PHYSICAL REVIEW E VOLUME 56, NUMBER 6 DECEMBER 1997

Dynamics and thermodynamics of complex fluids. I. Development of a general formalism

Miroslav Grmela
École Polytechnique de Montréal, Montréal, Quebec, Canada H3C 3A7

Hans Christian Öttinger
ETH Zürich, Department of Materials, Institute of Polymers and Swiss FIT Rheocenter,
CH-8092 Zürich, Switzerland

(Received 18 December 1996; revised manuscript received 6 August 1997)

We recognize some universal features of macroscopic dynamics describing the approach of a well-established level of description (that is, successfully tested by experimental observations) to equilibrium. The universal features are collected in a general equation for the nonequilibrium reversible-irreversible coupling (abbreviated as GENERIC). In this paper we formulate a GENERIC, derive properties of its solutions, and discuss their physical interpretation. The relation of the GENERIC with thermodynamics is most clearly displayed in a formulation that uses contact structures. The GENERIC is also discussed in the presence of noise. In applications we either search for new governing equations expressing our insight into a particular complex fluid or take well-established governing equations and cast them into the form of a GENERIC. In the former case we obtain the governing equations as particular realizations of the GENERIC structure; in the latter case we justify the universality of the GENERIC and derive some properties of solutions. Both types of applications are discussed mainly in the following paper [Phys. Rev. E **56**, 6633 (1997)]. [S1063-651X(97)06512-4]

PACS number(s): 05.70.Ln, 05.60.+w, 51.10.+y

I. INTRODUCTION

Our principal motivation for developing a general formalism for the dynamics of nonequilibrium systems comes from the modeling of rheological properties of complex fluids. We recall that the modeling of flow properties of simple fluids, such as water, is based on (i) an unambiguous choice of the state variables (the hydrodynamic fields) and (ii) the requirement of the conservation of the total mass, momentum, and energy. The requirement (ii) provides a general framework for the governing equations: They have the form of local conservation laws. In the modeling of complex fluids there is no unambiguous or universal choice of state variables and, consequently, a general framework for the time-evolution equations cannot simply be based on conservation laws. We here suggest replacing the requirement (ii) by a general equation for the nonequilibrium reversible-irreversible coupling, which we abbreviate as GENERIC. The reason why (i) has to be abandoned in the context of complex fluids is that the time evolution of the internal structure of complex fluids (e.g., the structure of the macromolecules composing them) cannot be separated from the time evolution of the hydrodynamic fields. The experience collected in rheological modeling strongly indicates that there is *no preferred universal set of state variables* for characterizing the internal structure. Their choice depends on the nature of the fluid. Consequently, if we want to say something about rheological modeling without specifying the fluid under consideration, we have to remain uncommitted to the choice of state variables. This in turn implies that the language and ideas to be used in formulating a GENERIC have to remain somewhat abstract.

How can one expect to formulate the general structure of the time-evolution equations for an unspecified set of state variables? Our formulation of the GENERIC is guided by *experimental observations*. The most fundamental observation is the approach to equilibrium; all time-evolution equations for complex fluids should be formulated such that the structure of the equations guarantees that global equilibrium is approached.

In order to explain the idea of using more general observations for formulating the GENERIC structure we introduce the notion of a *level of description*. We say that one level (level 1) is more microscopic (or less macroscopic) than another level (level 2) if the quantities used to describe the states, called state variables, on level 1 depict more details than the state variables used on level 2. For example, the level of fundamental particles is more microscopic than the level of hydrodynamics. The most macroscopic level is the level of equilibrium thermodynamics, on which states are described by two real numbers, and no time evolution takes place. If level 2 is successfully tested by experimental observations, then the GENERIC structure of the time-evolution equations on a more microscopic level 1 must be formulated such that level 1 and level 2 are *compatible* (that is, the experimental observations are reproducible and in agreement with predictions based on the corresponding dynamical theories). In this and the following paper [1], referred to as paper II, we shall always take the more macroscopic level 2 to be the level of equilibrium thermodynamics. The development of a GENERIC in the context of the compatibility with more microscopic levels of description will be studied elsewhere. In paper II we work out many particular examples. In the context of specific examples with specific choices of state variables, the abstract ideas developed here for unspecified state variables are clarified in a simpler and more familiar language (see paper II). The advantage of the abstract language of this paper is that many general results can be derived very efficiently: once for all applications.

If we have the choice of modeling experimental observations on a more microscopic or more macroscopic level, the advantage of adopting the more macroscopic level 2 is the relative simplicity of the governing equations and the straightforward access to the macroscopic properties of our direct interest. The disadvantage of level 2 is that the quantities through which the individual features of systems are expressed on level 2 can be obtained only from results of observations. The advantage of the more microscopic level 1 is its more fundamental nature. We also depend on experimental observations to specify the quantities through which the individual features are expressed on level 1, but these experimental observations are more fundamental. They penetrate into deeper knowledge of the physical nature of the system under consideration. The disadvantage of level 1 is the complexity of the passage from the governing equations to the macroscopic features of our direct interest.

Once we have accepted to use the approach to equilibrium as a fundamental experimental fact, how can we actually develop the GENERIC structure guaranteeing a time-evolution compatible with equilibrium thermodynamics? How can we recognize the features of the governing equations that guarantee that their solutions are compatible with the approach to equilibrium? The GENERIC structure that we present in this paper is a result of the *analysis of many particular examples*. This structure has emerged gradually [2,3] from an attempt to recognize common features. It should be pointed out that, with the exception of the Boltzmann equation, all the examples analyzed are for systems near equilibrium that may be described in excellent approximation by local equilibrium states on the next higher level of description. An extrapolation to more general situations is of a hypothetical nature.

In general, the analysis of the compatibility of two levels of description involves a *pattern recognition process*. In the spirit of the dynamical system theory the first thing that we shall do is to find the phase portrait on level 1, that is, the set of all solutions for all initial conditions and a family of parameters through which the individual features are expressed (e.g., Hamiltonians in the case of classical mechanics). We then look at the phase portrait as a ‘‘painting’’ and try to recognize some pattern in it, typically neglecting the fast contributions to the dynamics. In fact, we look for a pattern that represents the phase portrait obtained on level 2. From the extensively studied example of classical mechanics versus equilibrium thermodynamics we know that the pattern recognition may be achieved by some kind of coarse graining. From another example, namely, the Boltzmann kinetic theory versus hydrodynamics, we know that the pattern recognition consists of concentrating on a special part of the phase portrait, the part that is in the vicinity of local equilibrium solutions. Once the pattern has been extracted and found to be compatible with experimental observations, we can try to identify the structural features of the time-evolution equations on level 1 that lead to the pattern. It is important to stress that if we succeed in identifying the GENERIC structure leading to a certain pattern we provide a foundation of a specific realization of the GENERIC, not a foundation of a GENERIC in its abstract form. The GENERIC structure presented here can only be the result of many different case studies.

The paper is organized as follows. A general formulation of the structure of the time-evolution equation expressing its compatibility with equilibrium thermodynamics is presented in Sec. II. In Sec. III we look deeper into the relation between the GENERIC and the structure of thermodynamics, and into its formulation in the presence of noise. Illustrative examples are worked out in paper II. This paper and paper II are written in such a way that they can be read in either order, depending on whether one prefers to be motivated by considering the compatibility of two levels of description (this paper) or by discussing specific examples that include classical hydrodynamics, the nonisothermal kinetic theory of polymeric fluids, and chemical reactions (paper II).

II. COMPATIBILITY WITH EQUILIBRIUM THERMODYNAMICS

In this section we present a general formulation of the structure of a time-evolution equation expressing its compatibility with equilibrium thermodynamics. This GENERIC structure is presented as an extension of the Ginzburg-Landau equation. In Sec. II A we recall the classical Ginzburg-Landau equation and its shortcomings. In Sec. II B we consider the compatibility of a general time evolution with equilibrium thermodynamics. In Sec. II C we discuss the example of Boltzmann's kinetic equation.

A. Ginzburg-Landau equation

Let x denote an order parameter and $\Phi(x,T)$ the Helmholtz free energy, where T is the absolute temperature. At equilibrium, the order parameter x assumes the value x_{th} that minimizes Φ, i.e., x_{th} is a solution of

$$\frac{\delta\Phi}{\delta x}=0. \tag{1}$$

By $\delta/\delta x$ we denote the derivative with respect to x. If x is a function (for example, a density or concentration field) then $\delta/\delta x$ denotes the Volterra functional derivative. Ginzburg and Landau [4] have suggested that the time evolution that carries x to its equilibrium value x_{th} is described by the equation

$$\frac{dx}{dt}=-M\frac{\delta\Phi}{\delta x}, \tag{2}$$

where M is a positive-definite linear operator. Note that if x is a function of position in addition to time, then dx/dt should be read as $\partial x/\partial t$. Equation (2) is called a Ginzburg-Landau equation. We may regard it as a generic relaxation equation. It is important to point out that Eq. (2) has not been derived. It is an equation that is justified solely on the basis of comparing properties of its solutions with results of observations. The chosen observation is the approach of x to x_{th} for large times t (for $t\to\infty$).

The proof that solutions to Eq. (2) describe the approach to x_{th} as $t\to\infty$ proceeds as follows. From Eq. (2) we see immediately that

$$\frac{d\Phi}{dt}=-\left\langle\frac{\delta\Phi}{\delta x},M\frac{\delta\Phi}{\delta x}\right\rangle\leqslant 0 \tag{3}$$

by virtue of the positive definiteness of M, where $\langle,\rangle$ denotes the scalar product in the space of order parameters x. If Φ reaches a minimum at $x_{\rm th}$ then Φ is convex in the neighborhood of $x_{\rm th}$. The convexity together with the inequality (3) then implies that Φ plays the role of the Lyapunov function corresponding to the approach $x \to x_{\rm th}$ as $t \to \infty$. As time increases, the trajectories are trapped in smaller and smaller neighborhoods $U = \{x | \Phi(x) < \text{const}\}$ of $x_{\rm th}$.

Now we can regard x as a state variable on a well-established level 1. For example, x may stand for the one-particle distribution function (level 1 is then called the level of one-particle kinetic theory) or x may represent the five hydrodynamic fields (see paper II). Inspired by the Ginzburg-Landau equation, we look for a general time-evolution equation, a GENERIC, that would describe the experimentally observed approach to a more macroscopic level 2. In this paper, we follow Ginzburg and Landau and take level 2 as the level of equilibrium thermodynamics.

As in the case of the Ginzburg-Landau equation, we shall regard the GENERIC as an equation justified by the fact that its solutions agree with the experimental observation of the approach to equilibrium. We naturally require that the well-established governing equations, such as the Boltzmann kinetic equation or the Navier-Stokes-Fourier hydrodynamic equations, will all be particular realizations of the GENERIC. We can thus regard the development of the GENERIC as a search for a common structure of well-established time-evolution equations. As in the case of the Ginzburg-Landau equation, we would like to express the approach to equilibrium in a Lyapunov function. However, the right-hand side of the GENERIC cannot be the same as in the relaxation equation (2) because it has to contain also a convective term (for example, the Euler part of the Navier-Stokes-Fourier equations). Moreover, if the GENERIC is linearized about $x_{\rm th}$ (the equilibrium state approached as $t \to \infty$) then the relaxation and the convection parts are expected to obey the Onsager-Casimir symmetry [5,6]. In the general nonlinear case, the relaxation and the convection parts will be shown to be related also through the requirement of certain complementary degeneracies.

B. Formulation of the GENERIC

Let level 1 and the level of equilibrium thermodynamics (level 2) be found to be well established. This means that the experimental observations made are found to be reproducible on level 1 and that predictions based on the dynamical theory formulated on level 1 agree with the results of the observations. Moreover, the macroscopic systems under consideration are free from external influences so that they reach, as time goes on infinity, states, called equilibrium thermodynamics states, at which they can be well described by standard equilibrium thermodynamics. We now present a generic time-evolution equation on level 1 whose solutions are guaranteed to agree with the observation that the behavior of appropriately prepared systems can be well described by equilibrium thermodynamics (the preparation process consists of leaving the systems free of external influences for a sufficiently long time).

We begin by establishing the terminology. With the symbol x we denote state variables used on level 1; the set of all admissible states x is denoted by $\mathcal{M}$ (i.e., $x \in \mathcal{M}$). The set $\mathcal{M}$ is called the state space on level 1. The state variables of equilibrium thermodynamics are (n,e), where n denotes the number of particles per unit volume and e is the total energy per unit volume. We shall denote the state space of equilibrium thermodynamics with the symbol $\mathcal{N}$ [i.e., $(n,e) \in \mathcal{N}$].

To formulate the general time-evolution equation for the unspecified state variables x, we need the following structure in the state space $\mathcal{M}$.

1. Bundle structure. The state space $\mathcal{M}$ is represented as a bundle with the state space $\mathcal{N}$ of equilibrium thermodynamics as its base space, that is, $\mathcal{M} = (\mathcal{M}, \mathcal{N}, \Pi)$, where $\Pi: \mathcal{M} \to \mathcal{N}$ is the bundle projection.

2. Potentials (E,S). The potential $E: \mathcal{M} \to \mathbb{R}$ has the physical meaning of the total energy and the potential $S: \mathcal{M} \to \mathbb{R}$ has the physical meaning of the total entropy.

3. Poisson (nondissipative or reversible) kinematics. An operator L transforms the gradient $\delta E/\delta x$ of the energy E into a vector $L\,\delta E/\delta x$.

4. Ginzburg-Landau (dissipative or irreversible) kinematics. An operator M transforms the gradient $\delta S/\delta x$ of the entropy S into a vector $M\,\delta S/\delta x$.

The general equation describing the approach of x to states at which the behavior is well described by equilibrium thermodynamics is:

$$\frac{dx}{dt} = L\frac{\delta E}{\delta x} + M\frac{\delta S}{\delta x}. \tag{4}$$

This is the formulation of the GENERIC that extends the Ginzburg-Landau equation (2). In the rest of this subsection we shall give a complete and more precise formulation of the structure 1–4 and some additional degeneracy requirements. We shall also discuss its physical interpretation as well as properties of solutions of the GENERIC (4).

1. Bundle structure

Given the state variables x, we want to know how the equilibrium thermodynamic state variables (n,e) are expressed in terms of x. This means that we want to introduce a mapping

$$\Pi: \mathcal{M} \to \mathcal{N}, x \mapsto (n(x), e(x)). \tag{5}$$

This mapping can be interpreted as an introduction of coordinates into $\mathcal{M}$. Every $x \in \mathcal{M}$ can now be represented as a pair $x = (y,z)$, where $y \in \mathcal{N}$ and $z \in \Pi^{-1}(y)$ [$\Pi^{-1}(y) \subset \mathcal{M}$ is the inverse image of $y \in \mathcal{N}$]. In accordance with the established terminology of differential geometry, we call $\Pi^{-1}(y)$ a fiber over y. Again, by using the established terminology, we also regard $\mathcal{M}$ as a bundle $\mathcal{M} = (\mathcal{M}, \mathcal{N}, \Pi)$, where $\mathcal{M}$ is the total space, $\mathcal{N}$ is the base space, and Π is the bundle projection. We assume that Π is surjective (i.e., to every $y \in \mathcal{N}$ there is attached a fiber). It will also be useful to regard the introduction of the mapping Π [see Eq. (5)] as an introduction of two potentials (real-valued functions) in $\mathcal{M}$, namely, $n: \mathcal{M} \to \mathbb{R}, x \mapsto n(x)$ and $e: \mathcal{M} \to \mathbb{R}, x \mapsto e(x)$.

The considerations leading to the specification of Π are based on the physical interpretation of $x \in \mathcal{M}$ and of (n,e)

$\in \mathcal{N}$. For example, if x is the one-particle distribution function $f(\boldsymbol{r},\boldsymbol{v})$ ($\boldsymbol{r}$ and $\boldsymbol{v}$ stand for the position and velocity vectors), then

$$n=\frac{1}{V}\int d^3r \int d^3v\, f(\boldsymbol{r},\boldsymbol{v}) \tag{6}$$

and

$$e=\frac{1}{V}\int d^3r \int d^3v\, h(\boldsymbol{r},\boldsymbol{v}) f(\boldsymbol{r},\boldsymbol{v}), \tag{7}$$

where V is the volume of the region in which the system under consideration is confined and $h(\boldsymbol{r},\boldsymbol{v})$ is the energy of one particle.

2. Potentials (E,S)

The energy E and the entropy S are two real-valued functions of x. The individual features of the systems under consideration are expressed in these potentials. Roughly speaking, the internal interactions and all motions are expressed in E and the internal organization is in S. The methods developed and the experience gained in equilibrium statistical mechanics are usually found to be useful in the specification of E and S. We shall see a few examples later in this paper and many more in paper II.

We note that $e(x)$ introduced in the mapping Π equals $E(x)/V$. It is therefore superfluous to introduce $E(x)$ as a separate potential. However, since we shall often consider theories on one level only without specifying Π and since one might also be interested in bundle projections that do not involve $e(x)$, in general we need the potential $E(x)$.

3. Poisson (nondissipative or reversible) kinematics

We recall that in the context of classical mechanics of N particles the set of state variables is $x=(r,p)$, where $r=(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N)$, $p=(\boldsymbol{p}_1,\ldots,\boldsymbol{p}_N)$, and $(\boldsymbol{r}_i,\boldsymbol{p}_i)$ are the position and momentum vectors of the ith particle. The time evolution of x is governed by Hamilton's equations of motion

$$\frac{d}{dt}\begin{pmatrix} r \\ p \end{pmatrix} = L\begin{pmatrix} \partial E/\partial r \\ \partial E/\partial p \end{pmatrix}, \tag{8}$$

where

$$L=\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}. \tag{9}$$

The operator L (the cosymplectic matrix) represents the kinematics of (r,p). It expresses mathematically the fact that x is composed of two parts: One (r) denotes the position coordinates and the other (p) conjugates of the velocities associated with the position coordinates.

An analysis of many different choices of the state variables x (see paper II for several choices, for example, the classical hydrodynamic fields and the fields serving as state variables in the configuration space kinetic theory) revealed that all the operators L expressing the kinematics of $x \in \mathcal{M}$ share the following properties.

(a) The bracket

$$\{A,B\}=\left\langle \frac{\delta A}{\delta x}, L\frac{\delta B}{\delta x} \right\rangle \tag{10}$$

is a Poisson bracket; $\langle , \rangle$ denotes the scalar product and A,B are sufficiently regular functions $\mathcal{M}\to\mathbb{R}$. We say that Eq. (10) defines a Poisson bracket if the antisymmetry property $\{A,B\}=-\{B,A\}$ and the Jacobi identity $\{A,\{B,C\}\}+\{B,\{C,A\}\}+\{C,\{A,B\}\}=0$ hold. Note that L is allowed to be a function of x. It is easy to see that if L is independent of x (as it is, for example, in the case of classical mechanics), then the skew symmetry of L automatically implies both the antisymmetry of the bracket and the Jacobi identity. If L depends on x, then the Jacobi identity represents a severe additional restriction.

(b) Consider the following real-valued functionals on the state space $\mathcal{M}$: $E(x)$, $S(x)$, and the components of $\Pi(x)$. All these functionals except $E(x)$ are distinguished functions of the Poisson bracket (10). We say that a function $C:\mathcal{M}\to\mathbb{R}$ is a distinguished function of the bracket $\{,\}$ if $\{A,C\}=0$ holds for all A. From Eq. (10) we see that if C is a distinguished function, its gradient lies in the null space of L. The operator L is thus degenerate. We note that the operator L arising in classical mechanics [see Eq. (9)] is nondegenerate. In macroscopic dynamics, the degeneracy is essential to satisfy the entropy inequality (see the discussion of the properties of solutions at the end of this subsection). In other words, the appearance of dissipation and the appearance of degeneracy are closely related.

The operators L satisfying properties (a) and (b) above are called *Poisson operators*. Since these operators express mathematically the kinematics, we also use the term *Poisson kinematics*. Equation (4) with $M=0$ is a Poisson time-evolution equation (it is called a Hamiltonian time-evolution equation if L is nondegenerate). We call this time evolution a nondissipative or reversible time evolution.

4. Ginzburg-Landau (dissipative or irreversible) kinematics

The operator M in the GENERIC (4) is closely related to the operator appearing in the Ginzburg-Landau equation (2). We shall require that M satisfies the following properties.

(a) The bracket [called a Ginzburg-Landau (dissipative) bracket]

$$[A,B]=\left\langle \frac{\delta A}{\delta x}, M\frac{\delta B}{\delta x} \right\rangle \tag{11}$$

is symmetric, that is, $[A,B]=[B,A]$ for all A,B, and satisfies the positivity condition $[A,A]\geqslant 0$ for all A. By A,B we again denote sufficiently regular functions $\mathcal{M}\to\mathbb{R}$. The operator M depends in general on x.

(b) Consider again the real-valued functionals $E(x)$, $S(x)$, and the components of $\Pi(x)$. All these functionals except $S(x)$ are distinguished functions of the bracket (11). (We say that a function $C:\mathcal{M}\to\mathbb{R}$ is a distinguished function of the bracket $[,]$ if the equation $[A,C]=0$ holds for all A.) The operator M is thus degenerate since the gradients of the distinguished functions of the dissipative bracket lie in the null space of M. In macroscopic dynamics, the degeneracy of M is essential to satisfy the conservation of energy.

The reason why we call the kinematics expressed in M a dissipative or irreversible kinematics will become clear later when we discuss properties of solutions of the GENERIC (4). If $L=0$ in Eq. (4), then this equation becomes the Ginzburg-Landau equation (2) (we shall see the relationship between the potentials Φ and S later in this section). We note that the contributions involving the operators L and M in Eq. (4) are related to one another by *mutual degeneracy requirements*. The potential E that generates the nondissipative (Poisson) time evolution is a distinguished function of the dissipative (Ginzburg-Landau) bracket and, vice versa, the potential S that generates the dissipative time evolution is a distinguished function of the nondissipative bracket. Moreover, the components of $\Pi(x)$ are distinguished functions of both brackets $\{,\}$ and $[,]$.

In the analysis of solutions of Eq. (4), we shall see that the essential property of the bracket $[,]$ is the positivity $[A,A]\geqslant 0$ for all A. The symmetry $[A,B]=[B,A]$ and, in fact, also the linearity of $[A,B]$ regarded as a function of $\delta B/\delta x$ could be relaxed. From previous work (see [7] and also [2,8]), a need for a dissipative time evolution that is more general than the Ginzburg-Landau time evolution (2) might be expected if one wants to include the Guldberg-Waage dynamics arising in chemical kinetics into our consideration [9] (the so-called mass action law). We shall see in paper II that this dynamics can actually be cast in the form of Eq. (2); however, a generalization of Eq. (2) seems to be interesting and possibly unavoidable in some cases. For example, later in this section, we shall illustrate a more general version of the GENERIC with the Boltzmann kinetic equation [10]. This generalization (see [7] and also [2]) corresponds to the following modification of the dissipative bracket. Let Ψ, called a dissipative potential, be a real-valued function of gradients of functions $\mathcal{M}\rightarrow\mathbb{R}$. (In the context of particular physical applications it is in general necessary that the argument of Ψ is dimensionless, and this may cause some problems.) We require that $\Psi(0)=0$, Ψ reaches its minimum at 0, and Ψ is convex in the neighborhood of 0. We then introduce the generalized bracket

$$[A,B]=\left\langle \frac{\delta A}{\delta x}, \frac{\delta \Psi}{\delta(\delta B/\delta x)}\right\rangle. \tag{12}$$

We note immediately that $[A,A]\geqslant 0$ by virtue of the properties of Ψ and that in the special case when Ψ is a quadratic dissipative potential then Eq. (12) reduces to Eq. (11). The degeneracy requirements are formulated as follows. $\Pi(x)$ and $E(x)$ are distinguished functions of Eq. (12). We say that C is a distinguished function of $[,]$ if $[A,C]=[C,A]=0$ for all A. If Eq. (12) replaces Eq. (11) then Eq. (4) takes the form

$$\frac{dx}{dt}=L\frac{\delta E}{\delta x}+\frac{\delta\Psi}{\delta(\delta S/\delta x)}. \tag{13}$$

Equation (13) is a generalization of the GENERIC (4). We recall that Eq. (4) corresponds to the particular choice $\Psi(z)=(1/2)\langle z,Mz\rangle$ of the dissipative potential.

We have now compiled all the properties of the GENERIC building blocks E, S, L, and M. There are no further restrictions on the functional form of these quantities except certain regularity requirements that guarantee that all further mathematical operations are well defined.

5. Properties of solutions of the GENERIC

Details of solutions of the GENERIC (4) or (13) depend, of course, on the specific choice made in the bundle structure, potentials, and kinematics. There are, however, some properties of solutions of the GENERIC (4) or (13) that are shared by all particular realizations. These properties depend only on the general requirements about the bundle structure, potentials, and kinematics that were listed above. We regard these properties as a mathematical expression of the compatibility of the time evolution with equilibrium thermodynamics. We shall now present these properties.

Property 1. The time evolution takes place only in the fibers $\Pi^{-1}(n,e)$. In other words, $(n,e)\in\mathcal{N}$ are constants of motion, i.e.,

$$\frac{d\Pi(x)}{dt}=0. \tag{14}$$

This property arises as an immediate consequence of the degeneracy of the kinematics. From the physical point of view, Eq. (14) expresses the conservation laws for the state variables of equilibrium thermodynamics.

Property 2.

$$\frac{dE(x)}{dt}=0, \tag{15}$$

$$\frac{dS(x)}{dt}\geqslant 0. \tag{16}$$

These properties arise again as a direct consequence of the degeneracy of the kinematics and of the properties $\{A,A\}=0$ and $[A,A]\geqslant 0$.

From the physical point of view, Eq. (15) expresses the energy conservation and Eq. (16) the entropy inequality. Note that if $M=0$, that is, if Eq. (4) reduces to the Poisson time-evolution equation, then Eq. (16) becomes $dS/dt=0$. This means that all the potentials $\Pi(x)$, $E(x)$, and $S(x)$ are conserved.

Property 3. Our next task is to identify the time-independent solutions of the GENERIC and to study their stability. Also, we want to derive the fundamental thermodynamic relation implied by the GENERIC. We shall here discuss Eq. (4) only. The extension of the results to Eq. (13) is a straightforward exercise.

Properties 1 and 2 suggest that the time-independent solutions of the GENERIC (4) approached as $t\rightarrow\infty$ are the thermodynamic equilibrium states, denoted x_{th}, that maximize the entropy under the constraints $e(x)=\mathrm{const}$ and $n(x)=\mathrm{const}$. We now prove this statement.

We introduce the potential

$$\Phi=\Phi(x)=-S(x)+aE(x)+bN(x), \tag{17}$$

where a,b are constant coefficients, $N(x)=Vn(x)$ [see Eq. (5)], and V is the volume. The states x_{th} that maximize the entropy under the above constraints are solutions to

$$\frac{\delta\Phi}{\delta x}=0 \tag{18}$$

and a,b play the role of Lagrangian multipliers. Note that x_{th} is in fact a two-parameter family of states (a,b are the two parameters).

The degeneracy of the kinematics allows us to rewrite Eq. (4) as

$$\frac{dx}{dt}=\frac{1}{a}L\frac{\delta\Phi}{\delta x}-M\frac{\delta\Phi}{\delta x}. \tag{19}$$

This equation (or its corresponding form involving the dissipative potential Ψ) has been called in [2,3,11] a nonlinear Onsager-Casimir equation. The reason for this terminology will become clear in property 4 below.

We see now clearly that the states x_{th}, which are the solutions to Eq. (18), are time-independent solutions of Eq. (19) and thus also time-independent solutions of the GENERIC (4). Moreover, Eqs. (14)–(16) imply

$$\frac{d\Phi}{dt}\leqslant 0, \tag{20}$$

thus Φ plays the role of the Lyapunov function in the study of the stability of x_{th}. If Φ reaches its minimum at x_{th} and is convex in the neighborhood of x_{th} then we can conclude that the states x_{th} are approached as $t\to\infty$.

This proof of the approach to x_{th} remains, of course, formal unless we precisely specify the meaning of convergence (i.e., we explicitly introduce a topological structure in $\mathcal{M}$) and we discuss also the problem of the existence of solutions of Eq. (4). Ideally, the topological details as well as their physical interpretation should be provided for each particular realization of Eq. (4). In reality, this often appears to be rather difficult and thus we have to be content with the formal proof. For example, the details have not yet been fully clarified even in the context of the classical Boltzmann kinetic theory.

From what we have said so far about the states x_{th}, they are good candidates for the thermodynamic equilibrium states (i.e., the states at which the behavior of the system is found to be well described by equilibrium thermodynamics). In the remainder of this section we explicitly extract the structure of equilibrium thermodynamics from Eq. (4) and we elaborate the thermodynamic meaning of Φ reaching its nondegenerate minimum at x_{th} (since only then can we prove that $x\to x_{\mathrm{th}}$ as $t\to\infty$).

We recall the structure in $\mathcal{N}$ that expresses equilibrium thermodynamics.

(a) In addition to the state variables $(n,e)\in\mathcal{N}$ there is another state variable s, called entropy per unit volume, that is a function of (n,e) [i.e., $s=s(n,e)$]. This function is called a fundamental thermodynamic relation. It is in this relation that the individual features of the systems under consideration are expressed in equilibrium thermodynamics.

(b) The first derivatives of s with respect to n and e (denoted by $\partial s/\partial n=-\mu/T$ and $\partial s/\partial e=1/T$, where T is the temperature and μ is the chemical potential per particle) have the same status and importance as the state variables n, e, and s themselves. The transformations that replace (n,e,s) or some subset of them with $\partial s/\partial n$ and $\partial s/\partial e$ are called Legendre transformations. In order to replace (n,e) by (μ,T) we first introduce a function

$$\Phi(n,e,\mu,T)=-s(n,e)+\frac{1}{T}e-\frac{\mu}{T}n. \tag{21}$$

Then we look for solutions, denoted $(n,e)_{\mathrm{th}}$, of

$$\frac{\partial\Phi}{\partial n}=0,\quad \frac{\partial\Phi}{\partial e}=0. \tag{22}$$

If we now insert $(n,e)_{\mathrm{th}}$ into Eq. (21), then we obtain the Legendre transform $\tilde{s}(\mu,T)$ of $s(n,e)$, that is,

$$\Phi((n,e)_{\mathrm{th}},\mu,T)=\tilde{s}(\mu,T). \tag{23}$$

For later use we shall formulate the structure introduced above in a more geometrical language [12,13]. Let $T^*\mathcal{N}$ denote the cotangent bundle of $\mathcal{N}$. Locally, we denote its coordinates by (n,e,n^*,e^*), where $(n,e)\in\mathcal{N}$ and $(n^*,e^*)\in T^*_{(n,e)}\mathcal{N}$ [the cotangent space $T^*_{(n,e)}\mathcal{N}$ is the space of all covectors in the point (n,e)]. Next we construct the space $T^*\mathcal{N}\times\mathbb{R}$; its coordinates are (n,e,n^*,e^*,s), where $s\in\mathbb{R}$. This space has a natural contact structure defined by the one form $d\omega=ds-n^*dn-e^*de$. The Legendre transformations are the transformations that preserve this contact structure. The fundamental thermodynamic relation is expressed in the way that includes both the points (a) and (b) of the structure of equilibrium thermodynamics, as specification of a Legendre submanifold of $T^*\mathcal{N}\times\mathbb{R}$, that is, a submanifold on which $d\omega=0$. In local coordinates, the Legendre submanifold is the image of the mapping

$$(n,e)\mapsto\left(n,e,\frac{\partial s(n,e)}{\partial n},\frac{\partial s(n,e)}{\partial e},s(n,e)\right). \tag{24}$$

(c) In equilibrium thermodynamics, one has the identity

$$\tilde{s}(\mu,T)=-\frac{p}{T}, \tag{25}$$

where p is the pressure and $\tilde{s}$ is Legendre transform of s introduced in Eq. (23). This relation follows from the homogeneity of degree one of $S=S(N,E,V)$, where S,N,E are the total entropy, number of particles, and energy (not per unit volume) and V is the volume. The relation (25), that is, the relation $p=p(\mu,T)$, is the Gibbs-Duhem form of the relation $s=s(n,e)$.

Now we return to the setting of level 1. By comparing Eqs. (17) and (18) with Eqs. (21) and (22), we see that we can interpret the potential Φ in Eq. (17) as a potential arising in the Legendre transformation in $T^*\mathcal{M}\times\mathbb{R}$. We denote the local coordinates in $T^*\mathcal{M}\times\mathbb{R}$ by (y,z,y^*,z^*,s), where $x=(y,z)\in\mathcal{M}$, $y\in\mathcal{N}$ [i.e., $y=(n,e)$], $z\in\Pi^{-1}(y)$, $y^*\in T^*_y\mathcal{N}$, $z^*\in T^*_z\Pi^{-1}(y)$, and $s\in\mathbb{R}$. If we make the identification

$$a=\frac{1}{T},\quad b=-\frac{\mu}{T}, \tag{26}$$

then Eq. (17), having now the form

$$\Phi=\Phi(x)=-S(x)+\frac{1}{T}E(x)-\frac{\mu}{T}N(x), \tag{27}$$

is the potential arising in the Legendre transformation of $S(x)$ in $T^*\mathcal{M}\times\mathbb{R}$ that corresponds to $y^*=(-\mu/T,1/T)$ and $z^*=0$. Consequently, the potential (27) evaluated at x_{th} [we recall that x_{th} is defined as solution to Eq. (18)], becomes $-pV/T$ [compare with Eq. (25)], that is,

$$\Phi(x_{\text{th}})=-\frac{pV}{T}. \tag{28}$$

This relation [having the form $p=p(\mu,T)$ since x_{th} is a function of μ,T] is the fundamental thermodynamic relation implied by the GENERIC. Moreover, the states x_{th} [solutions of Eq. (18)] are indeed thermodynamic equilibrium states, that is, the states that are approached as $t\rightarrow\infty$ and that represent $\mathcal{N}$ in $\mathcal{M}$.

Before turning our attention to the next property we note that if $x\in\mathcal{M}$ has the meaning of a probability distribution (e.g., if x is the N-particle distribution function, where N is of the order of Avogadro's number) and $S(x)$ is an informational entropy [14], then Eqs. (18) and (27) can be interpreted as a search for the least-biased probability distribution, that is, the probability distribution that maximizes the informational entropy $S(x)$ subject to the constraints imposed by the available information [14]. The available information is, in the case of Eqs. (18) and (27), the information associated with the knowledge of the energy $E(x)$ and the number of particles $N(x)$. The coefficients $1/T$ and $-\mu/T$ play the role of the Lagrange multipliers. Jaynes [14] suggests to accept the maximization of the informational entropy subjected to constraints imposed by available information as a principle. We recall that in the case in which level 1 is the fully microscopic level of description (i.e., x is the N-particle distribution function, where N is of the order of Avogadro's number), then the Jaynes principle is just a reinterpretation of the ''Gibbs principle'' (i.e., the Gibbs recipe used in equilibrium statistical mechanics to pass from the fully microscopic level to the equilibrium thermodynamics level). The advantage of the Jaynes formulation is that it can be applied to the passage from a general level 1 to a general level 2 (provided, of course, we know how to express the informational entropy on level 1 and how to express level 2 as available information).

We see now that if we accept the GENERIC structure as a principle then the Jaynes principle arises as a consequence. The informational entropy arises as a generating function of dynamics on level 1, this quantity is maximized since we look for the state approached as the time goes to infinity (the entropy also plays the role of the Lyapunov function corresponding to this approach), and the available information is represented by the quantities that remain unchanged during the time evolution on level 1.

In many previous papers attempts have been made to generalize the concept of equilibrium entropy to nonequilibrium situations. The typical perspective is that, starting from the level of equilibrium thermodynamics, one looks for a more microscopic level involving time evolution and for a generalization of the concept of equilibrium entropy to that new level. In the GENERIC approach, on the other hand, we start on the more microscopic level of description and we formulate the structure of the time-evolution equation such that it guarantees the observed approach to equilibrium thermodynamics. One part of the proper structure is the potential $S(x)$, which generally satisfies the inequality (16) and coincides with the equilibrium entropy when evaluated for equilibrium states x_{th}. From this alternative perspective, we therefore interpret $S(x)$ as a nonequilibrium entropy arising in the confrontation of a more microscopic level with the level of equilibrium thermodynamics.

Property 4. If we now linearize Eq. (19) about x_{th}, we obtain

$$\frac{d\xi}{dt}=(TL_{\text{th}}-M_{\text{th}})H_{\text{th}}^{(\Phi)}\xi, \tag{29}$$

where we have used $a=1/T$ [see Eq. (26)], $x=x_{\text{th}}+\xi$, $L_{\text{th}}=L(x_{\text{th}})$, $M_{\text{th}}=M(x_{\text{th}})$, and $H_{\text{th}}^{(\Phi)}$ is the Hessian of Φ evaluated at x_{th}, that is,

$$H_{\text{th}}^{(\Phi)}=\left.\frac{\delta^2\Phi}{\delta x\,\delta x}\right|_{x_{\text{th}}}. \tag{30}$$

It follows directly from the properties of L and M that L_{th} is (formally) a skew symmetric linear operator and M_{th} is (formally) a symmetric linear operator. (We have to use the adjective ''formal'' since we do not specify the domains of the operators L_{th} and M_{th}.) In order to avoid problems with antisymmetric contributions to M (corresponding to dissipative dynamics without entropy production), we consider isolated systems (no external magnetic fields) and we assume that a sufficiently detailed level of description has been chosen (see problems caused by the transition from an inertial to a noninertial level of description in [15]). In addition, the degeneracy of L and M implies that both L_{th} and M_{th} are degenerate linear operators: The vectors $(\delta S/\delta x)|_{x_{\text{th}}}$ and $(\delta N/\delta x)|_{x_{\text{th}}}$ lie in the null space of L_{th} and the vectors $(\delta E/\delta x)|_{x_{\text{th}}}$ and $(\delta N/\delta x)|_{x_{\text{th}}}$ lie in the null space of M_{th}. These properties of L_{th} and M_{th} together with Eq. (29) constitute our formulation of the Onsager-Casimir reciprocity relations [5,6] (see also [16]; in that paper, it was shown that the Onsager-Casimir relations can only be assumed to be valid if there is a clear separation in time scales between the slow variables x retained in the description and all the other variables that occur in a more microscopic description of the system; in [16], any deviations from Onsager-Casimir symmetry are shown to be only of second order in the time-scale ratio for a suitable choice of variables). If we compare this formulation, which appeared as a consequence of the GENERIC structure, with the classical formulation [5,6] then we recognize two important features: (i) the degeneracy of L_{th} and M_{th} and (ii) the presence of the Hessian of Φ rather than the Hessian of S in Eq. (29) (the latter feature is shared by other theories of nonequilibrium dynamics). The point is that the equilibrium state x_{th} about which we are investigating the linearized dynamics is not the state that maximizes the entropy but the state that maximizes the entropy subjected to constraints imposed by available information (i.e., the state minimizing the potential Φ). Both of the above features are closely related to the conservation laws of the nonlinear time evolution. If the discussion is from the beginning limited to the linearized time evolution [5,6] then the linear spaces on which the time evolution takes place are automatically and without saying chosen in such a way that the time evolution is nondegenerate.

Property 5. Finally, we just note how the operators L and M transform under a one-to-one transformation $x \rightarrow x'$. It is easy to verify that

$$L = \frac{\partial(x)}{\partial(x')} L' \left[\frac{\partial(x)}{\partial(x')} \right]^T, \tag{31}$$

$$M = \frac{\partial(x)}{\partial(x')} M' \left[\frac{\partial(x)}{\partial(x')} \right]^T, \tag{32}$$

where L', M' are the operators L, M in the coordinates $x', \partial(x)/\partial(x')$ is the transformation matrix and $[\partial(x)/\partial(x')]^T$ is its transpose (that is, L' and M' are contracted from both sides with x'). As an example of the transformation $x \rightarrow x'$ we mention the transformation from hydrodynamics in the energy representation to hydrodynamics in the entropy representation (see paper II).

C. Boltzmann equation

The GENERIC structure introduced above can be used in two ways. First, we can accept it as a postulate and search for *its particular realizations in particular contexts*. This means that by using our physical insight into a particular system and situation, we suggest the state variables x, the bundle structure in $\mathcal{M}$, the potentials E, S, and the kinematics. In this way we arrive at dynamics that may appear to be a reformulation of an already known and well-established dynamics or at a new dynamical model. This will be illustrated in paper II.

We note that this first use of the GENERIC structure reminds us of the very familiar use of various algebraic and geometric structures in microscopic physics (for example, postulating a group and looking for its representations). The second use of the GENERIC consists of accepting level 1 and level 2 (equilibrium thermodynamics) theories as given, and by analyzing solutions of level 1 dynamics and comparing them with solutions of an appropriate realization of the GENERIC, we prove that the GENERIC structure indeed describes the approach of the chosen level 1 to equilibrium thermodynamics. This analysis thus amounts to a *derivation of the GENERIC in a particular context* of a specific theory. Also this second use of the GENERIC will be illustrated in paper II.

Since we want to regard this paper and paper II as two self-contained papers, we here briefly describe an example of a particular realization of the GENERIC. This example is not included in paper II, but it has already been mentioned in [3,17]. We choose level 1 to be the level of the Boltzmann kinetic theory [18] and level 2 to be the level of equilibrium thermodynamics. Experience shows that both levels are well established for externally unforced dilute gasses. For the applicability of equilibrium thermodynamics we, of course, need to prepare the gasses suitably. The preparation process consists of leaving the gasses a sufficiently long time without external influences. It is this preparation process that will be described by the GENERIC.

1. State variables and bundle structure

As the state variable x on level 1 we use the one-particle distribution function $f(\boldsymbol{r},\boldsymbol{v})$, where $\boldsymbol{r}$ and $\boldsymbol{v}$ denote the position and velocity vectors of one particle. The state variable y on level 2 is (n,e) as in Sec. II B:

$$x = f(\boldsymbol{r},\boldsymbol{v}), \quad y = (n,e). \tag{33}$$

The bundle projection Π is given by

$$\Pi : f(\boldsymbol{r},\boldsymbol{v}) \mapsto \left(\frac{1}{V} \int d^3r \int d^3v\, f(\boldsymbol{r},\boldsymbol{v}), \frac{1}{V} \int d^3r \int d^3v \frac{1}{2} m \boldsymbol{v}^2 f(\boldsymbol{r},\boldsymbol{v}) \right), \tag{34}$$

where m is the mass of one particle and V is the volume of the region in which the gas under consideration is confined. This bundle projection follows directly from the physical interpretation of the one-particle distribution function and the assumed absence of interactions among the particles.

2. Potentials E,S

The equation

$$E(x) = \int d^3r \int d^3v \frac{1}{2} m \boldsymbol{v}^2 f(\boldsymbol{r},\boldsymbol{v}) \tag{35}$$

again expresses that the only energy of the system is the kinetic energy of the particles. The expression

$$S(x) = -k_B \int d^3r \int d^3v\, f(\boldsymbol{r},\boldsymbol{v}) \ln f(\boldsymbol{r},\boldsymbol{v}) \tag{36}$$

is the famous Boltzmann H function (k_B is Boltzmann's constant; f is not dimensionless so that, strictly speaking, $\ln f$ cannot be formed; we should hence use a dimensionless quantity f/f_0, where f_0 is a suitable constant; since we are not interested in constant additive contributions to the entropy and in normalization factors for distribution functions we ignore f_0). We can either suggest this potential on the basis of known properties (Boltzmann's H theorem) of solutions of the Boltzmann equation (that is assumed to be known as a part of the experience included in level 1) or we can suggest it on the basis of relating entropy with a measure of information (see [14]). The first argument illustrates the second type of application of the GENERIC, while the second argument illustrates the first type of application.

From Eqs. (27) and (28) we can easily find the fundamental thermodynamic relation that is implied by Eqs. (34)–(36). The solution f_{th} of Eq. (18) is the Maxwell-Boltzmann distribution

$$f_{th}(\boldsymbol{r},\boldsymbol{v}) \propto \exp\left(\frac{\mu}{k_B T} \right) \exp\left(-\frac{m \boldsymbol{v}^2}{2 k_B T} \right). \tag{37}$$

The thermodynamic relation (28) is thus

$$\Phi(x_{\mathrm{th}}) = -k_{\mathrm{B}} \int d^3 r \int d^3 v\, f_{\mathrm{th}}(\boldsymbol{r},\boldsymbol{v}) = -\frac{pV}{T} \tag{38}$$

or, in a more explicit form,

$$\frac{\mu}{k_{\mathrm{B}}T} = \ln p - \frac{5}{2}\ln k_{\mathrm{B}}T + \mathrm{const}, \tag{39}$$

where the constant depends only on the particle mass m. This is the fundamental thermodynamic relation representing an ideal gas. As we have expected, by analyzing the equilibrium solutions of the Boltzmann kinetic equation, we have recovered the ideal gas fundamental thermodynamic relation.

3. Reversible kinematics

We introduce the Poisson bracket

$$\{A,B\} = \int d^3 r \int d^3 v \frac{f(\boldsymbol{r},\boldsymbol{v})}{m}\left[\frac{\partial}{\partial v_\gamma}\left(\frac{\delta A}{\delta f}\right)\frac{\partial}{\partial r_\gamma}\left(\frac{\delta B}{\delta f}\right) - \frac{\partial}{\partial v_\gamma}\left(\frac{\delta B}{\delta f}\right)\frac{\partial}{\partial r_\gamma}\left(\frac{\delta A}{\delta f}\right)\right], \tag{40}$$

where we use the summation convention. This Poisson bracket arises in a straightforward manner when we recall two facts. First, we note that in classical mechanics the time evolution of $(\boldsymbol{r},\boldsymbol{v})$ can be regarded as a group of canonical transformations and $f(\boldsymbol{r},\boldsymbol{v})$ as an element of the dual of the Lie algebra associated with this group. The second fact is a deep mathematical theory, introduced by Lie, that provides the dual of a Lie algebra with a canonical Poisson bracket (see, e.g., [19]).

4. Irreversible kinematics

The dissipation potential is given by

$$\Psi(X) = \int d1 \int d2 \int d1' \int d2'\, W(f;1,2,1',2')\left[\exp\left(\frac{X}{2}\right) + \exp\left(-\frac{X}{2}\right) - 2\right], \tag{41}$$

where $1 = (\boldsymbol{r}_1,\boldsymbol{v}_1)$, and $2 = (\boldsymbol{r}_2,\boldsymbol{v}_2)$ are the coordinates and velocities of two colliding particles before a collision, $1' = (\boldsymbol{r}_1',\boldsymbol{v}_1')$, $2' = (\boldsymbol{r}_2',\boldsymbol{v}_2')$ are the coordinates and velocities after the collision (if the particles are assumed to be point particles then $W=0$, except if $\boldsymbol{r}_1=\boldsymbol{r}_2=\boldsymbol{r}_1'=\boldsymbol{r}_2'$), W is the transition probability for the collision, and

$$k_{\mathrm{B}}X = \frac{\delta S}{\delta f(1)} + \frac{\delta S}{\delta f(2)} - \frac{\delta S}{\delta f(1')} - \frac{\delta S}{\delta f(2')}. \tag{42}$$

The transition probability W, which is closely related to the differential cross section for particle collisions, has the following properties: $W=0$ except if $(\boldsymbol{v}_1)^2+(\boldsymbol{v}_2)^2=(\boldsymbol{v}_1')^2+(\boldsymbol{v}_2')^2$ and $\boldsymbol{v}_1+\boldsymbol{v}_2=\boldsymbol{v}_1'+\boldsymbol{v}_2'$, in which case $W>0$; W is also symmetric with respect to the interchanges $(1,2)\rightarrow(2,1)$ and $(1',2')\rightarrow(2',1')$. We here again note the difficulty that arises due to the existence of physical dimensions of the potentials. The argument X of Ψ in Eq. (41) clearly has to be dimensionless. If we choose X as in Eq. (42), that is, if the potential is the entropy S, then X is indeed dimensionless. However, in the general definition of the dissipation bracket (12) we should be able to use in the argument of Ψ the gradient $\delta B/\delta f$ of any potential B. We therefore have to recognize that the gradients of the potentials appearing in Eq. (12) all need to be (made) dimensionless.

It is easy to verify that the above specifications comply with all the requirements included in the GENERIC structure and that this particular realization of GENERIC is identical to the Boltzmann kinetic equation. We can regard the above illustration either as an alternative introduction of the Boltzmann equation (in the spirit of the first type of application of the GENERIC) or as a derivation of the GENERIC structure in this particular context (in the spirit of the second type of application of the GENERIC). The information about solutions of the Boltzmann equation that allows us to arrive at the GENERIC formulation is the Boltzmann H theorem.

III. ALTERNATIVE FORMULATIONS OF THE GENERIC STRUCTURE

In this section we shall continue to confront two different levels of description. Our objective is to bring an additional physical insight into this discussion.

In Sec. III A we focus our attention on the structure of thermodynamics. We recall that one of the essential features of thermodynamics is the existence of conjugate state variables and the importance that they enjoy. The question then arises what the role of the conjugate variables in dynamics is. In Sec. III B we add a white noise to the right-hand side of the GENERIC. The setting that we obtain in this way can then be compared with the setting discussed previously by Onsager, Machlup, and others.

A. Contact dynamics

Conjugate state variables arise in both microscopic nondissipative dynamics (e.g., classical mechanics) and thermodynamics. The mathematical structures that provide a setting to deal with conjugate state variables are the symplectic and contact structures (see [20] for definitions of these structures and for the analysis of relations among them). This explains why some mathematical techniques that are associated with those structures, for example, the Legendre transformation, play an important role in both classical mechanics and thermodynamics. The physics that is behind the emergence of the conjugate variables in classical mechanics is, however, different from the physics that is behind the conjugate variables in thermodynamics. In classical mechanics the conjugate state variables (the momenta) arise due to the presence of the inertia in the time evolution. In other words, the conjugate state variable arises in classical mechanics since the equation governing the time evolution of the position coordinates is a second-order (in time) differential equation. On the other hand, in thermodynamics (and we may expect this also in dissipative dynamics) the main role of the conjugate state variable is to identify equilibrium states. We recall that, for example, the mechanical equilibrium is found by equating pressures (pressure is the state variable that is conjugate to the volume), the thermal equilibrium is found by equating the temperatures (temperature is the state variable that is conjugate to the entropy), etc. We shall now follow the conjugate state variables in the context of dynamics generated by the GENERIC. We again limit ourselves to the confrontation of level 1 with the level of equilibrium thermodynamics.

We have already formulated the structure of thermodynamics in terms of the contact structure in Sec. II B. We recall that in $\mathcal{N}$ the structure of equilibrium thermodynamics is represented by a Legendre submanifold in $T^*\mathcal{N}\times\mathbb{R}$. The local coordinates in $T^*\mathcal{N}\times\mathbb{R}$ are (y,y^*,w), where $y\in\mathcal{N}$ [i.e., $y=(n,e)$], $y^*\in T^*_y\mathcal{N}$ [i.e., $y^*=(-\mu/T,1/T)$], and $w\in\mathbb{R}$. The Legendre submanifold that represents thermodynamics, denoted by the symbol $\mathcal{L}^{(\mathcal{N})}$, is the image of the mapping (24) where s, called entropy, is a function $\mathcal{N}\rightarrow\mathbb{R}$. We also introduce a Legendre submanifold in $T^*\mathcal{M}\times\mathbb{R}$; we shall denote it by the symbol $\mathcal{L}^{(\mathcal{M})}$, as the image of the mapping

$$x\mapsto\left(x,\frac{\delta S(x)}{\delta x},S(x)\right), \tag{43}$$

where $S(x)$ is the potential arising in the GENERIC approach. The local coordinates in $T^*\mathcal{M}\times\mathbb{R}$ are (x,x^*,v), where $x\in\mathcal{M}$, $x^*\in T^*_x\mathcal{M}$, and $v\in\mathbb{R}$.

In order to study Legendre transformations of $\mathcal{L}^{(\mathcal{M})}$ we turn our attention to the potential Φ introduced in Eq. (27). With the help of this potential we introduce two additional Legendre submanifolds. The first, denoted $\mathcal{L}^{(\mathcal{M})}_{y^*}$, is the image of the mapping

$$x\mapsto\left(x,\frac{\delta\Phi(x)}{\delta x},\Phi(x)\right). \tag{44}$$

We note that Eq. (44) in fact represents a family of Legendre submanifolds in $T^*\mathcal{M}\times\mathbb{R}$; the family is parametrized by y^*. The second Legendre submanifold constructed with the help of the potential Φ is the submanifold denoted $\mathcal{L}^{(\mathcal{N})}_{\mathcal{M}}$, in $T^*\mathcal{N}\times\mathbb{R}$. This submanifold is defined as the image of the mapping

$$y^*\mapsto(N(x_{\mathrm{th}}),E(x_{\mathrm{th}}),y^*,\Phi(x_{\mathrm{th}})), \tag{45}$$

where x_{th} is a solution of $\delta\Phi/\delta x=0$. The submanifold $\mathcal{L}^{(\mathcal{N})}_{\mathcal{M}}$ [see Eq. (45)] is indeed a Legendre submanifold since it is a Legendre transform of the Legendre submanifold $\mathcal{L}^{(\mathcal{M})}$ [see Eq. (43)] corresponding to $z^*=0$, where $z^*\in T^*_z\Pi^{-1}(y)$. We can indeed verify directly that $E(x_{\mathrm{th}})=\delta\Phi(x_{\mathrm{th}})/\delta(1/T)$ and $N(x_{\mathrm{th}})=\delta\Phi(x_{\mathrm{th}})/\delta(-\mu/T)$.

Now we turn our attention to the time evolution in $T^*\mathcal{M}\times\mathbb{R}$. We look for the time evolution that satisfies the following requirements.

(i) The time evolution in $T^*\mathcal{M}\times\mathbb{R}$ preserves the canonical contact structure (given by the one form x^*dx-dv) of $T^*\mathcal{M}\times\mathbb{R}$. This means that the time evolution in $T^*\mathcal{M}\times\mathbb{R}$ is a one-parameter (the parameter is the time) family of Legendre transformations.

(ii) The time evolution in $T^*\mathcal{M}\times\mathbb{R}$ extends the time evolution governed by the GENERIC in the sense that the Legendre submanifolds $\mathcal{L}^{(\mathcal{M})}_{y^*}$ [see Eq. (44)] are invariant submanifolds of this time evolution and the time evolution restricted to these submanifolds is the time evolution governed by the GENERIC.

(iii) As the time goes to infinity, the time evolution on $\mathcal{L}^{(\mathcal{M})}_{y^*}$ brings each point of this Legendre submanifold to a fixed point that lies on the smaller Legendre submanifold $\mathcal{L}^{(\mathcal{N})}_{\mathcal{M}}$ imbedded in $T^*\mathcal{N}\times\mathbb{R}$ [see Eq. (45)].

We shall prove that all three requirements are verified for the following time evolution [21]:

$$\frac{dx}{dt}=-\frac{\delta K}{\delta x^*}, \tag{46a}$$

$$\frac{dx^*}{dt}=\frac{\delta K}{\delta x}+x^*\frac{\delta K}{\delta v}, \tag{46b}$$

$$\frac{dv}{dt}=K-\left\langle x^*,\frac{\delta K}{\delta x^*}\right\rangle, \tag{46c}$$

$$K(x,x^*)=\frac{1}{2}\langle x^*,M(x)x^*\rangle-\frac{1}{2}\left\langle\frac{\delta S(x)}{\delta x},M(x)\frac{\delta S(x)}{\delta x}\right\rangle-\left\langle x^*,L(x)\frac{\delta E(x)}{\delta x}\right\rangle, \tag{47}$$

where $\langle\ ,\ \rangle$ denotes the scalar product. The proof of (i) consists of the observation that Eq. (46) is a canonical form of dynamics preserving the contact structure (see, e.g., [20]). The potential K is called contact Hamiltonian. Property (ii) is proven by direct verification after expressing E and S in K in terms of Φ. We note also that on $\mathcal{L}^{(\mathcal{M})}_{y^*}$ the contact Hamiltonian K equals zero. Property (iii) is a direct consequence of properties (i), (ii), and property 3 of solutions to the GENERIC.

The contact Hamiltonian (47), for which all the Legendre submanifolds $\mathcal{L}^{(\mathcal{M})}_{y^*}$ are invariant submanifolds of the time evolution, is independent of y^*. Furthermore, since K is also independent of v, Eqs. (46a) and (46b) are of the Hamiltonian form.

We will now make a few remarks about the physical content and possible applications of Eq. (46). We first note that Eq. (46) is an equivalent reformulation of the GENERIC. Its main contribution is that it is a reformulation that throws additional light on the interrelationship between dissipative dynamics and thermodynamics. The essence of the reformulation is that the state space $\mathcal{M}$, on which the time evolution takes place in the original formulation of the GENERIC, is replaced by $\mathcal{L}^{(\mathcal{M})}_{y^*}$. This space is not bigger than $\mathcal{M}$ (if, for example, the dimension of $\mathcal{M}$ is finite then $\mathcal{M}$ and $\mathcal{L}^{(\mathcal{M})}_{y^*}$ have the same dimension), but it has a richer structure than $\mathcal{M}$. The new structure in $\mathcal{L}^{(\mathcal{M})}_{y^*}$ that is missing in $\mathcal{M}$ is the structure of a Legendre submanifold (in the mathematical interpretation) and the structure of thermodynamics (in the physical interpretation). This structure is then preserved during the time evolution so that the time evolution is a continuous sequence of Legendre transformations. Finally, as $t\rightarrow\infty$, all states settle on a Legendre submanifold that expresses mathematically the thermodynamics on level 2 that is implied by the GENERIC time evolution.

Another advantage of the reformulation (46) is that it gives us the possibility to formulate the GENERIC time evolution for discrete times. We recall, for example, that the discrete time Hamiltonian evolution is formulated as an iteration of a mapping that preserves the symplectic structure. Analogically, we can formulate discrete time GENERIC evolution as an iteration of a Legendre transformation (i.e., a mapping preserving the contact structure). In numerical solutions the time has to be discretized. It has been demonstrated in the context of Hamiltonian systems [22] that the time discretization that does not destroy the invariance of the symplectic structure has many advantages. We may expect that a similar situation will occur in the context of the GENERIC time evolution.

B. Liouville and Fokker-Planck formulations

In the Introduction we suggested that we should regard the passage from microscopic to macroscopic descriptions as a pattern recognition in the set of trajectories corresponding to the microscopic theory. Intuitively, we may expect that a good strategy in pattern recognition is to look at the trajectories in different settings. Features that are difficult to recognize in one setting may appear more clearly in other settings. In statistical mechanics, the standard first step in the passage to macroscopic descriptions is to present the particle trajectories as an evolution of a distribution function. In other words, the equations governing the time evolution of particles are replaced by the Liouville equation. Another very successful pattern recognition strategy is ‘‘to smear off’’ and then to look for the pattern. In statistical mechanics this strategy is usually achieved by adding noise to the governing equations. Under some conditions these equations then also lead to an equation governing the distribution function; however, the resulting equation is not the Liouville equation but the Fokker-Planck equation. We shall now apply both of these pattern recognition strategies to the GENERIC. We are particularly interested to observe as to whether the formulations of the GENERIC in other contexts are again particular, but different, realizations of the GENERIC.

The Liouville equation corresponding to the GENERIC is

$$\frac{\partial f(x,t)}{\partial t} = -\frac{\partial}{\partial x}\left[f(x,t)\left(L\frac{\partial E}{\partial x} + M\frac{\partial S}{\partial x}\right)\right], \tag{48}$$

where $f(x,t)$ is the distribution function (for clarity, we here reserve the symbol δ for derivatives with respect to the distribution function f and use the symbol ∂ for derivatives with respect to the state variables x, which may themselves be functions). We directly verify that Eq. (48) can also be written as

$$\frac{\partial f}{\partial t} = \hat{L}\frac{\delta\hat{E}}{\delta f} + \hat{M}\frac{\delta\hat{S}}{\delta f}, \tag{49}$$

where

$$\{A,B\} = \left\langle \frac{\delta A}{\delta f}, \hat{L}\frac{\delta B}{\delta f}\right\rangle = \int dx f\left[\frac{\partial}{\partial x}\left(\frac{\delta A}{\delta f}\right)\right] L\left[\frac{\partial}{\partial x}\left(\frac{\delta B}{\delta f}\right)\right], \tag{50}$$

$$[A,B] = \left\langle \frac{\delta A}{\delta f}, \hat{M}\frac{\delta B}{\delta f}\right\rangle = \int dx f\left[\frac{\partial}{\partial x}\left(\frac{\delta A}{\delta f}\right)\right] M\left[\frac{\partial}{\partial x}\left(\frac{\delta B}{\delta f}\right)\right], \tag{51}$$

$$\hat{E}(f) = \int dx f(x)E(x), \tag{52}$$

$$\hat{S}(f) = \int dx f(x)S(x). \tag{53}$$

By direct inspection we see that Eqs. (49)–(53) are particular realizations of the GENERIC in which $f(x)$ plays the role of the state variable. We also note that, in addition to $\hat{S}(f)$, there are many other distinguished functionals of $\{\ ,\ \}$ [for example, if L is independent of x, then $\int dx f \ln f$ is a distinguished functional of the bracket defined in Eq. (50)] and that the potentials (52) and (53) are only linear functions of the state variable f. The Liouville equation (48) or (49) has proven to be an excellent starting point to look at macroscopic theories but on its own is not very revealing. For example, due to the linearity of the potentials $\hat{E}(f)$ and $\hat{S}(f)$, we find no solution to the equation of $\delta\Phi/\delta f = 0$. However, this equation would be physically meaningful if we add the functional $-k_{\mathrm{B}}\int dx f \ln f$ to $\hat{S}(f)$. In fact, if $S(x)=0$, then $\delta\Phi/\delta f = 0$ would be solved by the Boltzmann distribution function.

We now proceed to the Fokker-Planck reformulation. We want to introduce a noise term into the GENERIC (4) so that the corresponding Fokker-Planck equation will be the particular realization of the GENERIC (49) with the brackets (50) and (51), the energy (52), and the entropy

$$\hat{S}(f) = \int dx f(x)[S(x) - k_{\mathrm{B}}\ln f(x)]. \tag{54}$$

In other words, the time evolution of the distribution function is assumed to be governed by the Fokker-Planck equation

$$\frac{\partial f(x,t)}{\partial t} = -\frac{\partial}{\partial x}\left[f(x,t)\left(L\frac{\partial E}{\partial x} + M\frac{\partial S}{\partial x}\right)\right] + k_{\mathrm{B}}\frac{\partial}{\partial x}\left[M\frac{\partial}{\partial x} f(x,t)\right]. \tag{55}$$

We note, however, that in this case the degeneracy requirement for $\hat{L}$ is not generally satisfied. From the physical point of view this is because the added noise plays the role of an external influence. We expect to obtain equations that possess the complete GENERIC structure if the noise becomes a state variable and we have another equation governing the time evolution of the noise.

The Fokker-Planck equation (55) is equivalent to the stochastic differential equation obtained by adding noise (and the divergence of M) to the GENERIC (4) [23],

$$dx = L\frac{\partial E}{\partial x}dt + M\frac{\partial S}{\partial x}dt + k_{\mathrm{B}}\frac{\partial M}{\partial x}dt + B\,dW_t, \tag{56}$$

where B is a solution of the equation

$$BB^T = 2k_{\mathrm{B}}M \tag{57}$$

and W_t is a multicomponent Wiener process, that is, a Gaussian process with first and second moments given by

$$\langle W_t\rangle = 0, \quad \langle W_t W_{t'}^T\rangle = \min(t,t')1 \tag{58}$$

or, more formally,

$$\left\langle \frac{dW_t}{dt}\right\rangle = 0, \quad \left\langle \frac{dW_t}{dt}\frac{dW_{t'}^T}{dt'}\right\rangle = \delta(t-t')1. \tag{59}$$

The expression (57) for B may be regarded as the *fluctuation-dissipation theorem* of the second kind (see Secs. 1.6 and 2.9 of [24]). In obtaining this theorem, we did not make any assumptions about being close to equilibrium or even local equilibrium and, interestingly, no temperature variable is required for formulating this fluctuation-dissipation theorem.

As an illustration of the stochastic dynamics (56) and (57) we refer the reader to the example of fluctuating hydrodynamics. With the specifications of L, M, E, S, and B given in paper II, Eq. (56) becomes the governing equation of the fluctuating hydrodynamics appearing, for example, in [25].

There are properties of solutions of Eq. (55) that can be extracted and that are of interest in the pattern recognition process leading to macroscopic properties. Following Onsager and Machlup [26] (see also [27,28]), we write the solutions to Eq. (55) as functional integrals involving the Lagrangian $A_0(x,\dot{x})$,

$$A_0 = \left\langle \left(\dot{x} - L\frac{\delta E}{\delta x} - M\frac{\delta S}{\delta x}\right), \frac{M^{-1}}{4k_{\mathrm{B}}}\left(\dot{x} - L\frac{\delta E}{\delta x} - M\frac{\delta S}{\delta x}\right)\right\rangle \tag{60}$$

(strictly speaking, M is degenerate; see [27,28] for a more careful discussion). In the saddle-point approximation, one looks for solutions of the Hamiltonian system corresponding to the Lagrangian (60). We hence realize that the dynamics arising in the Onsager-Machlup analysis takes place in the extended state space $T^*\mathcal{M}$. If the newly adopted state variable is set equal to zero, then the Hamilton equations reduce to the GENERIC. We note that the physics behind the Onsager-Machlup extension of dynamics from $\mathcal{M}$ to $T^*\mathcal{M}$ is very different from the physics behind the extension from $\mathcal{M}$ to $T^*\mathcal{M}\times\mathbb{R}$ discussed in Sec. III A.

Finally, we briefly mention related work of Graham and Tél (see review [28]), who introduce a general dissipative time-evolution equation. Their equation has the same form as our GENERIC except that it has less structure. The operator L is not required to be Poisson and, moreover, L and M are not required to possess the complementary degeneracy.

IV. CONCLUDING REMARKS

Universal features of macroscopic dynamics have been recognized and used by Onsager [5], Casimir [6], Ginzburg and Landau [4], and others [27,28]. The GENERIC approach that we introduce in this paper sums up results of these studies and contributes to them by introducing an additional structure, by developing different applications, and by throwing a light on the relation between dissipative dynamics and thermodynamics.

We have emphasized that, from the physical point of view, the GENERIC structure expresses the experimentally observed approach of one well-established level of description to another level of description that is more macroscopic and also well established, in particular, the approach to equilibrium. Time-evolution equations that do not describe this type of approach may, but in general will not possess this structure. For example, the equations governing the time evolution of externally forced systems that generate complex patterns (e.g., those discussed in [29]) will not in general possess the GENERIC structure. What will possess this structure will be equations expressing the approach of the time evolution of these driven systems formulated on more microscopic levels to the time evolution formulated in [29]. We hope to systematically discuss these applications of the GENERIC in a future paper. The main result emerging in these applications will be the thermodynamics of driven systems formulated on the levels of description used in [29].

The structure that makes the GENERIC approach very powerful in applications is the Poisson structure of the nondissipative part of the time evolution and the complementary degeneracy of the dissipative and nondissipative parts of the structure. The principal domain of applications that we have explored is hydrodynamics and kinetic theory of complex fluids while the applications developed previously (applications of a less complete universal structure) were, for the most part, limited to finite-dimensional dynamical systems. We regard the applications as the problem of finding particular realizations of the universal structure expressing the particular physics under consideration (similarly to, for example, the problem of finding a particular representation of a group).

ACKNOWLEDGMENTS

M.G. acknowledges financial assistance provided by the Natural Sciences and Engineering Research Council of Canada and by the Province of Québec through the Programme Coopération Internationale.

[1] H. C. Öttinger and M. Grmela, following paper, Phys. Rev. E **56**, 6633 (1997).

[2] M. Grmela, Phys. Rev. E **48**, 919 (1993); J. Chem. Phys. **85**, 5689 (1986).

[3] M. Grmela, Physica D **21**, 179 (1986); in *Rheological Modelling: Thermodynamical and Statistical Approaches*, edited by J. Casas-Vázquez and D. Jou, Lecture Notes in Physics Vol. 381 (Springer, Berlin, 1991), p. 99.

[4] *Collected Papers of L. D. Landau*, edited by D. ter Haar (Pergamon, Oxford, 1965).

[5] L. Onsager, Phys. Rev. **37**, 405 (1931); Phys. Rev. **38**, 2265 (1931).

[6] H. B. G. Casimir, Rev. Mod. Phys. **17**, 343 (1945).

[7] S. Sieniutycz, Chem. Eng. Sci. **42**, 2697 (1987).

[8] A. N. Beris and B. J. Edwards, *Thermodynamics of Flowing Systems with Internal Microstructure* (Oxford University Press, New York, 1994).

[9] C. M. Guldberg and P. Waage, *Etudes sur les Affinités Chimiques* (Brøgger and Christie, Christiana, 1867).

[10] Our very recent calculations suggest that even Boltzmann's kinetic equation can be written in the GENERIC form (4), so that the introduction of a dissipative potential is not actually required in this context.

[11] M. Grmela, Phys. Rev. E **47**, 351 (1993).

[12] R. Hermann, *Geometry, Physics and Systems* (Dekker, New York, 1973).

[13] W. L. Burke, *Applied Differential Geometry* (Cambridge University Press, Cambridge, 1985).

[14] E. T. Jaynes, Phys. Rev. **106**, 620 (1957); Phys. Rev. **108**, 171 (1957); *Maximum Entropy and Bayesian Methods*, edited by W. T. Grandy and L. H. Schick (Kluwer, Dordrecht, 1991).

[15] B. J. Edwards, A. N. Beris, and M. Grmela, Mol. Cryst. Liq. Cryst. **201**, 51 (1991).

[16] U. Geigenmüller, U. M. Titulaer, and B. U. Felderhof, Physica A **119**, 53 (1983).

[17] M. Grmela and D. Jou, J. Math. Phys. **34**, 2290 (1993).

[18] *Wissenschaftliche Abhandlungen von Ludwig Boltzmann*, edited by F. Hasenöhrl (Johann Ambrosius Barth, Leipzig, 1909).

[19] J. E. Marsden, *Lectures on Mechanics* (Cambridge University Press, Cambridge, 1992).

[20] V. I. Arnold, *Mathematical Methods of Classical Mechanics*, 2nd ed. (Springer, New York, 1989).

[21] M. Grmela, in *Proceedings of the CRM Workshop on Hamiltonian Systems, Transformation Groups and Spectral Transform Methods*, edited by J. Harnad and J. E. Marsden (Publications CRM, Montreal, 1990).

[22] J. M. Sanz-Serna and M. P. Calvo, *Numerical Hamiltonian Problems* (Chapman and Hall, London, 1994).

[23] H. C. Öttinger, *Stochastic Processes in Polymeric Fluids: Tools and Examples for Developing Simulation Algorithms* (Springer, Berlin, 1996).

[24] R. Kubo, M. Toda, and N. Hashitsume, *Statistical Physics II, Nonequilibrium Statistical Mechanics* (Springer, Berlin, 1985).

[25] L. D. Landau and E. M. Lifshitz, *Course of Theoretical Physics, Vol. 9, Statistical Physics, Part 2* (Pergamon, Oxford, 1992).

[26] L. Onsager and S. Machlup, Phys. Rev. **91**, 1505 (1953); S. Machlup and L. Onsager, *ibid.* **91**, 1512 (1953).

[27] M. S. Green, J. Chem. Phys. **20**, 1281 (1952); H. Grabert and M. S. Green, Phys. Rev. A **19**, 1747 (1979).

[28] R. Graham, in *Noise in Nonlinear Dynamical Systems, Vol. 1, Theory of Continuous Fokker-Planck Systems*, edited by F. Moss and P. V. E. McClintock (Cambridge University Press, Cambridge, 1989), p. 225.

[29] M. C. Cross and P. C. Hohenberg, Rev. Mod. Phys. **65**, 851 (1993).