt} + \overline{E}_{hy}$, and $\overline{\{A, B\}} = \overline{\{A, B\}}_{kt} + \overline{\{A, B\}}_{hy}$.

Comparing the analysis in this subsection with the analysis in the previous subsection, we have reached the paragraph that follows Eq. (8). Our next step is thus an introduction of a new fibration in $\mathcal{M}$. The physical motivation is the same as the one that led us to Eq. (9). We want to regard the macroscopic system under consideration as being described by hydrodynamic fields $(\rho, \boldsymbol{u}, s)$ and by the one particle distribution function f providing only a more detailed information that is not contained in the hydrodynamic fields. Taking inspiration from the transformation (9), we suggest

$$\rho(\boldsymbol{r}) = \overline{\rho}(\boldsymbol{r}) + m \int \mathrm{d}\boldsymbol{v}\, \overline{f}(\boldsymbol{r}, \boldsymbol{v}), \qquad \boldsymbol{u}(\boldsymbol{r}) = \overline{\boldsymbol{u}}(\boldsymbol{r}) + \int \mathrm{d}\boldsymbol{v}\, \boldsymbol{v}\overline{f}(\boldsymbol{r}, \boldsymbol{v}),$$

$$s(\boldsymbol{r}) = \overline{s}(\boldsymbol{r}) - \int \mathrm{d}\boldsymbol{v}\, \overline{f} \ln \overline{f}, \qquad f(\boldsymbol{r}, \boldsymbol{v}) = \overline{f}(\boldsymbol{r}, \boldsymbol{v}), \tag{32}$$

where m denotes mass of one particle. The transformation $(\overline{f}, \overline{\rho}, \overline{\boldsymbol{u}}, \overline{s}) \mapsto (f, \rho, \boldsymbol{u}, s)$ defined in Eq. (32) is clearly one-to-one. As in the previous subsection, straightforward calculations transform (31) into

$$\frac{\partial}{\partial t}(\rho, \boldsymbol{u}, s, f)^{\mathrm{T}} = L(E_\rho, E_{\boldsymbol{u}}, E_s, E_f)^{\mathrm{T}}, \tag{33}$$

where

$$E(\rho, \boldsymbol{u}, s, f) = \overline{E}_{kt}(\overline{\rho}(\rho, \boldsymbol{u}, s, f), \overline{\boldsymbol{u}}(\rho, \boldsymbol{u}, s, f), \overline{s}(\rho, \boldsymbol{u}, s, f), \overline{f}(\rho, \boldsymbol{u}, s, f))$$
$$+ \overline{E}_{hy}(\overline{\rho}(\rho, \boldsymbol{u}, s, f), \overline{\boldsymbol{u}}(\rho, \boldsymbol{u}, s, f), \overline{s}(\rho, \boldsymbol{u}, s, f), \overline{f}(\rho, \boldsymbol{u}, s, f)), \tag{34}$$

and the Poisson bivector L is determined by the Poisson bracket

$$\{A, B\} = \{A, B\}_{kt} + \{A, B\}_{hy} + \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{v} \left[mf\left(\frac{\partial}{\partial r_\alpha}(A_\rho)\frac{\partial}{\partial v_\alpha}(B_f) - \frac{\partial}{\partial r_\alpha}(B_\rho)\frac{\partial}{\partial v_\alpha}(B_f)\right) \right.$$

$$- f \ln f\left(\frac{\partial}{\partial r_\alpha}(A_s)\frac{\partial}{\partial v_\alpha}(B_f) - \frac{\partial}{\partial r_\alpha}(B_s)\frac{\partial}{\partial r_\alpha}(B_s)\frac{\partial}{\partial v_\alpha}(A_f)\right)$$

$$+ fv_\gamma\left(\frac{\partial}{\partial r_\alpha}(A_{u_\gamma})\frac{\partial}{\partial v_\alpha}(B_f) - \frac{\partial}{\partial r_\alpha}(B_{u_\gamma})\frac{\partial}{\partial v_\alpha}(A_f)\right) + f\left(\frac{\partial}{\partial r_\alpha}(A_f)B_{u_\alpha}\right)$$

$$\left. - \frac{\partial}{\partial r_\alpha}(B_f)A_{u_\alpha} \right], \tag{35}$$

$\{A, B\}_{kt}$ and $\{A, B\}_{hy}$ are the brackets (5) (with $i = 1$) and Eq. (30) except that the state variables are without bar. Eq. (33) represent the hierarchy of equations governing the time evolution in the kinetic-theory-hydrodynamics ensemble. We shall call it a kinetic-theory-hydrodynamics-ensemble hierarchy, or in an abbreviated form, a KTHE hierarchy. This hierarchy is written more explicitly in Eq. (40) below.

Now, we begin to discuss properties of solutions of Eq. (33). The conservation of the energy E and the number of moles N, provided E is given in Eq. (34) and

$$N(\rho, \boldsymbol{u}, s, f) = \frac{1}{m} \int d\boldsymbol{r}\, \rho(\boldsymbol{r}), \qquad (36)$$

is clearly verified. We can thus represent $x \equiv (\rho, \boldsymbol{u}, s, f)$ as $(x_{\text{fast}}, x_{\text{slow}})$ with $x_{\text{fast}} = (\rho, \boldsymbol{u}, s, f)$ and $x_{\text{slow}} \equiv (E, N)$ (another division of x into $(x_{\text{fast}}, x_{\text{slow}})$ will be made in Section 3).

We proceed with the discussion of properties of solutions of Eq. (33). We shall try to recognize in solutions of Eq. (33) the observation constituting the experimental basis of equilibrium thermodynamics. We shall follow now Boltzmann [11] rather than Gibbs and begin this discussion by modifying Eq. (33)

$$\frac{\partial}{\partial t}(\rho, \boldsymbol{u}, s, f)^{\mathrm{T}} = L(E_\rho, E_{\boldsymbol{u}}, E_s, E_f)^{\mathrm{T}} + \text{dissipation term}, \qquad (37)$$

where the dissipation term is required to be compatible with the nondissipative (Poisson) part of the time evolution equation (37) (i.e. with the first term on the right-hand side of Eq. (37)). We say that a dissipation term is compatible with the first term on the right-hand side of Eq. (37) if Eqs. (13) and (14) (with E given in Eq. (34) and N in Eq. (36)), and moreover, the dissipation condition (compare with Eq. (25))

$$\frac{dS}{dt} \geq 0, \qquad (38)$$

where $S = \int d\boldsymbol{r}\, s(\boldsymbol{r})$, hold. Many examples of the dissipation terms can be found in [16–30].

It is now easy to see that Eqs. (37) and (38) imply that Φ given in Eq. (21) with $x_{\text{slow}}^* = (1/T, -\mu/T)$ takes the role of the Lyapunov function corresponding to the approach (as the time goes to infinity) to solutions of Eq. (22). These states have been called in the general setting, presented in the previous subsection, thermodynamic states. In the particular setting discussed here these states are thermodynamic equilibrium states. We shall denote them by $(\rho, \boldsymbol{u}, s, f)_{\text{eq}}$. The fundamental thermodynamic equation of state implied by Eq. (37) is $\Phi^*(T, \mu) = -PV/T$, V denotes the volume.

Summing up, we have shown that solutions to the time evolution equations belonging to the family (37) (the family is parameterized by the two potentials E, S, and the dissipation term) satisfy the conservation of energy, conservation of the number of moles, and approach, as the time goes to infinity, equilibrium states (solutions of Eq. (22)) at which the classical equilibrium thermodynamics applies. Below, we shall make some additional observations about solutions of Eq. (37) with the two potentials E, S, remaining still unspecified.

Before embarking on this task we shall formulate Eq. (37) in a more abstract form as an equations governing the time evolution of the abstract state variable x used in the formulation of the thermodynamics (Th1)–(Th4). The time evolution of x is governed by

$$\frac{dx}{dt} = L(x) E_x + \frac{\partial \Psi}{\partial S_x}. \qquad (39)$$

In Eq. (39) we have written the dissipation term in the form that guarantees its compatibility with the first term on the right-hand side of Eq. (39). The compatibility is guaranteed provided Ψ, called hereafter a dissipation potential (see [21–25,27]), satisfies the following properties: (i) Ψ is a real valued and

sufficiently regular function of S_x, (ii) $\Psi(0) = 0$, (iii) Ψ reaches its minimum at 0, (iv) Ψ is convex in a neighborhood of 0, and finally (v) Ψ is appropriately degenerated so that Eqs. (13) and (14) are satisfied. Eq. (39) has been called in [27] general equation for non equilibrium reversible–irreversible coupling (GENERIC). It appeared gradually in [21–26]. Various less complete versions of this abstract equations have been called in [21–25] nonlinear Onsager–Casimir equations (NOC equations) since their linearized versions manifestly display the Onsager–Casimir symmetry. Having introduced Eq. (39), we can regard Eq. (37) as a particular, but still partial, realization of Eq. (39) (i.e. Eq. (37) is Eq. (39) in which x, L are specified, but S, E, Ψ still remain unspecified). We note that the time evolution described in Eq. (39) is generated by two potentials. The nondissipative time evolution (i.e. the time evolution for which $dS/dt = 0$) is generated by the energy E, the dissipative time evolution (i.e. the time evolution for which $dS/dt > 0$) is generated by the entropy S. The compatibility of the time evolution (39) with thermodynamics (Th1)–(Th4) would be more clearly manifested if the potential generating dynamics would be the same as the potential Φ (see Eq. (20)) that generates the Legendre transformations involved in the thermodynamics (Th1)–(Th4). This point has been recently taken in [31] where the geometry involved in the thermodynamics (Th1)–(Th4) and the time evolution (39) is systematically investigated. Examples of a version of Eq. (39) involving only one potential Φ will be introduced in Section 3 (see in particular Example 1 in Section 3.2).

We shall now proceed to discuss solutions of Eq. (37). First, we shall write the family of Eq. (37) explicitly

$$
\begin{aligned}
\frac{\partial \rho}{\partial t} &= -\frac{\partial}{\partial r_\alpha}(\rho E_{u_\alpha}) - \frac{\partial}{\partial r_\alpha}\int d\boldsymbol{v}\, f \frac{\partial}{\partial v_\alpha}(E_f), \\
\frac{\partial s}{\partial t} &= -\frac{\partial}{\partial r_\alpha}(s E_{u_\gamma}) + \frac{\partial}{\partial r_\alpha}\int d\boldsymbol{v}\, f \ln f \frac{\partial}{\partial v_\alpha}(E_f) + \sigma(\boldsymbol{r}), \\
\frac{\partial u_\alpha}{\partial t} &= -\frac{\partial}{\partial r_\gamma}(u_\alpha E_{u_\alpha}) - \frac{\partial}{\partial r_\alpha}p - \frac{\partial}{\partial r_\gamma}\tau_{\alpha\gamma}, \\
\frac{\partial f}{\partial t} &= -\frac{\partial}{\partial r_\alpha}\left(f \frac{\partial}{\partial v_\alpha}(E_f)\right) - \frac{\partial}{\partial r_\alpha}(f E_{u_\alpha}) + \frac{\partial}{\partial v_\alpha}\left(f \frac{\partial}{\partial r_\alpha}(E_f)\right) \\
&\quad + \frac{\partial}{\partial v_\alpha}\left(f \frac{\partial}{\partial r_\alpha}(E_\rho)\right) - \frac{\partial}{\partial v_\alpha}\left(f \ln f \frac{\partial}{\partial r_\alpha}(E_s) + \frac{\partial}{\partial v_\alpha}\left(f v_\gamma \frac{\partial}{\partial r_\alpha}(E_{u_\gamma})\right)\right) - \frac{\partial \Psi}{\partial(S_f)},
\end{aligned}
\tag{40}
$$

where the entropy production is given by

$$
\sigma(r) = \frac{1}{S_e}\int d\boldsymbol{v}\, S_f \frac{\partial \Psi}{\partial(S_f)},
\tag{41}
$$

the hydrostatic pressure by

$$
\frac{\partial}{\partial r_\alpha}p = \rho \frac{\partial}{\partial r_\alpha}E_\rho + s \frac{\partial}{\partial r_\alpha}E_s + u_\gamma \frac{\partial}{\partial r_\alpha}E_{u_\gamma} + \int d\boldsymbol{v}\, f \frac{\partial}{\partial r_\alpha}E_f,
\tag{42}
$$

(i.e. $p = -e + \rho E_\rho + s E_s + u_\gamma E_{u_\gamma} + \int d\boldsymbol{v} f E_f$, where e is the density of the energy E, $E = \int d\boldsymbol{r}\, e$ and the extra stress tensor by

$$
\tau_{\alpha\gamma} = \int d\boldsymbol{v}\, f v_\alpha \frac{\partial}{\partial v_\gamma}E_f.
\tag{43}
$$

In Eq. (40) we have partially specified the dissipation term by assuming that the explicit dissipation takes place only on the microscopic scale characterized by the distribution function f. We can verify easily that Eqs. (13), (14) as well as (38) are satisfied provided the dissipation potential Ψ satisfies the properties listed in the previous paragraph. Eqs. (40)–(43) are the KTHE hierarchy.

The first three equations in system (40) are the familiar balance equations of classical hydrodynamics except that the hydrodynamic fluxes and the source term in the entropy equation contain now new terms due to the fact that our view of the macroscopic system under consideration is more microscopic than the view taken in the classical hydrodynamics. We note new terms in all three fluxes (fluxes of mass, momentum end entropy). In the momentum balance equation the new terms in the momentum flux can also be interpreted as a modification of the local equilibrium assumption (Eq. (42) without the term involving f expresses the local equilibrium) and as an appearance of elasticity (appearance of the elastic part (43) of the extra stress tensor).

The fourth equation in system (40) is the kinetic equation of fluids subjected to external forces expressed on the level of classical hydrodynamics. Its physical interpretation is best revealed if we look at it as the Liouville equation corresponding to the time evolution equation of one particle

$$\frac{\mathrm{d}r_\alpha}{\mathrm{d}t} = \frac{\partial}{\partial v_\alpha}(E_f) + E_{u_\alpha}, \qquad \frac{\mathrm{d}v_\alpha}{\mathrm{d}t} = -\frac{\partial}{\partial r_\alpha}(E_f) - \frac{\partial}{\partial r_\alpha}(E_\rho) - \ln f \frac{\partial}{\partial r_\alpha}(E_{u_\gamma}) + \text{dissipation term}.$$
(44)

It is easy to verify that the Liouville equation corresponding to Eq. (44) is indeed the fourth equation in system (40). Since E involves always the kinetic energy the right-hand side of the first equation in system (44) is $(1/m)v_\alpha + (1/\rho)u_\alpha$. We see thus that v_α/ρ is, what is called in kinetic theory, a peculiar velocity. This finding is clearly compatible with our interpretation of f as an information extra to the information contained in hydrodynamic fields. The second, the third, and the fourth terms on the right-hand side of the second equation in (44) are forces originated and expressed in the hydrodynamic description. The force represented by the fourth term has already appeared before in the context of direct simulations (see [32] and also Section 3 of this paper). In this context it got the name a SLLOD force. The SLLOD-like force appeared also in [33] in the context of one particle kinetic theory of fluids subjected to a uniform shear flow. The dissipation term depends, of course, on the dissipation term appearing in Eq. (40) (the last term on the right-hand side of the fourth equation in system (40)). For example, if the dissipation term in system (40) is the Boltzmann collision term then the corresponding dissipation term in Eq. (44) is explicitly written in [17].

Finally, we may recall that another approach to the extension of classical hydrodynamics towards a more microscopic description has been developed in the so called fluctuating hydrodynamics [34]. In this setting the extra microscopic information is expressed in terms of quantities arising in stochastic calculus. We shall not attempt here to relate the approach presented in this subsection to the stochastic approach. Useful observations about the relation between the stochastic time evolution and the time evolution (39) can be found in [27].

2.3. Continuum–continuum-ensemble hierarchy

In Section 2.1 we took many different views of a single macroscopic system. The same thing we did in Section 2.2 with a different family of views. We still continue the same discussion in this subsection

except that the views are now different in a different way. In the two previous subsections the views were different because they belonged to different levels of description. In this subsection both views belong to the same level (we choose to regard the system under consideration as a continuum). The views are different because they focus on different aspects of dynamics namely on the large scale and the small scale motions of particles composing the macroscopic system. Indeed, the complex motion of the particles can be, roughly speaking, regarded as a superposition of a large scale motion and a small scale motion. Following the construction of ensembles developed in the previous subsections we shall introduce a new ensemble, we shall call it a continuum–continuum ensemble (or in short CC ensemble), as follows. The two continua are first regarded as independent. The time evolution of a continuum is seen in the classical continuum theory as a Lie group of transformations $\boldsymbol{R}^3 \to \boldsymbol{R}^3$. This then means that elements of the state space of a continuum is composed of two fields, one is a scalar field (we denote it by the symbol v, it has the physical interpretation of a volume) and a vector field the we denote by the symbol $\boldsymbol{u}$. The state variables, i.e. elements of $\mathcal{M}_1 \times \mathcal{M}_2$ thus $(v_1, v_2, \boldsymbol{u}_1, \boldsymbol{u}_2)$. We use the subscripts 1 and 2 to denote the first the second continuum, respectively.

What is the time evolution in $\mathcal{M}_1$ and $\mathcal{M}_2$? Since both continua are independent and their motion is seen as a Lie group of transformations $\boldsymbol{R}^3 \to \boldsymbol{R}^3$ their nondissipative dynamics is governed by Eq. (29) with the field s absent.

Next, we follow the construction of ensembles and introduce new fibration in $\mathcal{M}_1 \times \mathcal{M}_2$ by (compare with Eqs. (9) and (32))

$$\boldsymbol{u} = \boldsymbol{u}_1 + \boldsymbol{u}_2, \quad \boldsymbol{w} = \boldsymbol{u}_2, \quad \rho = \rho_0 v_1, \quad s = s_0 v_2, \tag{45}$$

where s_0 and ρ_0 are constants with appropriate physical dimensions. The transformation $(v_1, v_2, \boldsymbol{u}_1, \boldsymbol{u}_2) \mapsto (\rho, s, \boldsymbol{u}, \boldsymbol{w})$ defined in Eq. (45) is clearly one-to-one. We give the new state variables the following physical interpretation: ρ is the field of the overall mass density, s is the entropy field, $\boldsymbol{u}$ is the overall momentum field, and $\boldsymbol{w}$ is the field related (see Eq. (47) below) to the entropy flux.

Straightforward calculations lead us to the following Poisson bracket expressing kinematics of $(\rho, s, \boldsymbol{u}, \boldsymbol{w})$

$$\{A, B\} = \{A, B\}^{(30)} + \int \mathrm{d}\boldsymbol{r} \left[s \left(\frac{\partial}{\partial r_\alpha}(A_s) B_{w_\alpha} - \frac{\partial}{\partial r_\alpha}(B_s) A_{w_\alpha} \right) \right.$$
$$+ w_\gamma \left(\frac{\partial}{\partial r_\alpha}(A_{w_\gamma}) B_{u_\alpha} - \frac{\partial}{\partial r_\alpha}(B_{w_\gamma}) A_{u_\alpha} \right) + w_\gamma \left(\frac{\partial}{\partial r_\alpha}(A_{w_\gamma}) B_{w_\alpha} - \frac{\partial}{\partial r_\alpha}(B_{w_\gamma}) A_{w_\alpha} \right)$$
$$\left. + w_\gamma \left(\frac{\partial}{\partial r_\alpha}(A_{u_\gamma}) B_{w_\alpha} - \frac{\partial}{\partial r_\alpha}(B_{u_\gamma}) A_{w_\alpha} \right) \right], \tag{46}$$

where $\{A, B\}^{(30)}$ is the bracket introduced in Eq. (30) (now without the bar over the state variables). We note that both the total mass $M = \int \mathrm{d}\boldsymbol{r}\, \rho(\boldsymbol{r})$ and the total entropy $S = \int \mathrm{d}\boldsymbol{r}\, s(\boldsymbol{r})$ are Casimirs of the Poisson bracket (45).

The dissipation is now introduced in a similar way as in the previous subsection. We shall assume again that the direct dissipation takes place only on the small scale. In the context of our description this means that we let the dissipation potential to depend only on E_w.

The time evolution equations implied by this type of dissipation and by the kinematics (46) are

$$\frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial r_\alpha}(\rho E_{u_\alpha}), \qquad \frac{\partial u_\alpha}{\partial t} = -\frac{\partial}{\partial r_\gamma}(u_\alpha E_{u_\gamma}) - \frac{\partial}{\partial r_\alpha}p - \frac{\partial}{\partial r_\gamma}\tau_{\alpha\gamma},$$

$$\frac{\partial s}{\partial t} = -\frac{\partial}{\partial r_\alpha}(s E_{u_\alpha}) - \frac{\partial}{\partial r_\alpha}(s E_{w_\alpha}) + \sigma,$$

$$\frac{\partial w_\alpha}{\partial t} = -\frac{\partial}{\partial r_\gamma}(w_\alpha E_{u_\gamma}) - \frac{\partial}{\partial r_\gamma}(w_\alpha E_{w_\gamma}) - s\frac{\partial}{\partial r_\alpha}(E_s) - w_\gamma \frac{\partial}{\partial r_\alpha}(E_{u_\gamma}) - \frac{\partial \Psi}{\partial E_{w_\gamma}}, \qquad (47)$$

where the hydrostatic pressure p is given by

$$\frac{\partial}{\partial r_\alpha}p = \rho\frac{\partial}{\partial r_\alpha}(E_\rho) + u_\gamma\frac{\partial}{\partial r_\alpha}(E_{u_\gamma}) + s\frac{\partial}{\partial r_\alpha}(E_s) + w_\gamma\frac{\partial}{\partial r_\alpha}(E_{w_\gamma}), \qquad (48)$$

(i.e. $p = -e + \rho E_\rho + u_\gamma E_{u_\gamma} + s E_s + w_\gamma E_{w_\gamma}$, where e is the density of E). The extra stress tensor τ by

$$\tau_{\alpha\gamma} = w_\alpha E_{w_\gamma}, \qquad (49)$$

and the entropy production σ by

$$\sigma = \frac{1}{E_s}E_{w_\gamma}\frac{\partial \Psi}{\partial E_{w_\gamma}}. \qquad (50)$$

We can easily verify that both the energy E and the number of moles (36) are conserved. Moreover, the dissipation condition (38) is also verified provided the dissipation potential Ψ satisfies the properties listed in the paragraph following Eq. (39). Eqs. (47)–(50) represent another example of the realization of the abstract equation (39). Since Eqs. (47)–(50) govern the time evolution in the CC ensemble, we shall call them a CCE hierarchy.

The first three equations in the CCE hierarchy (47) are (as in Eq. (40)) the familiar equations of classical hydrodynamics. The fluxes appearing in these equations are however non-classical. The expression (48) for the scalar pressure represents a modification of the local equilibrium. The appearance of the extra stress tensor (49) then signifies that the fluid has a viscoelastic behavior. The second term on the right-hand side of the third equation in Eq. (47) is a divergence of the extra entropy flux $sE\boldsymbol{w}$. This gives the new state variable $\boldsymbol{w}$ its physical meaning.

The CCE hierarchy (47) can be brought closer to the governing equations of classical hydrodynamics by letting the dissipation potential depend also on $\Delta_{\alpha\beta} := (\partial/\partial r_\alpha)(E_{u_\beta}) + (\partial/\partial r_\beta)(E_{u_\alpha})$. With such dissipation potential Eq. (47) remains unchanged only Eqs. (49) and (50) change. The extra stress tensor gets a new term $-\partial \Psi/\partial \Delta_{\alpha\gamma}$ (the classical Navier–Stokes term if Ψ is a quadratic potential) and the entropy production gets a new term $(1/E_s)\Delta_{\alpha\beta}(\partial \Psi/\partial \Delta_{\alpha\beta})$.

Finally, we note that the CCE hierarchy presented above shares some features with other types of two fluid models (e.g. the two fluid model introduced in the theory of superfluidity [34]) and with extended irreversible thermodynamics [35–37]. The starting point of the latter theory is an extension of the set of state variables by considering the fluxes appearing in the classical hydrodynamic equations as independent state variables. Since our $\boldsymbol{w}$ is essentially the entropy flux (see Eq. (47)), its appearance is natural in the context of extended irreversible thermodynamics (EIT). However, since the classical formulation of EIT [37] does not use Poisson structures and remains thus linear (in the sense that only the entropy production that is a quadratic function of the thermodynamic forces is considered) the time evolution equations

(47) are different from the equations arising in ELT. For example, the extra stress tensor (49), being quadratic or higher order in $\boldsymbol{w}$, is absent in the classical EIT. A more general formulation of EIT in which higher order nonlinearities are introduced as higher order perturbations has been suggested by Lebon. Preliminary results indicate that in this analysis the extra stress tensor (49) does appear. The formulation of EIT that uses the Poisson structures and is thus fully nonlinear has been developed in [38]. In closing, we also note that the idea of two continua, physically interpreted as material and caloric, has already appeared in [39] in the context of the attempt to develop a complete Lagrangian description (Lagrangian in both material and thermal motions). Sieniutycz and Berry [40] have used still another motivation for introducing a similar two continua model.

3. External forces

In this section we turn our attention back to the main subject of this paper, namely to externally driven complex fluids. In the previous section we have developed multilevel descriptions and a general formulation of thermodynamics. The former is clearly essential if the level on which the external force is defined and the level on which dynamics of the macroscopic system under consideration is formulated are not identical. We shall now explain, in general terms, the pertinence of the latter. Illustrations are then developed in Sections 3.1 and 3.2.

We begin by evoking the following well known experience: majority of both isolated and externally driven systems can be prepared in such a way that their behavior is found to be well described in a setting that is more macroscopic than the setting of completely microscopic theories (classical or quantum mechanics of particles). The preparation process usually consists of waiting for a while without applying on them any additional external influence. For example, isolated macroscopic systems can be prepared in such a way that their behavior is found to be well described by classical equilibrium thermodynamics (in other words, the isolated macroscopic systems are let to approach equilibrium states). Many driven systems (e.g. the Bénard system). can be prepared in such a way that they are found to be well described in the setting of classical hydrodynamics.

What are the consequences, in the theoretical analysis of dynamics of macroscopic systems, of the above experience? This question represents the basis of our investigation and our view of classical equilibrium thermodynamics and thermodynamics of driven systems. It clearly distinguishes our viewpoint from the viewpoints of thermodynamics of driven systems explored previously (see e.g. [1]). Let $\mathcal{M}$ denote a microscopic state space, $x \in \mathcal{M}$, and $\mathcal{P}$ a set of quantities through which the individual features are described (e.g. in the setting of classical mechanics $\mathcal{P}$ is the set of Hamiltonians). Elements of $\mathcal{P}$ will be denoted by the symbol p. Let a phase portrait in $\mathcal{M}$ be a collection of trajectories passing through all $x \in \mathcal{M}$ for a family of $p \in \mathcal{P}$. To pass from the time evolution in $\mathcal{M}$ to the observed more macroscopic description means to recognize a pattern in the phase portrait. The pattern that we look for is the pattern expressing the observed macroscopic description. Let the state space of the more macroscopic description be denoted by $\mathcal{M}_{\text{slow}}$, $x_{\text{slow}} \in \mathcal{M}_{\text{slow}}$, the quantities through which the individual features are expressed by $\mathcal{Q}$. $q \in \mathcal{Q}$. For example, for isolated systems we can choose $\mathcal{M}_{\text{slow}}$ to be the state space of equilibrium thermodynamics (note that $\mathcal{Q}$ is in this case the set of all fundamental thermodynamic relations $S = S(E, N, V)$). How shall we recognize the pattern in the phase portrait? As we recalled in the previous section in the context of the pattern expressing the classical equilibrium thermodynamics, we can follow two paths. One on which we analyze in detail the particle trajectories in $\mathcal{M}$ and the other on which we first

appropriately modify the equation governing the time evolution of x and then analyze solutions of this modified equation. We suggest that we can follow the same strategy also in the process of recognizing the patterns expressing the macroscopic time evolution of driven systems. In particular, we suggest that the final stage of the pattern recognition process described in Section 2 as thermodynamics (Th1)–(Th4) is common to all pattern recognition processes in phase portraits. In other words, we are suggesting that the experimentally established fact of the existence of a macroscopic description (in both isolated and driven systems) always leads to a thermodynamic theory in the state space used in the macroscopic description (i.e. in $\mathcal{M}_{slow}$). The thermodynamical theory is always a particular realization (appearing in the pattern recognition process) of the general thermodynamics (Th1)–(Th4). The first formulation of this idea has appeared in [41]. Its further developments have been reported in [42,43].

We shall now formulate the time evolution representing the approach of the time evolution in $\mathcal{M}$ to the time evolution in $\mathcal{M}_{slow}$. We begin by noting that we have already written an equation of this type, namely Eq. (39), for the special case in which $\mathcal{M}$ is left unspecified but $\mathcal{M}_{slow} = \mathcal{M}_{eq\,th} :=$ state space of equilibrium thermodynamics (i.e. elements of $\mathcal{M}_{eq\,th}$ are (E, N, V)). In this special case no time evolution in $\mathcal{M}_{slow}$ takes place. Now we turn our attention to the general case in which also $\mathcal{M}_{slow}$ is left unspecified. We shall write the equation governing the time evolution of $x \in \mathcal{M}$ representing the approach of the time evolution in $\mathcal{M}$ to the time evolution in $\mathcal{M}_{slow}$ as follows:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = L(x)\Phi_x + dissipation\,term, \tag{51}$$

where L, Φ and the dissipation term are required to satisfy the following properties:

L is a Poisson bivector $\tag{52}$

$$\text{Eq. (51)} \Rightarrow \Pi\left(\frac{\mathrm{d}x}{\mathrm{d}t}\right) = \frac{\mathrm{d}x_{slow}}{\mathrm{d}t} = 0, \tag{53}$$

$$\text{Eq. (51)} \Rightarrow \frac{\mathrm{d}\Phi}{\mathrm{d}t} \leq 0, \tag{54}$$

Φ is the potential (20) generating Legendre transformations. $\tag{55}$

As we have already mentioned in the context of an additional insight into the generating potentials has arisen recently [31] in the setting in which the thermodynamics (Th1)–(Th4) and the time evolution equation (51) are fully integrated into one embracing geometrical picture. The development of such setting (see [31]) is out of the scope of this paper. The requirements (52) and (53) address the degeneracy of the Poisson bivector L and the dissipation potential involved in the dissipation term. Eq. (53) is clearly an extension of Eqs. (13) and (14) that are associated with Eq. (39). We also recall that for a given $\mathcal{M}$ and a given time evolution in $\mathcal{M}$ the choice of $\mathcal{M}_{slow}$ is not arbitrary. There are two routes leading to the choice of $\mathcal{M}_{slow}$. First, it is the pattern recognition in the phase portrait in $\mathcal{M}$. Second, we get to know $\mathcal{M}_{slow}$ and the time evolution in it as a result of observations. For example, this is the way we got to know classical hydrodynamics. What remains is to identify the projection operator $\Pi : \mathcal{M} \rightarrow \mathcal{M}_{slow}$. Its identification should come again as a result of the pattern recognition process in the phase portrait in $\mathcal{M}$ but in practice Π is usually suggested on the basis of ad hoc albeit well physically founded considerations.

What remains now is to study in detail particular examples. In such study we expect to meet other arguments and results that have been developed independently in various particular contexts. It is obvious

that we cannot follow this program very far in this paper. What we shall do is that we shall consider in some detail one external force, namely the imposed temperature or pressure, in the context of a whole spectrum of levels (Section 3.1). In order to convey however the main feature of this type of analysis, namely its unifying nature, we shall very briefly and without details mention also the situation arising in the presence of other types of external forces (Section 3.2). Only one simple example (Example 1 in Section 3.2) will be worked out with all details.

3.1. Imposed temperature and pressure

To impose the temperature means to put the system under consideration (we shall call it a fluid) into a contact, allowing exchange of heat, with another system that we shall call a thermal bath. Both systems together will be called an enlarged system. The enlarged system is an isolated system. The initial stage of its evolution is the thermal equilibration of the fluid and the thermal bath. This means that the fast state variables in this stage of the time evolution are $E_c^{(fl)}$ and $E_c^{(th.b)}$ describing the thermal motion (the subscript "c" denotes "caloric" (fl) refers to the fluid and (th.b) to the thermal bath). The final equilibration is achieved when the entropy $S_c(E_c^{(fl)}, E_c^{(th.b)}) = S_c^{(fl)}(E_c^{(fl)}) + S_c^{(th.b)}(E_c^{(th.b)})$ reaches its maximum. This means that (since $E_c^{(fl)} + E_c^{(th.b)} = \text{const.}$)

$$\frac{dS_c^{(fl)}}{dE_c^{(fl)}} = \frac{dS_c^{(th.b)}}{dE_c^{th.b}} = \text{const.} := \frac{1}{T}. \tag{56}$$

The initial stage in the time evolution of the enlarged system we can be also regarded as a process of preparation of the fluid subjected to the influence of thermal bath.

In the subsequent time evolution we shall follow only the fluid (now a driven system). The external influence is expressed by Eq. (56). Let the state variables of the fluid be (x, S_c, V, N) (we shall omit the superscript (fl) since we consider now only the fluid). In these state variables x are the fast state variables and $dE_c/dS_c = T$ (the imposed temperature) together with V, N are the slow variables. The first thing that we have to do therefore is to pass from (x, S_c, V, N) to (x, T, V, N). This is clearly achieved by the Legendre transformation so that the fast time evolution (both nondissipative and dissipative) of the prepared fluid will be generated by

$$\Phi(x, T, V, N) = (E(x, S_c, V, N) - T(S_0(x) + S_c))|_{(\partial(E(x,S_c,V,N) - T(S_0(x)+S_c))/\partial S_c = 0)}. \tag{57}$$

In Eq. (57) we denote by $S_0(x)$ the part of the total entropy expressible in terms of the state variables x (the total entropy $S = S_0(x) + S_c$). The thermodynamics of the system driven by an imposed temperature (i.e. thermodynamics in the space of slow state variables (T, V, N), i.e. in this case $(T, V, N) \in \mathcal{M}_{slow}$) is determined by Φ given in Eq. (57) evaluated at x_{th} that is a solution of $\partial \Phi/\partial x = 0$ (it is also the x approached as the time goes to infinity). Such is clearly the standard equilibrium thermodynamic free energy. The thermodynamics of systems driven by an imposed temperature is thus the standard equilibrium thermodynamics expressed in the state variables (T, V, N).

Now, we present some examples (i.e. some particular choices of x) in detail. First, we consider the setting of classical equilibrium thermodynamics, i.e. is absent and $S_c = S$. In this case there is, of course, no time evolution. The passage $(V, N, S) \mapsto (V, N, T)$ is the Legendre transformation constituting an integral part of the mathematical formulation of classical equilibrium thermodynamics. From the physical point of view, this reflects the well known fact that the validity of classical equilibrium thermodynamics

is not limited to isolated systems. Also systems driven by being in appropriately restricted contact with exterior of the system (imposed temperature, pressure, and chemical potential) are described by classical equilibrium thermodynamics. The inclusion of Legendre transformations into the formulation of equilibrium thermodynamics is best expressed mathematically by, first, enlarging the set of state variables and, second, by introducing a contact structure in the set of the enlarged thermodynamic state variables. The contact structure is the structure that is invariant under the Legendre transformations. The enlarged set of state variables is composed of (V, N, S, T, P, μ).

Next, we consider the setting of classical hydrodynamics. In this setting the state variables x are the hydrodynamic fields $(\rho(\boldsymbol{r}), \boldsymbol{u}(\boldsymbol{r}), s(\boldsymbol{r}))$ (see Section 2.2), the time evolution is governed by the time evolution equation (37) with s and f missing (the Poisson bivector L is given in Eq. (30) with $\bar{s}$ missing and $\bar{\rho}, \bar{\boldsymbol{u}}$ replaced by $\rho, \boldsymbol{u}$) and the energy E generating the time evolution in Eq. (37) is replaced by the free energy $\Phi(x, V, N, T)$ given in Eq. (57) with $S_0(x)$ missing. This is, of course, the well known way the isothermal fluids are treated in classical hydrodynamics.

In the setting of extended hydrodynamics of complex fluids we proceed in way. In this setting the state variables x include the classical hydrodynamic fields, also other fields or distribution functions describing the internal structure of the complex fluids. The only difference now is that the part of the entropy denoted in Eq. (57) is not identically equal to zero as in the case of classical equilibrium thermodynamics or classical hydrodynamics but it is a quantity that has to be specified. Many examples of x and $S_0(x)$ can be found in [18–30].

In the following example we consider the setting of the so called direct molecular simulations. We choose $x = (\boldsymbol{r}, \boldsymbol{v}) \in \boldsymbol{M}_n$, where $\boldsymbol{r} = (\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n), \boldsymbol{v} = (\boldsymbol{v}_1, \ldots, \boldsymbol{v}_n), \boldsymbol{r}_i, \boldsymbol{v}_i$ are position coordinates and momenta of the ith particle. First, we shall recall how we investigate in this setting the isolated systems and then we shall extend the investigation to the systems subjected to an imposed temperature or pressure.

The equations governing the time evolution of x are

$$\frac{\mathrm{d}x}{\mathrm{d}t} = LE_x, \tag{58}$$

where $E(x)$ is the energy and

$$L = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix},$$

i.e. the Poisson bracket in $\boldsymbol{M}_n$ is the canonical Poisson bracket

$$\{A, B\}_{\mathrm{cl\,mech}} = \sum_{i=1}^{n} (A_{\boldsymbol{r}_i} B_{\boldsymbol{v}_i} - B_{\boldsymbol{r}_i} A_{\boldsymbol{v}_i}). \tag{59}$$

Now we look for properties of solutions of Eq. (58) that will reveal the classical equilibrium thermodynamics implied by Eq. (58). Following the discussion in Section 2 we can follow two paths. The first one consists of constructing the phase portrait in $\boldsymbol{M}_n$ and then extracting from it a pattern representing classical equilibrium thermodynamics. On the second path we pass first to distribution functions and then formulate a realization of Eq. (39) that replaces Eq. (58). The second path has been described in Section 2. What is new and interesting is that if we choose the number of particles $n \sim 10^3$ then, with the assistance of computers, we can also follow the first path. We make here only two comments about the way equilibrium thermodynamics is extracted from Eq. (58) in molecular simulations. We

have defined the phase portrait in $\boldsymbol{M}_n$ as a set of trajectories passing through all $x \in \boldsymbol{M}_n$ for a family of energies $E(x)$. An investigation of the literature shows that the calculations are usually done only for one specific energy. As for the pattern recognition process, it usually consists of various averaging. More sophisticated pattern recognition processes involve a comparison of nearby trajectories (see e.g. [10]).

By calculating the phase portrait corresponding to Eq. (58) we consider the situation $E = \text{const.}$ Now, we proceed to the case in which $T = \text{const.}$ rather than $E = \text{const.}$ First, we ask as to whether we can also in this case use computers and follow the first path. We shall briefly follow it. According to the general strategy outlined at the beginning of this subsection, the first thing that has to be done is to replace the energy E by the free energy Φ. We thus have to know how to express the entropy in terms of $x \in \boldsymbol{M}_n$. Since the entropy has to be a Casimir of the Poisson bracket expressing kinematics in $\boldsymbol{M}_n$, i.e. the Poisson bracket (59), and since the canonical Poisson bracket (59) is nondegenerate (i.e. the only Casimirs are $C = \text{const.}$) this cannot be done. We thus have to begin by extending the state space $\boldsymbol{M}_n$ to a bigger state space $\boldsymbol{M}$ in which we would be able to express the entropy. In order to keep the "computer friendliness" of the governing equations, the extended state space $\boldsymbol{M}$ has to remain finite dimensional. We shall not embark here on a systematic discussion of this problem. Below, we shall only note that some of the choices of $\boldsymbol{M}$ and the time evolution in them that have been reported in the literature can be cast into the setting of Eq. (57) in which E is replaced by Φ and the canonical Poisson bracket (58) by another Poisson bracket (see also [44,45]).

Inspired by the continuum–continuum ensemble (Section 2.3) we introduce the extra state variables through which we shall express the entropy as state variables of a fictitious fluid. We shall choose them to be the position coordinates and momenta of "phantom particles", one state variable, denoted Ω closely related to entropy (see Eq. (65)), and another one, denoted ϵ, related to the entropy flux (see the fourth equation in Eq. (66)). In the illustration developed below we try to use the smallest number of state variables. We shall, therefore, omit interactions among the phantom particles (we can thus omit the position vectors of the phantom particles) and we shall consider only one such particle. Its momentum will be denoted by the symbol $\boldsymbol{V}$. The complete set of state variables $x \in \boldsymbol{M}$ in this illustration is thus

$$\boldsymbol{M} \ni x \equiv (\boldsymbol{r}_1, \boldsymbol{v}_1, \dots \boldsymbol{r}_n, \boldsymbol{v}_n, \boldsymbol{V}, \Omega, \epsilon). \tag{60}$$

The Poisson kinematics of these state variables, replacing in $\boldsymbol{M}$ the Poisson kinematics determined by Eq. (59), is determined by the following Poisson bracket:

$$\{A, B\} = \sum_{i=1}^{n} (A_{r_{i\alpha}} B_{v_{i\alpha}} - B_{r_{i\alpha}} A_{v_{i\alpha}}) + \Omega(A_\Omega B_\epsilon - B_\Omega A_\epsilon) - V_\alpha(A_{V_\alpha} B_\epsilon - A_\epsilon B_{V_\alpha}). \tag{61}$$

The first term is the canonical Poisson bracket of particle coordinates and momenta, the second term expresses advection of Ω with ϵ and the third term advection of $\boldsymbol{V}$ with ϵ. It easy to verify that Eq. (61) is indeed a Poisson bracket (the Jacobi that is the only property that is not obvious, can be verified by a direct calculation).

Next, we pass to new sate variables in which $\boldsymbol{v}_i$ are replaced by $\boldsymbol{w}_i = \boldsymbol{v}_i + \boldsymbol{V}, i = 1, 2, \dots, n$. The transformation is clearly one-to-one and the Poisson bracket (53) becomes (to simplify the notation we

write again $\boldsymbol{v}_i$ instead of $\boldsymbol{w}_i$)

$$\{A, B\} = \sum_{i=1}^{n}(A_{r_{i\alpha}}B_{v_{i\alpha}} - B_{r_{i\alpha}}A_{v_{i\alpha}}) + \Omega(A_{\Omega}B_{\epsilon} - B_{\Omega}A_{\epsilon}) - V_{\alpha}(A_{V_{\alpha}}B_{\epsilon} - A_{\epsilon}B_{V_{\alpha}})$$

$$-\sum_{i=1}^{n}V_{\alpha}(A_{v_{i\alpha}}B_{\epsilon} - A_{\epsilon}B_{v_{i\alpha}}). \tag{62}$$

The corresponding time evolution equations are

$$\frac{\mathrm{d}r_{i\alpha}}{\mathrm{d}t} = \Phi_{v_{i\alpha}}, \qquad \frac{\mathrm{d}v_{i\alpha}}{\mathrm{d}t} = -\Phi_{r_{i\alpha}-V_{\alpha}-\Phi_{\epsilon}}, \qquad \frac{\mathrm{d}\Phi}{\mathrm{d}t} = \Omega\Phi_{\epsilon},$$

$$\frac{\mathrm{d}\epsilon}{\mathrm{d}t} = -\Omega\Phi_{\Omega} + V_{\alpha}\Phi_{V_{\alpha}} + \sum_{i=1}^{n}V_{\alpha}\Phi_{v_{i\alpha}}, \tag{63}$$

where Φ is given in Eq. (57). If we choose, as an example, the energy to be

$$E = \sum_{i=1}^{n}\frac{v_{i\alpha}^2}{2m} + \frac{1}{2}K\epsilon^2 + V_{\mathrm{pot}}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n), \tag{64}$$

where m is the mass of one particle, K is a parameter and V_{pot} is the potential energy among the particles, and the entropy to be

$$S = -\ln \Omega^3, \tag{65}$$

then the time evolution equation (63) become

$$\frac{\mathrm{d}r_{i\alpha}}{\mathrm{d}t} = \frac{v_{i\alpha}}{m}, \qquad \frac{\mathrm{d}v_{i\alpha}}{\mathrm{d}t} = -\frac{\partial V_{\mathrm{pot}}}{\partial r_{i\alpha}} - KV_{\alpha}\epsilon,$$

$$\frac{\mathrm{d}V_{\alpha}}{\mathrm{d}t} = -KV_{\alpha}\epsilon, \qquad \frac{\mathrm{d}\Omega}{\mathrm{d}t} = K\Omega\epsilon, \qquad \frac{\mathrm{d}\epsilon}{\mathrm{d}t} = -3T + \sum_{i=1}^{n}\frac{V_{\alpha}v_{i\alpha}}{m}. \tag{66}$$

These time evolution equations are very similar to the time evolution equations introduced by Nosé and Hoover [46–48] on the basis of another type of considerations. Nose point of view is the following: we look for the time evolution equations (equations governing the time evolution of particle coordinates and momenta and a finite number of additional state variables) for which the corresponding Liouville equation admits the microcanonical distribution function as its stationary solution. This function then, if integrated over the added state variables, is required to turn into classical canonical distribution function. We can easily verify that this is indeed the case for Eq. (66): since Φ remains constant during the time evolution, the microcanonical distribution function $\delta(\Phi - \mathrm{const.})$ is an admissible stationary solution of the Liouville equation corresponding to Eq. (66). If this function is integrated over $\boldsymbol{V}$, Ω, and ϵ it becomes the classical canonical distribution function.

It is clear that everything that we said above about fluids subjected to an imposed temperature can be simply adapted to the systems subjected to an imposed pressure. The entropy has to be replaced by

volume, temperature by pressure and free energy by enthalpy. Here we shall only recall explicitly the formulation used in direct molecular simulations. As the state variables we choose

$$x \equiv (\boldsymbol{r}_1, \boldsymbol{v}_1, \ldots, \boldsymbol{r}_n, \boldsymbol{v}_n, \boldsymbol{V}, \epsilon), \tag{67}$$

where $\boldsymbol{V}$ is the overall volume and ϵ the "volume flux" (its physical meaning is revealed in the dynamics introduced below). The Poisson kinematics of the state variables (67) we choose to be

$$\{A, B\} = \sum_{i=1}^{n} (A_{r_{i\alpha}} B_{v_{i\alpha}} - B_{r_{i\alpha}} A_{v_{i\alpha}}) + V(A_V B_\epsilon - B_V A_\epsilon) + \sum_{i=1}^{n} r_{i\alpha} (A_{r_{i\alpha}} B_\epsilon - B_{r_{i\alpha}} A_\epsilon)$$

$$- \sum_{i=1}^{n} v_{i\alpha} (A_{v_{i\alpha}} B_\epsilon - B_{v_{i\alpha}} A_\epsilon). \tag{68}$$

The first term in the bracket (68) is the canonical Poisson bracket (59) of classical mechanics. The next three terms express advection of $V, \boldsymbol{r}_i$ and $\boldsymbol{v}_i$, respectively, by ϵ. It is easy to verify by direct calculations that Eq. (68) is indeed a Poisson bracket. The time evolution of the fast state variables is governed now by the enthalpy H. We shall choose it to be

$$H = \sum_{i=1}^{n} \frac{v_{i\alpha} v_{i\alpha}}{2m} + V_{\text{pot}}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n) + \frac{1}{2} K \epsilon^2 + PV, \tag{69}$$

where P is the imposed pressure, m is the mass of one particle, K is a parameter, and V_{pot} is the potential energy. The time evolution equations corresponding to Eqs. (68) and (69) are

$$\frac{dr_{i\alpha}}{dt} = \frac{v_{i\alpha}}{m} + Kr_{i\alpha}\epsilon, \qquad \frac{dv_{i\alpha}}{dt} = -\frac{\partial V_{\text{pot}}}{\partial r_{i\alpha}} - Kv_{i\alpha}\epsilon,$$

$$\frac{dV}{dt} = KV\epsilon, \qquad \frac{d\epsilon}{dt} = -PV + \frac{v_{i\alpha} v_{i\alpha}}{m} - r_{i\alpha} \frac{\partial V_{\text{pot}}}{\partial r_{i\alpha}}. \tag{70}$$

These equations have been derived previously, on the basis of completely different considerations, in [49].

Now we turn our attention to the second path. We thus look for a realization of Eq. (51) whose solutions will show the approach to the equilibrium states with $T = \text{const}$. Here, we shall abandon the requirement of the "computer friendliness" and allow the extended state space to be an infinite dimensional space. We shall denote it by the symbol $\mathcal{M}$. We suggest to regard the particles in the context of the KTH ensemble introduced in Section 2.2. Elements of $\mathcal{M}$ are chosen to be $x = (\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n, \boldsymbol{v}_1, \ldots, \boldsymbol{v}_n, f_1(\boldsymbol{r}_1, \boldsymbol{v}_1), f_2(\boldsymbol{r}_1, \boldsymbol{v}_1, \boldsymbol{r}_2, \boldsymbol{v}_2)$, higher order distribution functions), where f_1 and f_2 are the one and two particle distribution functions, respectively. For the sake of simplicity we shall continue only with f_1. The time evolution of $x \in \mathcal{M}$ is easily obtained from Eq. (26). If we choose the energy to be $E = \sum_{i=1}^{n} [f_n((v_i)^2/2m + V_{\text{pot}}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_n)) + \text{a term independent of } f_n]$ and the entropy S to be independent of f_n then Eq. (26) can be written as

$$\frac{dr_{i\alpha}}{dt} = \frac{v_{i\alpha}}{m} + \frac{\partial \Phi_{f_1}}{\partial v_{i\alpha}}, \qquad \frac{dv_{i\alpha}}{dt} = -\frac{\partial V_{\text{pot}}}{\partial r_{i\alpha}} - \frac{\partial \Phi_{f_1}}{\partial r_{i\alpha}},$$

$$\frac{\partial f_{1(1)}}{dt} = -\frac{\partial}{\partial r_{i\alpha}} \left(f_1 \frac{\partial \Phi_{f_1}}{\partial v_{i\alpha}} \right) + \frac{\partial}{\partial v_{i\alpha}} \left(f_1 \frac{\partial \Phi_{f_1}}{\partial r_{i\alpha}} \right) - \frac{\partial \Psi}{\partial \Phi_{f_{1(1)}}}. \tag{71}$$

In the second equation of system (26) we have replaced f_n by the Klimontovich distribution function and added a dissipation term (the term on the right-hand side). A more detailed specification and analysis of solutions of Eq. (71) is out of the scope of this paper.

3.2. Imposed hydrodynamic flows and boundary conditions

External forces that have played the most important role in rheology are imposed hydrodynamic flows in particular then the imposed mass flows. A large majority of rheological measurements are observations of reactions of complex fluids to the application of these forces. The theoretical setting relating to the rheological measurements has to therefore involve hydrodynamic fields together with other state variables (we shall denote them by the symbol x_{int}) that characterize the internal structure most directly influenced by the imposed hydrodynamic flows. For example, in the setting discussed in Section 2.2, x_{int} is the one particle distribution function. The state variables of rheological models (we shall denote them by the symbol x_{rheo}) are thus

$$x_{\text{rheo}} \equiv (\text{hydrodynamic fields}, x_{\text{int}}). \tag{72}$$

A general framework for such setting has been developed in Section 2.2. To obtain a rheological model the framework has to be filled with physical insight about the fluid under consideration. The framework is particularly useful in showing what sort of insight is needed, how to express it in mathematical terms, and how to put everything together to arrive at an intrinsically consistent model. Many rheological models, both old (derived before on the basis of other considerations) and new (derived for the first time by using the framework) have been now formulated in this way.

We recall that the framework serving as the pivotal point in the construction of the rheological models guarantees that the whole system (both the complex fluid under consideration and the hydrodynamic flows) reaches an equilibrium thermodynamic state if left undisturbed. This is indeed experimentally observed. We are thus making the first successful confrontation of our models with experiments. There are, however, other more interesting rheological observations with which we want to confront our models. In these observations the hydrodynamic flows are considered to be imposed from outside and thus the complex fluid under consideration is seen as a driven system. We shall now take this point of view.

First, we recall how we calculate results of rheological observations. In the equations governing the time evolution of x_{rheo} we look only at the equations governing the time evolution of x_{int} (e.g. in Eq. (40) is the fourth equation) in which the terms involving hydrodynamic fields are considered to be known external forces. After solving these equations (we shall talk about boundary conditions later in this section) we insert the solution into the expressions for extra stress tensor and heat flux appearing in the equations governing the time evolution of hydrodynamic fields (see Eq. (43)). These are then the quantities constituting the output of traditional rheological measurements. At this point we may appreciate that the framework (39) shows clearly how to express the external forces in the equation governing the time evolution of x_{int}, see Eq. (44) in the context of direct molecular simulations) and how to express results of rheological measurements in terms of x_{int} (see Eqs. (43) and (49)).

But this is not all. We can also derive thermodynamics of complex fluids subjected to external hydrodynamic forces. We shall call it flow-thermodynamics, or if we use the Greek word for flow, a rheo-thermodynamics. In the rest of this section we shall make a few comments about how this thermodynamics can be derived and what may be its usefulness.

From the large body of knowledge created in the last, say, 60 years in rheology we take only one result: the comparison of results of rheological measurements with theoretical predictions shows that in the large majority of situations there exists an appropriate mesoscopic theoretical setting (an appropriate choice of x_{int}) providing a realistic description of complex fluids subjected to external hydrodynamic forces (we emphasize at this point that the choice of x_{int} is not expected to be universal). This experimental observation constitutes the experimental basis of rheo-thermodynamics. Indeed, following the discussion at the beginning of this section we can now deduce consequences of this experimental observation. Let x_{rheo} and the corresponding time evolution equations represent a theoretical setting that is found to be in agreement with results of rheological measurements. Let us now take a more microscopic point of view in which the state variables are chosen to be more detailed than x_{rheo}. We shall denote them by the symbol $x_{rheo}^{(micro)}$,

$$x_{rhoe}^{(micro)} \equiv (\text{hydrodynamic fields, } x_{int}^{(micro)}), \tag{73}$$

where $x_{int}^{(micro)}$ represents the more detailed internal state variables. The state variables x_{int} are obtained from $x_{int}^{(micro)}$ by a projection (we shall denote it by the symbol, i.e. $\mathcal{M}_{int} = \Pi \mathcal{M}_{int}^{(micro)}$, where $\mathcal{M}_{int}$ is the state space whose elements are x_{int} and $\mathcal{M}_{int}^{(micro)}$ is the state space whose elements are $x_{int}^{(micro)}$. As an example, we can think of x_{int} as about the conformation tensor $\boldsymbol{c}$ and of $x_{int}^{(micro)}$ as about configuration space distribution functions $\psi(\boldsymbol{R})$, where $\boldsymbol{R}$ is the end-to-end vector of a model-macromolecule; the projection II is given by $c_{\alpha\beta} = \int d\boldsymbol{R} \, R_\alpha R_\beta \psi(\boldsymbol{R})$. Since, we consider here the complex fluids as driven systems we look now only at the time evolution in and in $\mathcal{M}_{int}$ and in $\mathcal{M}_{int}^{(micro)}$. The experimental observation that we are taking as the experimental basis of the rheo-thermodynamics implies that the time evolution in $\mathcal{M}_{int}^{(micro)}$ has to approach, as the time goes to infinity, the time evolution in $\mathcal{M}_{int}$.

We emphasize that neither the time evolution in $\mathcal{M}_{int}^{(micro)}$ nor the time evolution in $\mathcal{M}_{int}$ is, in general, expected to be governed by equations of the form (39) or (51). It is only the part of the time evolution in $\mathcal{M}_{int}^{(micro)}$, namely the part describing the approach of the time evolution in $\mathcal{M}_{int}^{(micro)}$ to the time evolution in $\mathcal{M}_{int}$, that is expected to be governed by the time evolution equation of this form.

We have seen that the process of solving the time evolution equations in $\mathcal{M}_{int}^{(micro)}$ brings us the function Φ (it arises as the function generating the approach of the fast time evolution to the slow time evolution) which, if put into the context of thermodynamics (Th1)–(Th4), see Section 2.1, brings the rheo-thermodynamics. The following examples and questions will indicate the physical significance of this theory.

Example 1. This is a toy example that is not however without a physical content. It appeared first in [43] in the context of thermodynamics of glasses. The example is simple enough to be worked out completely in all details. It can serve as a specific illustration of both Eqs. (39) and (51) and of the thermodynamics of driven systems. The presentation of the example that appeared in the first version of this paper was discussed extensively with Hans Christian Oettinger. Thanks to the discussion this new version is free of several mistakes in calculations that I made in the first version. The discussion led also to a better understanding of the physics involved in the example.

We introduce three levels of description: Level 0, Level 1, and Level 2.

Level 0: This is the level of classical equilibrium thermodynamics, the state variables are: $\mathcal{M}_0 \ni x_0 = (n, e)$, where $n = N/V$, $e = E/V$, V denotes the volume, we assume it to be a constant. The fundamental thermodynamic relation in $\mathcal{M}_0$ is $s_0 = s_0(n, e)$. No time evolution takes place in $\mathcal{M}_0$.

Level 1: The state variables on this level are $\mathcal{M}_1 \ni x_1 = (n, e, p)$. The fundamental thermodynamic relation in $\mathcal{M}_1$ is $s_{1,0} = s_{1,0}(n, e, p)$. The projection $\Pi_{1,0} : \mathcal{M}_1 \to \mathcal{M}_0$ is defined by $(n, e, p) \mapsto (n, e)$. The time evolution in $\mathcal{M}_1$ describing the approach to equilibrium thermodynamics (i.e. the approach of the Level 1 description to the Level 0 description) is governed by a realization of Eq. (39) corresponding to $x = x_1$, $\{A, B\}_{1,0} \equiv 0$, $\Psi_{1,0} = (1/2)\Lambda_{1,0}((s_{1,0})_p)^2$, where $\Lambda_{1,0} > 0$ is a function of x_1. With these specifications, Eq. (39) becomes

$$\frac{dn}{dt} = 0, \qquad \frac{de}{dt} = 0, \qquad \frac{dp}{dt} = \Lambda_{1,0}(s_{1,0})_p. \tag{74}$$

Eq. (74) represents the time evolution arising in the confrontation of Levels 1 and 0. We note that this particular realization of Eq. (39) involves only one generating potential, namely $s_{1,0}(x_1)$. We use the indices 1, 0 to indicate the origin of the generating potential. The generating potential is always introduced in the confrontation of two levels. If we change the levels we change the generating potential. This will be well illustrated in this example. The entropy s_0 introduced on Level 0 is obtained from $s_{1,0}$ by following the time evolution to its completion, i.e. to equilibrium states that are solutions of $(s_{1,0})_p = 0$. We thus have $s_0(n, e) = s_{1,0}(n, e, p)|_{(s_{1,0})_p=0}$.

Level 2: The state variables on this levels are $\mathcal{M}_2 \ni x_2 = (n, e, p, q)$. The fundamental thermodynamic relation in $\mathcal{M}_2$ is $s_{2,0} = s_{2,0}(n, e, p, q)$. The projection $\Pi_{2,0} : \mathcal{M}_2 \to \mathcal{M}_0$ is defined by $(n, e, p, q) \mapsto (n, e)$. The time evolution in $\mathcal{M}_2$ describing the approach to equilibrium thermodynamics (i.e. to Level 0) is governed by a realization of Eq. (39) corresponding to $x = x_2$, $\{A, B\}_{2,0} = (A_p B_q - B_p A_q) + ((s_{2,0})_e)^{-1}[(s_{2,0})_q(A_e B_p - B_e A_p) + (s_{2,0})_p(A_q B_e - B_q A_e)]$, $\Psi_{2,0} = 1/2\Lambda_{2,0}(s_{2,0})_q^2$ where $\Lambda_{2,0} > 0$ is a function of x_2. (We can easily prove that $\{A, B\}_{2,0}$ is a Poisson bracket by noting that the canonical Poisson bracket $\{A, B\} = A_p B_q - B_p A_q$ written in the state variables $(n, s_{2,0}, p, q)$ transforms into $\{A, B\}_{2,0}$, under the one-to-one transformation $(n, s_{2,0}, p, q) \mapsto (n, e, p, q)$, i.e. we assume that $(s_{2,0})_e > 0$) With these specifications, Eq. (39) becomes

$$\frac{dn}{dt} = 0, \qquad \frac{de}{dt} = 0, \qquad \frac{dp}{dt} = -((s_{2,0})_e)^{-1}(s_{2,0})_q,$$
$$\frac{dq}{dt} = ((s_{2,0})_e)^{-1}(s_{2,0})_p + \Lambda_{2,0}(s_{2,0})_q. \tag{75}$$

Eq. (75) represents the time evolution arising in the confrontation of the Levels 2 and 0. This particular realization of Eq. (39) involves again only one generating potential, namely $s_{2,0}(n, e, p, q)$. This is simply because the energy is one of the state variables. Following the time evolution, we arrive eventually at the equilibrium states determined by $(s_{2,0})_q = 0$, $(s_{2,0})_p = 0$. Consequently, $s_0(n, e) = s_{2,0}(n, e, p, q)|_{(s_{2,0})_q=0,(s_{2,0})_p=0}$.

So far, the system under consideration, i.e. the system represented by the three levels presented above, has been externally unforced. As the time goes to infinity, the system evolves to equilibrium states. Now, we shall prevent the approach to equilibrium states. This can be achieved either by an external influence, i.e. by applying an external force and thus modifying Eqs. (74) and (75), or by keeping Eqs. (74) and (75) unchanged but choosing in them the coefficients Λ in such a way that Eqs. (74) and (75) will describe the time evolution during which some internal constraints are created. The internal constrains then prevent the

completion of the approach to equilibrium. The latter situation arises in glasses. In the context of modeling the time evolution of glasses, the state variable p can be interpreted as a concentration of holes in the hole theory of liquids or as a local volume on the molecular level. The state variable q is then interpreted as the velocity-type state variable corresponding to p (see more in [43]). In any case, let us assume now that Level 0 becomes inaccessible. Moreover, let us also assume that the results of observations show that Level 1 provides still a good description. Our problem now is to find thermodynamics on Level 1 of the systems that are prevented from reaching the Level 0 description. Following the strategy outlined at the beginning of Section 3, we seek this thermodynamics in the confrontation of Level 2 with Level 1. Since, according to our assumed experimental evidence, the time evolution on Level 1 is still found to describe well the behavior of the systems that are prevented from reaching the Level 0 description, the time evolution on Level 2 has to show an approach the time evolution on Level 1. To find thermodynamics on Level 1 means to find a realization of Eq. (51) describing such approach. The potential arising in the realization will be then the potential determining the thermodynamics that we seek.

To simplify the analysis of the asymptotic behavior of solutions to Eq. (75), we shall make two assumptions: (i) we assume that q in Eq. (75) evolves faster than the rest of the state variables, and (ii) $s_{2,0}(n, e, p, q) = s_{1,0}(n, e, p) - (1/2)a(n, e, p)q^2$ where a is a real valued and positive function. The simplest way to estimate $a(n, e, p)$ is the following. By passing from Level 1 to Level 2 the energy gets a new term proportional to q^2. We shall write it as $(1/2m)q^2$. This is because q plays the role of the "momentum that is associated with p". The energy on Level 1, we shall denote it by the symbol ϵ, becomes $\epsilon(e, p) = e - (1/2m)q^2$. We introduce $s_{2,0}(n, e, p, q) := s_{1,0}(n, \epsilon(e, q), p) \sim s_{1,0}(n, e, p) - (1/2)aq^2$ where $a = (1/m)(s_{1,0})_e$.

The two assumptions introduced above imply that q becomes small as the time goes to infinity. We shall thus keep in Eq. (75) only the terms that are linear in q. We also see easily that, as the time goes to infinity, the time evolution governed by Eq. (75) will be concentrated about a manifold, we shall call it $\mathcal{M}_{\text{closure}}$, that is given by $\mathcal{M}_2 \supset \mathcal{M}_{\text{closure}} = \{x_2 \in \mathcal{M}_2 | (\mathrm{d}q/\mathrm{d}t)_{\text{Eq. (75)}} = 0\}$. If we then evaluate Eq. $(\mathrm{d}p/\mathrm{d}t)_{\text{Eq. (75)}}$ at $\mathcal{M}_{\text{closure}}$, we see that the resulting equation is identical with Eq. $(\mathrm{d}p/\mathrm{d}t)_{\text{Eq. (74)}}$ provided $\Lambda_{1,0} = ((s_{1,0})_e)^{-2}(\Lambda_{2,0})^{-1}$ This relation expresses the kinetic coefficients introduced on Level 1 in terms of the kinetic coefficients introduced on the more microscopic Level 2.

We proceed to identify the equation governing the approach of Level 2 to Level 1. We can convince ourselves easily that this equation is

$$\frac{\mathrm{d}n}{\mathrm{d}t} = 0, \qquad \frac{\mathrm{d}e}{\mathrm{d}t} = 0, \qquad \frac{\mathrm{d}p}{\mathrm{d}t} = 0, \qquad \frac{\mathrm{d}q}{\mathrm{d}t} = \Lambda_{2,1}(\varphi_{2,1})_q, \tag{76}$$

where $\Lambda_{2,1} > 0$ is a function of $(\Lambda_{1,0}, \Lambda_{2,0}, s_{1,0})$ and $\varphi_{2,1}(n, e, p, q)$ is a new thermodynamic potential introduced below. It is easy to verify that Eq. (76) is indeed a particular realization of Eq. (51) in which $x = (n, e, p, q)$, $\Psi_{2,1} = (1/2)\Lambda_{2,1}((\varphi_{2,1})_q)^2$ and the generating potential is $\varphi_{2,1}$.

Now, we specify $\varphi_{2,1}(n, e, p, q)$. It is easy to see that if we follow the time evolution of Eq. (76) we reach states that are solutions of $(\varphi_{2,1})_q = 0$. These states form a manifold (called $\mathcal{M}_{\text{th}}$ in the terminology introduced in the abstract thermodynamics (Th1)–(Th4)). We shall require that this manifold is identical with the manifold $\mathcal{M}_{\text{closure}}$, i.e. we shall require that $\mathcal{M}_{\text{closure}} \equiv \{x_2 \in \mathcal{M}_2 | (\mathrm{d}q/\mathrm{d}t)_{\text{Eq. (75)}} = 0\} \equiv \mathcal{M}_{\text{th}} = \{x_2 \in \mathcal{M}_2 | (\varphi_{2,1})_q = 0\}$. Moreover, we shall require that $\varphi_{2,1}|_{q=0} = s_{1,0}$. In order to find such $\varphi_{2,1}$, we shall make a Legendre transformation of $s_{2,0}$ with respect to q and identify $\varphi_{2,1}$ with the generating potential $\Phi(n, e, p, q; q^*)$ of this transformation with appropriately chosen q^*. We thus proceed as follows: first, we introduce, in the usual way, the generating potential Φ by $\Phi(n, e, p, q; q^*) = s_{2,0}(n, e, p, q) - q^*q$.

Next, we choose q^* by requiring that the equation $(\Phi)_q = 0$ has the same solutions as the equation $(dq/dt)_{\text{Eq. (75)}} = 0$. We see easily that this requirement leads to $q^* := q^{*(\text{closure})} = -(s_{1,0})_p/((s_{1,0})_e \Lambda_{2,0})$. Consequently $\varphi_{2,1}(n, e, p, q) = \Phi(n, e, p, ; q^*)|_{q^*=q^{*(\text{closure})}} = s_{2,0}(n, e, p, q) + (s_{1,0})_p(s_{1,0})_e \Lambda_{1,0} q$. The Legendre transform $s_{2,0}(n, e, p, q)$ is $s_{2,0}^*(n, e, p, q^*) = s_{1,0}(n, e, p) + (q^*)^2/2a$ and consequently the entropy $s_1(n, e, p)$ determining thermodynamics on Level 1 of systems that are prevented from reaching Level 0 is given by

$$s_1(n, e, p) = s_{2,0}^*(n, e, p, q^*)|_{q^*=q^{*(\text{closure})}} = s_{1,0}(n, e, p) + \frac{(\Lambda_{1,0})^2((s_{1,0})_e)^2((s_{1,0})_p)^2}{2a}. \tag{77}$$

In Eq. (77) we used the relation $\Lambda_{1,0} = ((s_{1,0})_e)^{-2}(\Lambda_{2,0})^{-1}$ obtained previously. We note that s_1 involves the quantity $\Lambda_{1,0}$ that appears in Eq. (74) in the dissipative part of the time evolution (in the dissipation potential $\Psi_{1,0}$). In the context of glasses, this result correlates well with results of observations according to which glasses in the vicinity of glass transition show a singular behavior in both thermodynamic quantities (as e.g. specific heat) and dynamic quantities (as e.g. the viscosity or the relaxation time). If we calculate specific heat from the entropy (77) we obtain (see more in [43]) a relation between specific heat and the relaxation time (note that the relaxation time is proportional to $(\Lambda_{1,0})^{-1}$).

We would like to emphasize that in order to arrive at the nonequilibrium entropy s_1 on Level 1 that expresses the entropy of systems that are prevented from reaching Level 0, we needed Level 2. The entropy s_1 arises when the state space on Level 1 is taken to be $\mathcal{M}_{\text{closure}}$ (i.e. a manifold embedded in $\mathcal{M}_2$) rather than $\mathcal{M}_1$ that is the state space introduced on Level 1. We also note the importance of the role that the Legendre transformations play in the construction of s_1 (we have already seen this in the examples discussed in Section 3.1). We can interpret $q^* = q^{*(\text{closure})}$ as an external force keeping the system from collapsing to the Level 0 equilibrium.

In closing this example, we recall Muschik's viewpoint [50] of the concept of entropy of constrained (driven) systems: the entropy of an unconstrained (reference) system equals the entropy of the constrained (forced) system plus Δs that is the entropy created in the process that takes place after removing the constraints. If the unconstrained states are Level 0 equilibrium states and the constrained states are Level 1 states then Muschik's argument shows how to obtain the Level 1 entropy of constrained systems on the basis of just the Level 1 dynamics. As we have emphasized already several times (see also [2]), we do not expect this to be possible. However, we shall show below that Muschik's argument leads to Eq. (77) provided the argument is appropriately applied in the three level setting. Let the constrained (nonequilibrium) state on Level 2 be a state with $q = 0$ (as we see from the fourth equation in system (75) this state will evolve in time if $(s_{2,0})_p \neq 0$). Its entropy is $s_{2,0}|_{q=0} = s_{1,0}$. Let the unconstrained states on Level 2 be the states with $q \in \mathcal{M}_{\text{closure}}$. Their entropy will be denoted by s_1. According to Muschik's argument $s_1 = s_{1,0} + \Delta s$, where Δs is the entropy created in the Level 2 evolution from states with $q = 0$ to states with $q \in \mathcal{M}_{\text{closure}}$. If we succeed to show that Δs equals to the second term on the right-hand side of Eq. (77) then the consistency with Muschik's argument is proven. Let us estimate Δs from Eq. (75) we see easily that the entropy production $ds_{2,0}/dt$ equals $\Lambda_{2,0}(aq)^2$. We now have to integrate this entropy production over the time needed to reach $q \in \mathcal{M}_{\text{slow}}$. Since $q^2(t) \sim e^{-(2\Lambda_{2,0}a)t}$ we have $\Delta s \sim ((1/2a)\Lambda_{2,0})(\Lambda_{2,0}(aq)^2)|_{q \in \mathcal{M}_{\text{closure}}} = (1/2a)(\Lambda_{1,0})^2((s_{1,0})_e)^2((s_{1,0})_p)^2$. In the last equality we have used $\Lambda_{1,0} = ((s_{1,0})_e)^{-2}(\Lambda_{2,0})^{-1}$ derived previously. We thus see that Eq. (77) is indeed consistent with argument provided the argument is appropriately applied in the three level setting.

Example 2. In this example we consider an isolated gas whose time evolution is found to be well described on the level of classical hydrodynamics and also on the level of the Boltzmann kinetic theory. The role of the more microscopic state space $\mathcal{M}$ is thus played by $\mathcal{M}_{kt}$ (the state space whose elements are one particle distribution functions f_1) and the slow state space $\mathcal{M}_{slow}$ is $\mathcal{M}_{hy}$. In this example we do not use the setting of the KTH ensemble developed in Section 2.2. This is because our objective in this example is to relate rather than to combine the kinetic theory and hydrodynamics descriptions. By relating we mean showing how solutions to the kinetic equation are well approximated, as the time goes to infinity, by solutions to hydrodynamic equations. The problem of relating the Boltzmann kinetic theory and classical hydrodynamics is an old problem, going back to Boltzmann himself, Chapman [51] and Enskog [52]. It should be interesting to see how our point of view presents itself in this context.

First, we recall the main idea of the Chapman–Enskog approach. By applying the standard projection $\mathcal{M}_{kt} \rightarrow \mathcal{M}_{hy}$ on the Boltzmann kinetic equation we obtain equations governing the time evolution of the hydrodynamic fields. The right-hand side of these equations still involves however the one particle distribution function. We thus need to express it in terms of the hydrodynamic fields. In other words, we look for a manifold, called a closure manifold (denoted by $\mathcal{M}_{closure}$), that is an immersion of $\mathcal{M}_{hy}$, in $\mathcal{M}_{kt}$. Manifold $\mathcal{M}_{closure}$ should be the manifold about which the time evolution in $\mathcal{M}_{kt}$ is concentrated as the time goes to infinity. Chapman and Enskog devised a method, a sort of perturbation method for finding asymptotic solutions to the Boltzmann equation, leading to $\mathcal{M}_{closure}$.

Comparing this setting with the setting of the previous example, we note that our starting point is again a family of three levels of description. The Level 0 remains to be the same as in the previous example, Level 1 is the level of classical hydrodynamics, and Level 2 is the level of kinetic theory. We recall that both the Boltzmann kinetic equation and the governing equations of classical hydrodynamics are particular realizations of Eq. (39) (see [21–28]). The essence of the analysis leading to thermodynamics on Level 1 implied by the dynamics on Level 2 is the same as in Example 1. What is different are the details in the mathematical analysis. For example, the asymptotic analysis that led us to Eq. (76) will be replaced by the Chapman–Enskog analysis. We now briefly sketch the analysis. We begin by asking the following question: what is the time evolution describing the approach of the time evolution in $\mathcal{M}_{kt}$ to the time evolution in $\mathcal{M}_{hy}$. We recall that we know that such approach exists since we know from experimental observations that both classical hydrodynamics and kinetic theory provide adequate descriptions. Following our point of view, the equation we look for will be a particular realization of Eq. (51) with $x \equiv f_1$ and $\mathcal{M}_{slow} \equiv \mathcal{M}_{hy}$. Let us suppose that we have found such equation. We have thus found the generating function Φ and consequently (by putting this function into the structure of thermodynamics (Th1)–(Th4)) thermodynamics in $\mathcal{M}_{hy}$. How this information relates to the information provided by the Chapman Enskog method? We see immediately that the thermodynamic manifold $\mathcal{M}_{th}$ introduced in (Th4) has to be identical with the closure manifold $\mathcal{M}_{closure}$. The thermodynamic relation (23) (recall that in this example x_{slow} are hydrodynamic fields) represents however a new result. Let us try to see how this relation looks like.

We note that if we choose in Eq. (51) $L \equiv 0, \Phi$, given in Eq. (20) with S being the Boltzmann expression for entropy, and the dissipation term being the Boltzmann collision term, then this realization of Eq. (51) satisfies all the requirements (recall that $\mathcal{M}_{hy}$ is indeed the nullspace of the Boltzmann collision term and the inequality (54) is the Boltzmann theorem). The manifold $\mathcal{M}_{th}$ is in this case the $\mathcal{M}_{closure}^{(0)}$ corresponding to the zero Chapman–Enskog approximation (i.e. $\mathcal{M}_{closure}^{(0)}$ is composed of local Maxwellian distribution functions) and the fundamental thermodynamic relation (23) in $\mathcal{M}_{hy}$, is the local

equilibrium thermodynamic relation. We see thus that in this particular example the new information arising if our point of view is followed is the familiar local thermodynamic relation.

Next, we pass to the first Chapman–Enskog approximation and arrive at $\mathcal{M}^{(1)}_{\text{closure}}$. We then naturally ask: what is the realization of Eq. (51), in particular then, what is the potential Φ appearing in it, for which $\mathcal{M}_{\text{th}} \equiv \mathcal{M}^{(1)}_{\text{closure}}$, and consequently, what is the resulting fundamental thermodynamic relation in $\mathcal{M}_{\text{hy}}$. We refer to Section 4 of [25] where some answers to these questions can be found. We only note here that since the first Chapman–Enskog approximation involves quantities entering the Boltzmann collision term (the dissipative part of the Boltzmann equation), the fundamental thermodynamic relation in $\mathcal{M}_{\text{hy}}$ corresponding to the first Chapman–Enskog approximation will also involve such quantities.

Example 3. In this example, we look at extensions of classical hydrodynamics. We choose Level 0 to be the level of classical hydrodynamics, Level 1 the level of extended irreversible thermodynam-ics (EIT, see [37]), and Level 2 a level that we shall call an extended EIT. The state variables are: $\mathcal{M}_0 \ni x_0 = $ (classical hydrodynamic fields), $\mathcal{M}_0 \ni x_1 = (x_0,$ extra stress tensor, heat flux), $\mathcal{M}_2 \ni x_2 = (x_1,$ higher order fluxes). The time equations governing the time evolution equations of x_1 (i.e. equations of the type (74) if we make an analogy with the setting of Example 1) have been introduced in [35–37] by requiring the compatibility of the Level 1 and the Level 0 in the sense that the dissipation inequality (38) holds. The entropy $s_{1,0}(x_1)$ becomes in this way related to the time evolution equations. Two methods allowing to find such relation have been developed in [35–37]. First, it is a method, used in [35,36] and predominantly then in [37], that is based on the requirement that the entropy production is only a quadratic function of the extra stress tensor and the heat flux. The second method, used in [35,36], is more general. It does not require the type of linearization required in the first method. The inequality (38) is seen in the second method as a constraint that is then dealt with by using the method of Lagrange multipliers. In order to be able to arrive at specific results with this method, the authors in [35,36] require the time evolution equations to possess additional structure. For example, they assume that the right-hand side of the time evolution equations is a sum of two terms, one is the divergence of a flux and the other one does not involve derivatives (this is a very restrictive assumption). The method based on the search for an appropriate realization of Eq. (39) is in fact an alternative method (i.e. the third method) that can be used to relate $s_{1,0}$ and the equations governing the time evolution in EIT (see [38]).

Now we turn to externally driven systems. We shall consider the systems that are found, by making the comparison with results of experimental observations, to be well described on Level 1 (i.e. in the context of EIT). For example, such systems are simple fluids driven by imposed mass or heat flows. As we have argued in this paper, the entropy $s_{1,0}$, obtained in the confrontation of Level 1 and Level 0, is not the entropy that should be used in the context of such driven systems. The entropy that should be used in the context of such driven systems is the entropy s_1 (we use the notation used in Example 1) that arises in the confrontation of Level 2 and Level 1. This type of confrontation has not yet been investigated systematically in the context of extended hydrodynamic theories.

Example 4. In this example we remain in the domain of classical rheology. The complex fluids are polymeric fluids, the more microscopic state space $\mathcal{M}^{(\text{micro})}_{\text{int}}$ is the space composed of configuration space distribution functions $\psi(\boldsymbol{R})$, where $\boldsymbol{R}$ is the end-to-end vector of a model-macromolecule, the more macroscopic state space $\mathcal{M}_{\text{int}}$ is composed of the configuration tensors $\boldsymbol{c}$ (the projection operator Π is given by $c_{\alpha\beta} = \Pi\psi := \int \mathrm{d}\boldsymbol{R}\, R_\alpha R_\beta \psi(\boldsymbol{R})$), and the external forces are imposed mass flows. The

relation between the time evolution in $\mathcal{M}_{\text{int}}^{(\text{micro})}$ and $\mathcal{M}_{\text{int}}$ is discussed for example in [53]. We recall that the zero approximation to the closure manifold $\mathcal{M}_{\text{closure}}$ is in this case the manifold composed of van Wiechen–Booij distribution functions [54] (playing in this example the role of the local Maxwellian distribution functions that have arisen in Example 2). We also note that this example has been discussed already in the first exposition of thermodynamics of driven systems in [41]. It has been shown recently by Keunings and his collaborators [55,56] that if the external forces are imposed elongational flows then dynamical phase transitions may occur. This then means that the manifold $\mathcal{M}_{\text{closure}}$ may be composed of two or more leafs. It should be therefore particularly interesting to investigate the rheo-thermodynamics (i.e. look for the potential Φ arising in the appropriate realization of Eq. (51)) of the fluids studied by Keunings.

Example 5. Gorban and Karlin [57,58] have recently undertaken a very elegant geometrical analysis of reductions in dynamical systems. Following Gorban and Karlin we would be able, for example, to formulate and analyze very elegantly and precisely the reduction of the Level 2 dynamics (75) to the Level 1 dynamics (74). In particular, Gorban and Karlin developed a very powerful method for identifying $\mathcal{M}_{\text{closure}} \subset \mathcal{M}_2$. Following their analysis, we would be able to find $\mathcal{M}_{\text{closure}}$ that represents more faithfully the asymptotic solutions of Eq. (75) than $\mathcal{M}_{\text{closure}} = \{x_2 \in \mathcal{M}_2 | (\mathrm{d}q/\mathrm{d}t)_{\text{Eq. (75)}} = 0\}$ that we have found. In the recent paper [59], the authors promise to use their approach to tackle also externally forced systems.

Example 6. The choice of x_{int} in rheological models is determined by requiring dynamical closeness of the models. We say that a model is dynamically closed if predictions of the model and results of the measurements associated with the model are found to be reproducible (for example, we would find hydrodynamic description without say, energy field dynamically unclosed; the observations made without controlling the temperature would not be found reproducible). In the context of a microscopic theory, the dynamical closeness of a model means that the time evolution described in the model is well separated from the time evolution of the additional details that are included in the microscopic description. It is certainly appreciated if x_{int} can be directly measured but this does not have to be the case. These quantities are measured indirectly by making comparisons of measured quantities (as for example extra stress tensors) with predictions of the model. The question of measurability of x_{int} becomes more serious if we are required to specify initial and boundary conditions for x_{int}. Since we do not measure x_{int} we usually also do not control them. Let $x_{\text{int}} \equiv (x_{\text{int}}^{(1)}, x_{\text{int}}^{(2)})$, where $x_{\text{int}}^{(1)}$ is the part of the internal state variables that we control and thus we can specify the initial and boundary conditions for them. The state variables $x_{\text{int}}^{(2)}$ are not controlled and their values on boundaries are thus determined in the process of the time evolution. Following our point of view we thus propose to look at the time evolution of $x_{\text{int}}|_{\text{boundary}}$ describing approach to the time evolution of $x_{\text{int}}^{(1)}|_{\text{boundary}}$. This type of consideration will then lead us to a thermodynamic theory of boundary conditions (we may call it boundary-thermodynamics). We believe that the recent discussion of boundary conditions for x_{int} presented in [60] shares some common features with the approach suggested above.

Summing up, we have shown in this section the provenance of thermodynamics of driven systems, a few illustrations, and a large unexplored territory. We emphasize that we see thermodynamics of driven systems in the time evolution describing approach of a microscopic dynamics to the mesoscopic dynamics and not in the mesoscopic dynamics itself. For example, we are suggesting to look for thermodynamics of the Bénard system (horizontal layer of a fluid heated from below) in the time evolution describing

the approach of, say, a kinetic theory description to the standard hydrodynamics description (Bousinesq equations) and not in the time evolution generated by the Bousinesq equations themselves. Still another interesting open problem is to find a relation between Jongschaap's Matrix method [61] (that has arisen from the previous Jongschaap's discussion of driven systems [62] and from results reported in [63]) and thermodynamics of driven systems. Some observations about the relation between Jongschaap's method and Eq. (39) have been reported in [64] and recently in [31].

4. Concluding remarks

We shall summarize the new results obtained in this paper by passing briefly through the process of the creation of rheological models and pointing out the places at which results of this paper provide a new assistance.

We begin with a physical insight that we assume have been collected in an attempt to express and understand certain family of experimental observations of polymeric fluids. We want now to formulate the insight in a way that will allow us to explore all its consequences and will bring us certain understanding of the observed phenomena. We thus proceed to formulate a rheological model. The insight that we collect is usually of two types, one that is more or less directly related to the observed macroscopic flow properties, and the other that arises in our attempt to imagine molecular origins of the observed behavior. We begin therefore to formulate two models, one macroscopic and the other molecular. Both models we formulate as two different realizations of the structure expressed in Eq. (37). We recall that this strategy has two main advantages: (i) the process of formulating the model is well organized, and (ii) agreement of predictions of the model with certain fundamental experimental observations is guaranteed. The new assistance in the process of searching for realizations of Eq. (37) that this paper offers is in showing a method for finding the Poisson bivector for a large variety of choices of the internal state variables (Section 2).

Let us assume that we have already formulated the two models, one macroscopic and the other molecular (both as realizations of Eq. (39)). The two models are two separate and essentially independent formulations of two separate and essentially independent insights. We are now in position to increase our understanding of the physics involved in the observed phenomena by relating the two models. Following the spirit of Section 3 we focus our attention on the identification of the time evolution equation describing the approach of the molecular time evolution to the macroscopic time evolution (a realization of the abstract equation (51)). As we have seen in Section 3 this analysis promises to bring us the following new information: (i) we identify the closure manifold and are thus able to express the material characteristics entering the macroscopic model in terms of the molecular material characteristics entering the molecular model, (ii) we arrive at rheo-thermodynamic fundamental relation in the state space of the macroscopic model. This thermodynamic relation represents indeed a new information on the macroscopic level of description (an information that is not included in the original macroscopic model).

The usefulness of the abstract setting (39) has been demonstrated on many examples. Among the recent illustrations we can mention the application in the hydrodynamics of radiation [65], in the kinetic theory and hydrodynamics of fluids composed of particles experiencing the rigid body motion [66,67], in the non-Fickian mass transport in polymers [68], in non-Fourier heat propagation [69], in rheology of immiscible mixtures [70,71], in non-isothermal rheology [38], and in many other fields discussed or mentioned in this workshop. We hope that a burst of activities of the similar intensity will be directed in the future also towards the abstract setting (51).

Acknowledgements

References

[1] R. Graham, Noise and nonlinear dynamical systems, in: F. Moos, P.V.E. McClintock (Eds.), Theory of Continuous Fokker–Planck Systems, Vol. 1, Cambridge University Press, Cambridge, 1989, p. 225.

[2] M.C. Cross, P.C. Hohenberg, Pattern formation outside equilibrium, Rev. Mod. Phys. 65 (1993) 851–1112.

[3] P.J. Morrison, J.M. Greene, Phys. Rev. Lett. 45 (1980) 790.

[4] W. Gibbs, Elementary Principles of Statistical Mechanics, Dover, 1960.

[5] M.S. Green, in: B. Jancovici (Ed.), Cargese Lectures in Theoretical Physics, Gordon and Breach, London, 1966.

[6] M.S. Green, J. Math. Phys. 9 (1968) 875.

[7] M.S. Green, R.E. Nettleton, J. Chem. Phys. 29 (1958) 1365.

[8] J. Yvon, Correlations and Entropy in Classical Statistical Mechanics, Pergamon Press, Oxford, 1969.

[9] N.S. Krylov, Work on the Foundation of Statistical Mechanics, Princeton University Press, Princeton, NJ, 1979.

[10] V. Latore, M. Baranger, Kolmogorov–Sinai entropy rate versus physical entropy, Phys. Rev. Lett. 82 (1999) 520–523.

[11] L. Boltzmann, Wissenschaftliche Abhandlungen von Ludwig Boltzmann, Chelsea, NY, 1968.

[12] H.B. Callen, Thermodynamics, Wiley, NY, 1963.

[13] E.T. Jaynes, in: M. Tribus, R.D. Levine (Eds.), The Maximum Entropy Formalism, MIT University Press, Cambridge, 1978.

[14] R. Luzzi, A.R. Vasconcellos, Fortschr. Phys. Prog. Phys. 38 (1990) 887.

[15] M. Grmela, R. Luzzi, J.G. Ramos, A.R. Vasconcellos, Termodinamica, Note de Fisica IFGF 16, Universidade Estadual de Campinas, Instituto de Física Gleb Wataghin, 1999.

[16] I.E. Dzyaloshinskii, G.E. Volovick, Poisson brackets in condensed matter physics, Ann. Phys. (NY) 125 (1980) 67–97.

[17] M. Grmela, Contemp. Math. 28 (1984) 125.

[18] A.N. Kaufman, Phys. Lett. A 100 (1984) 419.

[19] P.J. Morrison, Phys. Lett. A 100 (1984) 423.

[20] P.J. Morrison, Phys. D 18 (1986) 410.

[21] M. Grmela, Bracket formulation of diffusion-convection equations, Phys. D 21 (1986) 179–212.

[22] M. Grmela, Bracket formulation of dissipative fluid mechanics equations, Phys. Lett. A 102 (1984) 355–358.

[23] M. Grmela, Bracket formulation of dissipative time evolution equations, Phys. Lett. A 111 (1985) 36–40.

[24] M. Grmela, Hamiltonian dynamics complex fluids, J. Phys. A Math. General 22 (1989) 342–348.

[25] M. Grmela, Weakly nonlocal hydrodynamics, Phys. Rev. E 47 (1993) 351–368.

[26] A.N. Beris, B.J. Edwards, Thermodynamics of Flowing Systems With Internal Microstructure, Oxford University Press, Oxford, 1994.

[27] M. Grmela, H.C. Öttinger, Dynamics and thermodynamics of complex fluids. I. Development of a general formalism, Phys. Rev. E 56 (1997) 6620–6632.

[28] H.C. Öttinger, M. Grmela, Dynamics and thermodynamics of complex fluids. II. Illustrations of a general formalism, Phys. Rev. E 56 (1997) 6633–6655.

[29] B.J. Edwards, An analysis of single and double generator thermodynamics formalisms for the macroscopic description of complex fluids, Part I, J. Nonequilib. Thermodyn. 23 (1998) 301–333.

[30] B.J. Edwards, A.N. Beris, H.C. Öttinger, An analysis of single and double generator thermodynamics formalisms for the macroscopic description of complex fluids Part II 23 (1998) 334–350.

[31] M. Grmela, Geometry of Nonequilibrium Thermodynamics, 1999, preprint.

[32] D.J. Evans, G.P. Morriss, Statistical Mechanics of Nonequilibrium Liquids, Academic Press, New York, 1990.

[33] M. Lee, J.W. Dufty, Transport far from equilibrium: uniform shear flow, Phys. Rev. E 56 (1997) 1733.

[34] D. ter Haar (Ed.), Collected Papers of Landau, Pergamon Press, Oxford, 1965.

[35] I. Müller, Zeit. Phys. 198 (1967) 329.

[36] I. Müller, T. Ruggeri, Rational Extended Thermodynamics, Springer, New York, 1998.

[37] D. Jou, J. Casas-Vazquez, G. Lebon, Extended Irreversible Thermodynamics, Springer, Berlin, 1996.

[38] M. Grmela, D. Jou, J. Casas-Vazquez, Nonlinear and Hamiltonian extended irreversible thermodynamics, J. Chem. Phys. 108 (1998) 7937–7945.

[39] M. Grmela, J. Teichmann, Lagrangian formulation of the Maxwell–Cattaneo hydrodynamics, Int. J. Eng. Sci. 21 (1983) 297–313.

[40] S. Sieniutycz, R.S. Berry, Open Syst. Inf. Dyn. 4 (1997) 15.

[41] M. Grmela, Reductions in dynamical theories, J. Chem. Phys. 85 (1986) 5689–5697.

[42] M. Grmela, Thermodynamics of driven systems, Phys. Rev. 48 (1993) 919–930.

[43] M. Grmela, A. Cournoyer, On thermodynamics of glasses, Open Syst. Inf. Dyn. 5 (1998) 67–88.

[44] M. Grmela, Coupling between microscopic and macroscopic dynamics in NEMD. Part I, Phys. Lett. A 174 (1993) 59–65.

[45] M. Grmela, Coupling between microscopic and macroscopic dynamics in NEMD. Part II, Phys. Lett. A 182 (1993) 270–276.

[46] S. Nosé, J. Chem. Phys. 81 (1984) 511.

[47] S. Nosé, Mol. Phys. 52 (1984) 255.

[48] W.G. Hoover, Phys. Rev. A 31 (1985) 1695.

[49] W.G. Hoover, Phys. Rev. A 34 (1986) 2499.

[50] W. Muschik, J. Nonequilib. Thermodyn. 4 (1979) 277.

[51] S. Chapman, T.S. Cowling, Mathematical Theory of Non-Uniform Gases, Cambridge University Press, Cambridge, 1958.

[52] D. Enskog, in: S. Brush (Ed.), Kinetic Theory, Vol. 3, Pergamon Press, London, 1972.

[53] R.B. Bird, O. Hassager, R.C. Armstrong, C.F. Curtiss, Dynamics of Polymeric Fluids, Vol. 2, Wiley New York, 1987.

[54] P.H. van Wiechen, H.C. Booij, J. Eng. Math. 5 (1971) 89.

[55] R. Keunings, On the Peterlin approximation for finitely extensible dumbbells, J. Non-Newtonian Fluid Mech. 68 (1997) 85–100.

[56] R. Sizaire, G. Lielens, L. Jaumain, R. Keunings, J. Legat, On the hysteretic behaviour of dilute polymer solutions in relaxation following elongational flow, J. Non-Newtonian Fluid Mech. 82 (1999) 233–253.

[57] A.N. Gorban, I.V. Karlin, The method of invariant manifold and regularization of accustic spectra, Transport Theory Stat. Phys. 23 (1994) 559.

[58] A.N. Gorban, I.V. Karlin, Thermodynamic parametrization, Phys. A 190 (1992) 393.

[59] A.N. Gorban, I.V. Karlin, V.B. Zmijevskij, S.V. Dymova, Reduced description in the reaction kinetics, Phys. A 275 (2000) 361.

[60] H. Struchtrup, W. Weiss, Maximum of the local entropy production becomes minimal in stationary processes, Phys. Rev. Lett. 80 (1998) 5048–5051.

[61] R.J.J. Jongschaap, H.H. Haas, K.H. Damen, A generic matrix representation of configuration tensor rheological models, J. Rheol. 38 (1994) 769–796.

[62] R.J.J. Jongschaap, About the role of constraints in the linear relaxational behaviour of thermodynamic systems, Phys. A 94 (1978) 521–544.

[63] M. Grmela, Stress tensor in generalized hydrodynamics, Phys. Lett. A 111 (1985) 41–44.

[64] B.J. Edwards, H.C. Öttinger, R.J.J. Jongschaap, On the relationship between thermodynamic formalisms for complex fluids, J. Nonequilib. Thermodyn. 22 (1997) 356–373.

[65] M. Grmela, D. Jou, J. Casas-Vazquez, Radiation hydrodynamics and thermodynamics, J. Nonequilib. Thermodyn. 23 (1998) 203–225.

[66] M. Grmela, P.G. Lafleur, Kinetic theory and hydrodynamics of rigid body fluids, J. Chem. Phys. 109 (1998) 6973–6981.

[67] M. Grmela, A. Ait-Kadi, P.G. Lafleur, Suspensions of fibres in viscoelastic fluids, J. Chem. Phys. 109 (1998) 6956–6972.

[68] A. Elafif, M. Grmela, G. Lebon, Rheology and diffusion in simple and complex fluids, J. Non-Newtonian Fluid Mech. 86 (1999) 253–275.

[69] M. Grmela, G. Lebon, Finite speed propagation of heat: a nonlocal and nonlinear approach, Phys. A 248 (1998) 428–441.

[70] M. Grmela, A. Ait-Kadi, Rheology of immiscible inhomogeneous blends, J. Non-Newtonian Fluid Mech. 77 (1998) 191–199.

[71] M. Grmela, A. Ait-Kadi, L.A. Utracki, Blends of two immiscible and rheologically different fluids, J. Non-Newtonian Fluid Mech. 77 (1998) 253–259.