Thermodynamics of driven systems

Miroslav Grmela

Ecole Polytechnique de Montreal, Montreal, Canada H3C 3A7

A geometrical formulation of thermodynamics is carried in this paper to a domain that includes dynamics and driven systems. Let it be known from experience that the behavior of an externally unforced or a driven system is well described in a state space N. The thermodynamics of the system is a geometrical structure in N that arises from an analysis of the time evolution in a more microscopic (i.e., depicting more details) state space M. If in particular the system is externally unforced then the state space N can be chosen to be the state space N_{ET} of equilibrium thermodynamics. The geometrical structure in N_{ET}, obtained by analyzing the time evolution in a more microscopic state space M, appears to be the geometrical formulation of classical equilibrium thermodynamics. The general formulation of thermodynamics introduced in this paper is illustrated by the example of a k-component system undergoing a chemical reaction.

I. INTRODUCTION

An effort to understand thermodynamics and to facilitate and extend its applications has led, in the past 200 years, to several different formulations of thermodynamics. As an example, we mention the formulation geared to engineering applications [1], the formulation based in hydrodynamics [2], and the formulation based on Gibb's equilibrium statistical mechanics [3]. Each formulation explores in detail some facets of thermodynamics; none can claim to encompass all of them. In this paper we take the geometrical formulation and carry it to a domain that includes dynamics and driven systems.

The geometrical interpretation of thermodynamics has been introduced in [4–9]. Within this interpretation, thermodynamics is formulated as geometry of a manifold. The physical content and usefulness of this formulation is extensively discussed in [4–9]. Alternative arguments indicating the usefulness of the geometrical formulation are introduced in this paper. Thermodynamics is regarded in this paper as a theory arising in the analysis of dynamics. The manifold representing thermodynamics is a manifold that distinguishes itself by its notable dynamical properties. If the system under consideration is externally unforced, then, according to experience, time evolution brings all states to time-independent equilibrium states. The manifold representing thermodynamics is the manifold of equilibrium states. If, on the other hand, the system under consideration is a driven system, then, again according to experience (see details in Sec. III), the time evolution does not carry all states to the time-independent equilibrium states but to states that evolve in time at a slower pace. The manifold composed of such states, called a slow manifold, is the manifold representing thermodynamics of driven systems. The standard analysis of driven systems that consists of an analysis of the slow time evolution can be now supplemented by a thermodynamic analysis. The thermodynamic analysis consists of an analysis of the approach of the fast to the slow time evolution. Such an analysis introduces a geometry into the slow manifold.

In Sec. II we discuss externally unforced systems and in Sec. III driven systems. An illustration (a k-component system undergoing a chemical reaction) is worked out in Sec. IV. The point of view of thermodynamics introduced in Secs. II and III can become useful only if it is clearly formulated. The clear formulation requires the use of the language of differential geometry. Well-known demonstrations of the usefulness of geometry in other domains of physics (e.g., in general relativity, classical mechanics, gauge field theories, etc.) should facilitate the acceptance of the geometrical point of view in thermodynamics. A very clear introduction of geometrical concepts used in this paper can be found, for example, in [9–11].

II. THERMODYNAMICS OF EXTERNALLY UNFORCED SYSTEMS

Let us begin our analysis on a level of description on which externally unforced systems are seen to evolve in time. The state variables used on this level of description will be denoted by the symbol u, the state space by the symbol M (i.e., $u \in M$). For example, we can think of u as representing a one-particle distribution function or the five hydrodynamic fields. We would like to introduce the time evolution in M that reproduces the well-known experimental observation of the approach to time-independent equilibrium states. From an analysis of solutions of the time-evolution equations we expect to arrive at thermodynamics.

The first question that we have to address is thus the question of what the dynamics in M is. Of course, the dynamics will be different for different systems. In fact, the thermodynamics is also different for different systems, but, as it is well known, there is a very useful general formulation of thermodynamics of which thermodynamics of particular systems are particular realizations. Since we

focus our attention on the aspects of the dynamics that are related to thermodynamics, we can expect that there may exist a general formulation of dynamics of which the dynamics of particular systems will be particular realizations. To find such general dynamics, we shall follow two routes. First, we analyze particular cases (e.g., the Boltzmann kinetic equation or the Navier-Stokes-Fourier hydrodynamic equations) and try to extract from them some common features. Second we concentrate on the properties of dynamics of externally unforced systems that have already been recognized as being generally valid. One such property is certainly the Onsager-Casimir relations characterizing, in general terms, dynamics in a small neighborhood of the time-independent equilibrium states.

Following both routes, we have arrived at the time-evolution equation, which we call a nonlinear Onsager-Casimir (NOC) equation. This equation is suitable for discussing thermodynamics. Roughly speaking, the well-known and extensively tested with experimental observations linear Onsager-Casimir equation is extended to a nonlinear equation by generalizing the skew symmetry of a linear operator to the property of being a Hamiltonian operator and by generalizing the symmetry of a linear operator to the property of being an operator generated by a convex potential. A record of the passage of the first route (i.e., the analysis of particular cases) can be found in [12–16]. The structure that appears to be common to all well-established (i.e., extensively tested with results of our experimental observations) dynamical theories (which include, among others, the Boltzmann kinetic equation and the hydrodynamic equations of simple and complex fluids) is indeed the structure of the NOC equation.

In the rest of this section we shall introduce the NOC equation and derive some properties of its solutions. These properties will be shown to be in agreement with results of certain fundamental experimental observations made on externally unforced systems.

A. Nonlinear Onsager-Casimir equation

Common feature of all mathematical formulations of the time evolution are collected in the concept of a dynamical system. The time evolution that takes place in a state space M is generated by a vector field. The abstract nonlinear Onsger-Casimir equation will be introduced by introducing a structure in M (Sec. II A 1) and a vector field in M (Sec. II A 2). We shall use the following notation. Elements of M, called state variables, are denoted by u, i.e., $u \in M$. By T^*M we denote the cotangent bundle having M as its base space. Elements of T^*M are (u, u^*), where $u \in M$ and $u^* \in T_u^*M$. By N_{ET} we denote the state space of equilibrium thermodynamics. Elements of N_{ET} are denoted by v, i.e., $v \in N_{\text{ET}}$. If the system under consideration is a one-component system, then $v \equiv (n, e) \in \mathbb{R}^2$, where n is the number of moles per unit volume and e is the energy per unit volume. By T^*N_{ET} we denote the cotangent bundle having N_{ET} as its base space. Its elements are $(v, v^*) \in T^*N_{\text{ET}}$. Following the notation used in thermodynamics, $v^* \equiv (-\mu/T, 1/T)$,

where μ is the chemical potential and T is the temperature.

1. State space M

The structure in M is introduced in five points $(M1)–(M5)$.

(M1): M is a linear space ; $\langle \, , \, \rangle$ denotes the inner product in M.

(M2): M is a bundle $(M, N_{\text{ET}}, \Pi_{\text{ET}})$, M is the total space, N_{ET} is the base space, and $\Pi_{\text{ET}}: M \to N_{\text{ET}}$ is the bundle projection.

(M3): A real-valued function s: $M \to \mathbb{R}$, called an entropy, is introduced in M. This function plays two roles. First, it introduces thermodynamics in M, and, if combined with the bundle structure $(M2)$, also in N_{ET} (see Sec. II C). Second, it serves, if combined with the bundle structure $(M2)$, as a generating function of the time evolution (see Sec. II A 2).

(M4): A Poisson bracket $\{A, B\}$ is introduced in M. By $A, B, \ldots$ we denote sufficiently regular functions $M \to \mathbb{R}$. We shall introduce a Poisson operator L by

$$\{A, B\} = \langle \partial A / \partial u, L(u) \partial B / \partial u \rangle , \tag{1}$$

where $\partial A / \partial u$ denotes the gradient of A. The Poisson bracket (1) is required to be degenerate so that (4), introduced in Sec. II A 2, holds. We recall that $\{A, B\}$ is a Poisson bracket if $\{A, B\}$ is a linear function of $\partial A / \partial u$ and $\partial B / \partial u$, $\{A, B\} = -\{B, A\}$, and $\{A, B\}$ satisfies the Jacobi identity. From the physical point of view, the Poisson bracket expresses mathematically kinematics in M. In dynamics, the role of the Poisson operator L is to transform a covector (gradient of a function) into a vector (see Sec. II A 2).

(M5): A real-valued function Ψ: $T^*M \to \mathbb{R}$, called a dissipative potential, is introduced in T^*M. It is required to satisfy the following properties: (i) $\Psi(u, 0) = 0$; (ii) Ψ reaches its minimum at $u^* = 0$; (iii) Ψ is a convex function of u^* in a neighborhood of $u^* = 0$; and (iv) Ψ is degenerate so that (4), introduced in Sec. III A 2, holds. The role of Ψ in dynamics is to transform a covector (gradient of a function) into a vector (see Sec. II A 2).

2. Vector field on M

The vector field on M is introduced in two points (VF1) and (VF2).

(VF1): The generation function of dynamics is

$$\Phi(u, v^*) = -s(u) + \langle v^*, \Pi_{\text{ET}}(u) \rangle , \tag{2}$$

where $s(u)$ is introduced in $(M3)$, Π_{ET} in $(M2)$, and $\langle \, , \, \rangle$ denotes the inner product in N_{ET}.

(VF2): The gradient $\partial \Phi / \partial u$ of the generating function Φ is transformed into a vector field by the Poisson structure $(M4)$ and the dissipative potential $(M5)$,

$$\frac{\partial u}{\partial t} = L(u) \frac{\partial \Phi}{\partial u} - \frac{\partial \Psi}{\partial \left[\dfrac{\partial \Phi}{\partial u} \right]} . \tag{3}$$

Both L and Ψ are required to be degenerate [see $(M4)$

and $(M5)$] so that no time evolution takes place on the base space N_{ET}, i.e.,

$$\frac{\partial \Pi_{ET}(u)}{\partial t} = 0 \ . \tag{4}$$

The time-evolution equation (3) is called a nonlinear Onsager-Casimir equation since its structure can be regarded as a nonlinear extension of the Onsager-Casimir reciprocity relations (see observation 2 in Sec. II B 2). It has been shown [12–16] that the Boltzmann kinetic equation, the Navier-Stokes-Fourier hydrodynamic equations, as well as many other dynamical equations arising, for example, in theory of complex fluids [14,15] are particular realizations of the NOC equation. Particularly simple realizations of Eq. (3) will be discussed in Sec. IV.

B. Properties of solutions of the NOC equation

We make now several observations about properties of solutions of the NOC equation (3).

Observation 1

If $u \in M$ follows the trajectory generated by (3), then

$$\frac{d\Phi(u)}{dt} \leq 0 \ . \tag{5}$$

Indeed,

$$\frac{d\Phi}{dt} = \left\langle \frac{\partial \Phi}{\partial u}, \frac{\partial u}{\partial t} \right\rangle$$

$$= \left\langle \frac{\partial \Phi}{\partial u}, L \frac{\partial \Phi}{\partial u} \right\rangle + \left\langle \frac{\partial \Phi}{\partial u}, \frac{\partial \Psi}{\partial(\partial \Phi/\partial u)} \right\rangle \ ,$$

$$\left\langle \frac{\partial \Phi}{\partial u}, L(u) \frac{\partial \Phi}{\partial u} \right\rangle = 0 \ ,$$

since

$$\{\Phi, \Phi\} = 0 \ , \quad \left\langle \frac{\partial \Phi}{\partial u}, \frac{\partial \Psi}{\partial(\partial \Phi/\partial u)} \right\rangle \geq 0$$

due to the properties $(M5)$ of the dissipative potential Ψ. The generating function can be thus regarded as a Lyapunov function associated with the approach (as $t \to \infty$) of solutions of (3) to the states satisfying $\partial \Phi/\partial u = 0$. These states do not change in time and will be shown to be thermodynamic equilibrium states (see Sec. II C). It has to be emphasized that, due to the lack of information about the topological structure of the state space M, the inequality (5) does not by itself suffice to prove the existence of solutions to (3) and therefore also the existence of the approach to the thermodynamic equilibrium states. The approach to equilibrium states implied by (5) remains thus only formal. Equilibrium thermodynamics implied by (3) will be presented in Sec. II C.

Observation 2

Let u_0 be a solution of $\partial \Phi/\partial u = 0$, $u = u_0 + \xi$, and

$$\frac{\partial \xi}{\partial t} = P^- \xi + P^+ \xi \tag{6}$$

be Eq. (3) linearized about u_0. We can easily see that $\Phi_0'' P^+$ is a formally skew-adjoint and $\Phi_0'' P^-$ a formally self-adjoint linear operator; Φ_0'' denotes the Hessian of Φ evaluated at u_0. We have to insist again on formal self-adjointness and skew-adjointness since we do not provide enough information about the topological structure of the state space M and about the domains of P^+ and P^-. The properties of P^+ and P^- noted above represent a general formulation of the Onsager-Casimir reciprocity relations [17,18]. Since Eq. (3), if linearized about u_0, implies the Onsager-Casimir reciprocity relations, Eq. (3) can be regarded as a nonlinear extension of the Onsager-Casimir reciprocity relations. This is the reason why we call Eq. (3) a nonlinear Onsager-Casimir equation.

Observation 3

If the dissipative potential $\Psi \equiv 0$, then Eq. (3) represents a Hamiltonian dynamical system [19]. Existing results about trajectories of Hamiltonian systems can be thus used to analyze solutions of Eq. (3) with $\Psi \equiv 0$. The generating function of the Hamiltonian dynamics is the function Φ. Its physical interpretation will be discussed in Sec. II C. We note that if $\Psi \equiv 0$, then the equality sign in (5) holds. We can therefore call the first term on the right-hand side of Eq. (3) a nondissipative part of the NOC equation. We recall that the dynamics that arises in the complete microscopic theory (in which the system under consideration is viewed as composed of elementary particles) is known to be Hamiltonian. The nondissipative part of the NOC equation thus retains this feature of the completely microscopic dynamics.

Observation 4

If $L(u) \equiv 0$ in (3), then Eq. (3) reduces to the gradient dynamics introduced by Ginzburg, Landau [20], Cahn, and Hilliard [21]. In many well-known particular realizations of the NOC equation, the dissipative potential Ψ is a quadratic function of u^* (e.g., the dissipative potential arising in the Navier-Stokes-Fourier hydrodynamic equations [15]). In the case of the Boltzmann kinetic equation, the dissipative potential is similar to the dissipative potential that arises in chemical kinetics (see [15] and Sec. IV).

Observation 5

We have seen in observation 1 that the NOC equation (3) agrees with the observation of the approach to thermodynamic equilibrium states (see also Sec. II B). This observation by itself cannot be regarded, however, as the only empirical basis of the NOC equation. A dynamical equation exhibiting an approach to some subspace of the state space does not have to, for example, possess the generalized Hamiltonian structure introduced in (3). We recall that we have introduced the structure of the NOC equation by extracting common features of well-established (i.e., well tested with observations) mesoscopic dynamical equations. The empirical basis of the NOC equation remains thus to be rather indirect. The question arises as to whether there exist observations that could be

regarded as a direct empirical basis of the NOC equation. We conjecture that these observations may be observations of certain regularity (structural stability) of the approach. A precise mathematical formulation of the meaning of the regularity as well as a precise formulation of the observation remains an open problem. We recall here only two known results that are distantly related to this problem. First, we recall that analysis of Onsager according to which the Onsager-Casimir relations (i.e., the structure of the NOC equation seen in the linearized NOC equation) are related to the time reversibility of the completely microscopic dynamics [17]. An attempt to relate the Onsager-Casimir relations to the structural stability of the linear time evolution has been made in [22]. Second, we recall results reported in [23]. According to these results, the existence of an additional local conservation law in dynamics whose governing equations are local conservation laws implies certain regularity of trajectories. If $\Psi \equiv 0$, then (5) represents an additional conservation law. But, of course, the NOC equation is not a system of local conservation laws and if $\Psi \neq 0$, then (5) is a dissipation law rather than a conservation law. We believe, however, that the results proven in [23] may serve as an inspiration for proving similar results for the NOC equation (3).

C. Thermodynamics

We saw in observation 1 that solutions in Eq. (3) exhibit a (formal) approach (as $t \rightarrow \infty$) to states satisfying

$$\frac{\partial \Phi}{\partial u} = 0 . \tag{7}$$

In this subsection we shall confront Eq. (3) with the observation according to which behavior of externally unforced systems at the states approached as $t \rightarrow \infty$ [i.e., the states satisfying (7)] is well described by equilibrium thermodynamics.

If we follow $\Phi(u(t))$ as $t \rightarrow \infty$, we arrive at $\Phi(u_T(v^*), v^*)$, where $u_T(v^*)$ is a solution of (7). This follows from (5) (see also observation 1). We shall now argue that u_T is a thermodynamic equilibrium state and $\Phi(u_T(v^*), v^*)$ specifies the equilibrium thermodynamics implied by (3). We note that

$$V \frac{\partial \phi_T}{\partial(-\mu/T)} = Vn \left[u_T \left(-\frac{\mu}{T}, \frac{1}{T} \right) \right] ,$$

$$V \frac{\partial \phi_T}{\partial(1/T)} = Ve \left[u_T \left(-\frac{\mu}{T}, \frac{1}{T} \right) \right] , \tag{8}$$

where

$$\Phi \left[u_T \left(-\frac{\mu}{T}, \frac{1}{T} \right), -\frac{\mu}{T}, \frac{1}{T} \right] = V\phi_T \left(-\frac{\mu}{T}, \frac{1}{T} \right) ,$$

$$\Pi_T(u) = (n(u), e(u)) .$$

If we want to identify $n(u_T)$ with the thermodynamic state variable n (having the meaning of the number of moles per unit volume) and $e(u_T)$ with the thermodynamic variable e (having the meaning of energy per

unit volume), then we see that (8) becomes the familiar thermodynamic relations provided

$$\phi_T \left[-\frac{\mu}{T}, \frac{1}{T} \right] = -P , \tag{9}$$

where P is the thermodynamic pressure. This relation (see [6]) is the fundamental thermodynamic relation representing the complete knowledge of the equilibrium thermodynamic behavior. The relation (9) can be transformed, by using the Legendre transformation, to its dual form

$$s = s(n, e) \tag{10}$$

in N_{ET}. By s we denote the equilibrium entropy, i.e., $s = s(u_T)$. It is useful to formulate equilibrium thermodynamics in such a way that both (9) and (10) appear manifestly as two forms of one relation. Following [7-9] we introduce thermodynamics as Legendre submanifold in $T^* N_{ET} \times \mathbb{R}$. We recall that $T^* N_{ET} \times \mathbb{R}$ has a natural contact structure defined by the one form $d\omega = ds - v^* dv$, where $s \in \mathbb{R}$, $v \in N_{ET}$, $v^* \in T_v^* N_{ET}$. The Legendre submanifold is the submanifold on which $d\omega \equiv 0$ [9]. Locally, the Legendre submanifold is the image of

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

Legendre transformations are the transformations preserving the contact structure and transforming a Legendre submanifold into another Legendre submanifold.

The above formulation of thermodynamics in N_{ET} suggests that the relation $s = s(u)$ introduced in $(M3)$ (see Sec. II A 1) should be regarded as a fundamental thermodynamic relation in M. Thermodynamics in M is thus introduced as a Legendre submanifold in $T^* M \times \mathbb{R}$. Locally, the Legendre submanifold is the image of $u \mapsto (u, \partial s / \partial u(u), s(u))$. The generating function Φ introduced in (2) can be regarded as a function generating the Legendre transformation associated with the bundle structure in M for which $v'^* = 0$, where $v'^* \in T^* N'_{ET}$, $N'_{ET} = \Pi_{ET}^{-1}(v)$ is the fiber attached to $v \in N_{ET}$. The passage from the fundamental thermodynamic relation $s = s(u)$ in M to the fundamental thermodynamic relation $s = s(n, e)$ in the base space N_{ET} is thus realized by the Legendre transformation generated by Φ. Because of this role of Φ in thermodynamics, we shall call Φ also a thermodynamic potential. It can be shown [24,14] that the Gibbs recipe (introduced in equilibrium statistical mechanics) that allows us to pass from the fundamental thermodynamic relation in the state space used in the completely microscopic description to the fundamental thermodynamic relation in N_{ET} can also be cast into the form of a Legendre transformation.

Since contact geometry provides the setting for formulating thermodyamics, we can ask the question as to whether the NOC equation (3) can also be put into this setting. We thus look for a vector field in $T^* M \times \mathbb{R}$ that generates the time-evolution preserving the contact structure defined by the one form $ds - v^* dv$ and that is, in

some sense, the same as the vector field (3). The time-evolution preserving the contact structure can be seen as a sequence of Legendre transformations similarly as the time evolution arising in classical mechanics can be seen as a sequence of canonical (i.e., preserving the symplectic structure) transformations. The question has been answered in [25]. We introduce a function K: $T^*M \times \mathbb{R} \rightarrow \mathbb{R}$, called a contact Hamiltonian, by

$$K(u,u^*) = \Psi(u^*) - \Psi\left[\frac{\partial \Phi}{\partial u}\right] - \left\langle u^*, L(u)\frac{\partial \Phi}{\partial u}\right\rangle \quad (11)$$

and a vector field on $T^*M \times \mathbb{R}$ by

$$\frac{\partial u}{\partial t} = -\frac{\partial K}{\partial u^*} ,$$

$$\frac{\partial u^*}{\partial t} = \frac{\partial K}{\partial u} - u^*\frac{\partial K}{\partial s} , \quad (12)$$

$$\frac{ds}{dt} = K - \left\langle u^*, \frac{\partial K}{\partial u^*}\right\rangle .$$

We observe that the time evolution generated by (12) indeed preserves the contact structure [(12) is a canonical formulation of a contact vector field [10,11]] and that Legendre submanifolds that are locally images of $u \mapsto (u, \partial \Phi/\partial u(u), \Phi(u))$ are invariant submanifolds of $T^*M \times \mathbb{R}$. The vector field (12) restricted to these invariant submanifolds is equivalent to (3).

III. THERMODYNAMICS OF DRIVEN SYSTEMS

In the preceding section we have arrived at thermodynamics of externally unforced systems by observing the approach to equilibrium. The thermodynamic description in N_{ET} is less detailed (i.e., more macroscopic) than the description in M in which the time evolution takes place. A state $u \in M$ evolves in time in two stages. First, the trajectory that passes through u reaches, as $t \rightarrow \infty$, a state $v \in N_{\mathrm{ET}}$. Then, the trajectory continues in N_{ET}. Since, however, N_{ET} is composed of constants of motion, no time evolution takes place in N_{ET}. We shall therefore refer to the time evolution in M as a fast time evolution and to the time evolution in N_{ET} as a still time evolution. The split of the time evolution into two stages can be expressed as follows:

$$\text{time evolution in } M \approx \begin{cases} \text{fast time evolution in } M \\ \text{(approach to } N_{\mathrm{ET}}) \\ \text{still time evolution in } N_{\mathrm{ET}} \\ \text{governed by } \dfrac{dn}{dt} = 0 , \dfrac{de}{dt} = 0 . \end{cases}$$

$$(13)$$

The sign $\approx$ in (3) means that solutions of the time evolution equations on the left- and the right-hand sides of (13) are in some sense close. The analysis of the time evolution in M continued in Sec. II by introducing a hypothesis that the fast time evolution is governed by the NOC equation. This then led us to the introduction of thermodynamics in N_{ET}.

In driven systems, the approach to equilibrium is not observed. This is because the external forces prevent the system from reaching the thermodynamic equilibrium states. We do observe, however, also in driven systems, the approach of a detailed (microscopic) description to a less detailed (more macroscopic) description that uses N as its state space. We recall the experience that behavior of many driven systems is found to be well described by state variables v which are more macroscopic than the state variables used in the complete microscopic theory in which the systems are regarded as composed of elementary particles. If we thus describe the time evolution in a state space M that is more microscopic than N, we have to observe in trajectories in M an approach to N. For example, the behavior of a horizontal layer of a fluid subjected to the gravitational force and a vertical temperature gradient (Bénard system) is found to be well described by using hydrodynamic state variables. In the case of Bénard system, the state space N is thus composed of hydrodynamic fields. The observed existence of a description in N then means that the time evolution in M can be split into the time evolution in M approaching N (we shall call it a fast time evolution) and the time evolution in N (we shall call it a slow time evolution)

$$\text{time evolution in } M \approx \begin{cases} \text{fast time evolution in } M \\ \text{(approach to } N) \\ \text{slow time evolution in } N . \end{cases}$$

$$(14)$$

The observation (14) does not suffice to introduce thermodynamics of driven systems just as the observation (13) did not suffice to introduce thermodynamics of externally unforced systems. The trajectories approaching N have to be examined in some detail. Inspired by the discussion in observation 5 (Sec. II B) we introduce a hypothesis that the approach to N is governed also by the NOC equation. We emphasize that we do not expect that the approach to the still time evolution will be governed by the same equation as the approach to the slow time evolution. What we expect is that these two equations will be two different realizations of the abstract NOC equation (i.e., the two equations will have, in general, two different Poisson brackets, generating functions and dissipative potentials). In the context of externally unforced systems, the hypothesis that the approach of fast to still time evolution is governed by the abstract NOC equation was justified by showing that this is indeed the case in many well-studied particular examples. For instance, we have proven that if on the left-hand side of (13) is the Boltzmann kinetic equation or the Navier-Stokes-Fourier hydrodynamic equations, then the sign $\approx$ means a complete equivalence. There are no such extensively studied examples of the approach of fast to slow time evolution. The hypothesis that the fast time evolution is governed by the NOC equation is much less justified in (14) than in (13). We expect that the sign $\approx$ in (14) will rarely, if ever, signify an exact equivalence. The right-hand side of (14) should be regarded only as a model of the left-hand side.

The experience expressed in (14) together with the hypothesis that the fast time evolution is governed by the NOC equation will lead us to thermodynamics in N in the

same way as the experience (13) together with the same hypothesis led us to thermodynamics in N_{ET} in Sec. II. The only change that has to be made in Sec. II is to replace the state space N_{ET} used in equilibrium thermodynamics by the state space N composed of slow state variables. We thus keep the same state space M, but change its structure. The bundle structure is now (M,N,Π) with the bundle projection Π: $M \rightarrow N$. Also the entropy $s(u)$, the dissipative potential Ψ, and the Poisson bracket are in general different if $N \neq N_{ET}$. This then means that also the generating function Φ introduced in (2) is different,

$$\Phi(u,v^*) = -s(u) + \langle v^*, \Pi(u) \rangle .$$ (15)

The states that satisfy (7) [with Φ given in (15)] will be called thermodynamic states (we shall denote them by the symbol u_T). The vector field generating the fast time evolution is still the vector field (3), but L, Φ, Ψ are in general different than those used in (3) generating the fast time evolution in (13). We end this section by two remarks. Illustrations of thermodynamics of driven systems in the state space N composed of slow state variables will be worked out in Sec. IV.

Remark 1. We recall that thermodynamics introduced in Sec. II has been interpreted as a geometrical structure in the state space N_{ET} (namely, as a Legendre submanifold in $T^*N_{ET} \times \mathbb{R}$ equipped with its canonical contact structure). Similarly, if we replace N_{ET} by N, the thermodynamics in N is a geometrical structure in N (more specifically, a Legendre submanifold in $T^*N \times \mathbb{R}$). A geometrical structure in a state space is, of course, time independent. If we speak in thermodynamics of externally unforced systems about the time evolution of entropy, we mean the time evolution of $s(u)$ with $u \in M$ following the trajectory M generated by the fast time evolution. We note [see the inequality (7)] that $s(u)$ can only grow or remain unchanged as the time progresses. The entropy $s(u)$ becomes the entropy s, which participates in the specification of the thermodynamic (geometrical) structure in N_{ET}, only after it has been evaluated at u_T [i.e., $s = s(u_T)$]. To sum up, in the context of (13) we have only one time evolution, namely the fast time evolution. The time evolution of entropy thus has to be the fast time evolution.

Now we turn our attention to driven systems. In this case we deal with two time evolutions, the fast and the slow [see (14)]. The time evolution of entropy can be thus fast or slow. The fast time evolution is the time evolution of $s(u)$ where $u \in M$ follows the fast time evolution in M. Since the inequality (7) holds, $s(u)$ can only grow or remain unchanged. As $t \rightarrow \infty$, $s(u)$ tends to $s(u_T) = s(v)$, which is then the entropy that participates in the specification of the geometric (thermodynamical) structure in N. In N, another time evolution takes place, namely the slow time evolution. We can therefore think of $s(v(t))$ where v follows the trajectory in N generated by the slow time evolution. Since $s(v)$ is regarded as a part of the structure in N, this time evolution does not have a clear physical (or mathematical) meaning. What does have, however, a clear meaning is the question of

how the time evolution in N (i.e., the slow time evolution) is related to the geometric (thermodynamical) structure of N. We expect that these two features of dynamics in N are related since, if we regard (14), the geometrical (thermodynamic) structure in N and the slow dynamics in N are in fact two aspects of solutions of the time evolution equations in M [i.e., the time-evolution equations appearing on the left-hand side of (14)]. We can indeed regard the right-hand side of (14) as a partial solution of the time-evolution equations appearing on the left-hand side of (14). The relation between the thermodynamic structure in N and the time evolution in N can be investigated more closely only by entering into a more detailed analysis of trajectories in M [i.e., solutions of the equations appearing on the left-hand side of (14)]. As an example of the relation that might be revealed in this study, we recall the observation made in [26] according to which driven systems seem to evolve, in some situations, to a critical state (i.e., a point where the geometrical structure in N is singular). In our formulation this means that trajectories in N approach, in some situations, the points in which the geometrical (thermodynamic) structure in N is singular.

Remark 2. We recall that if M is chosen to be the state space used in completely microscopic description in which the systems under consideration are regarded as composed of elementary particles, then the introduction of thermodynamics presented in Sec. II C is an equivalent reformulation of the Gibbs equilibrium statistical mechanics. In this case the entropy $s(u)$ is the same for all systems; the individual features of the systems are expressed only in the bundle structure (see [24,14]). In this section we have introduced a thermodynamic potential Φ by analyzing the observation (14). We can ask the question as to whether and how the thermodynamic potential introduced in this section can be regarded as a generalization of the thermodynamic potentials arising in the Gibbs equilibrium statistical mechanics. The answer to this question is affirmative. The thermodynamic potentials introduced in [27–29] are indeed of the same type as those arising in this section. The physical intuition on which generalization of the Gibbs equilibrium statistical mechanics introduced in [27–29] is based is a suggestion to regard entropy as a measure of information. If we take the point of view of thermodynamics of driven systems introduced in [27–29], then the discussion presented in this section represents the following contribution. We indicate an alternative way of seeing the thermodynamic potential Φ. We show that this potential can be obtained by analyzing solutions of the time evolution in M. The right-hand side of (14) where Φ arises represents a result of an analysis of solutions of the time-evolution equation appearing on the left-hand side of (14). Thermodynamics of driven systems is clearly put into the context of dynamics. In addition, the interpretation of Φ as a function generating a geometrical structure in N is also useful in the search for Φ and for its physical interpretation.

IV. ILLUSTRATION

In this section we introduce several illustrations of Eqs. (13) and (14) and the thermodynamics that is associated

with them. We look for illustrations that are interesting from the physical point of view and simple from the mathematical point of view. Illustrations of this type can be found, for example, in chemical kinetics. We consider in this section a k-component system (the k components are denoted by symbols $A^{(1)}, \ldots, A^{(k)}$) undergoing one chemical reaction

$$0 \rightleftharpoons \sum_{i=1}^{k} \nu_i A^{(i)} , \qquad (16)$$

where $\nu_1, \ldots, \nu_k$ are stoichiometric coefficients. Let $A^{(1)}, \ldots, A^{(k')}$ be reactants (i.e., $\nu_1, \ldots, \nu_{k'}$ are negative) and $A^{k'+1}, \ldots, A^{(k)}$ products of the reaction (i.e., $\nu_{k'+1}, \ldots, \nu_k$ are positive). The system will be considered to be isothermal and spatially homogeneous. We shall analyze it in the following three state spaces.

(i) N is a k-dimensional space and its elements are $(n_1, \ldots, n_k)$, denoting the number of moles (per unit volume) of the components.

(ii) N_{ET} is the state space of equilibrium thermodynamics; N_{ET} is a $(k-1)$-dimensional space, its elements $(m_2, \ldots, m_k)$ are linear combinations of $n_1, \ldots, n_k$ that remains unchanged during the reaction (16) [see (20)].

(iii) M is a $(k+1)$-dimensional space with elements $(n_1, \ldots, n_k, \mathscr{J})$, where $n_1, \ldots, n_k$ have the same meaning as in N and $\mathscr{J}$ is a quantity related to the rate J of the reaction (16) [see (32)]. We shall call M an extended state space of classical chemical kinetics.

In all three state spaces introduced above, the remaining state variable is the temperature T. Since we limit ourselves in this section to the analysis of isothermal systems, we put $T = 1$ so that the temperature will disappear from our notation.

A. Externally unforced system [Eq. (13)]

The state space N is the state space in which chemical systems are analyzed in classical chemical kinetics. By using the classical analysis, the left-hand side of Eq. (13) is the time evolution equation

$$\frac{dn_i}{dt} = -\nu_i J , \qquad (17)$$

where

$$J = \overleftarrow{k} n_{k'+1}^{\nu_{k'+1}} \cdots n_k^{n_k} - \overrightarrow{k} n_1^{-\nu_1} \cdots n_{k'}^{-\nu_{k'}} \qquad (18)$$

is the reaction rate given by the mass action law; $\overrightarrow{k}$ and $\overleftarrow{k}$ are rate coefficients of the forward and the backward reactions. Our objective now is to recast (17) and (18) into the form of the NOC equation [i.e., into the right-hand side of Eq. (13)].

We begin by introducing the structure into N (see Sec. II A 1). The bundle structure of N is $N = (N, N_{\mathrm{ET}}, \Pi^N_{\mathrm{ET}})$, where

$$(n_1, \ldots, n_k) \xrightarrow[\Pi^N_{\mathrm{ET}}]{} (m_2, \ldots, m_k) , \qquad (19)$$

$$m_i = \nu_1 n_i - \nu_i n_1, \quad i = 2, \ldots, k . \qquad (20)$$

We can easily verify that m_i, $i = 2, \ldots, k$, remain unchanged in time if $n_1, \ldots, n_k$ evolve according to (17). The generating function (2) is

$$\Phi^{(N)}(n_1, \ldots, n_k, m_2^*, \ldots, m_k^*)$$

$$= \phi_k^{(N)}(n_1, \ldots, n_k) - \sum_{i=2}^{k} m_i^*(\nu_1 n_i - \nu_i n_1) , \qquad (21)$$

where $\phi^{(N)}$ is the free energy that is left at this point unspecified. The time-evolution equations (17) and (18) are clearly only dissipative equations so that the Poisson structure is absent from N. Hence the NOC equation is

$$\frac{dn_i}{dt} = -\frac{\partial \Psi^{(N)}}{\partial(\partial \Phi^{(N)}/\partial n_i)} , \qquad (22)$$

where $\Psi^{(N)}$ denotes the dissipative potential.

Our problem now is to identify $\Psi^{(N)}$ and $\phi^{(N)}$ so that (22) is an equivalent reformultion of (17) and (18). First, we turn our attention to the degeneracy requirement (4). We note that if we let $\Psi^{(N)}$ depend on $\partial \Phi^{(N)}/\partial n_i$ only through its dependence on the chemical affinity

$$a^{(N)} = \sum_{i=1}^{k} \nu_i \frac{\partial \Phi^{(N)}}{\partial n_i} \qquad (23)$$

[note that $\sum_{i=1}^{k} \nu_i(\partial \Phi^{(N)}/\partial n_i) = \sum_{i=1}^{k} \nu_i(\partial \phi^{(N)}/\partial n_i)$], then (22) satisfies the degeneracy requirement (4). Equation (22) becomes moreover equivalent to (17) provided

$$J = \frac{\partial \Psi^{(N)}}{\partial a^{(N)}} . \qquad (24)$$

We note that if (24) holds, then

$$\frac{d\Phi^{(N)}}{dt} = -a^{(N)} \frac{\partial \Psi^{(N)}}{\partial a^{(N)}} \leq 0 \qquad (25)$$

since $\Psi^{(N)}$ satisfies the properties $(M5)$ (see Sec. II A 1). What remains to be done is to specify $\Psi^{(N)}$ and $\phi^{(N)}$ so that (24) is equivalent to (18). This problem has in fact already arisen in a different type of consideration of chemical kinetics (for a recent review see [30]). We shall make therefore only a few remarks. First, we note that the problem, as stated, has many solutions. Let us see one of them.

We choose the ideal gas free energy

$$\phi^{(N)}(n_1, \ldots, n_k) = \sum_{i=1}^{k} (n_i \ln n_i + C_i n_i) , \qquad (26)$$

where $C_1, \ldots, C_k$ are parameters. It is easy to verify that if

$$\Psi^{(N)}(a^{(N)}) = W(n_1, \ldots, n_k)(a^{(N)} + e^{-a^{(N)}} - 1) , \qquad (27)$$

where $W > 0$ is a parameter [note that the dissipative potential (27) satisfies the requirement $(M5)$—see Sec. II A 1] and $W = \overleftarrow{k} n_{k'+1}^{n_{k'+1}} \cdots n_k^{\nu_k}$, $\overleftarrow{k}/\overrightarrow{k} = \exp[\sum_{i=1}^{k} \nu_i(1 + C_i)]$, then indeed (24) transforms into (18). We also note that if $a^{(N)}$ is small (i.e., only states close to the equilibrium state are considered), then (27) is well approximated by $\frac{1}{2} W(a^{(N)})^2$ and (24) reduces to the time-evolution equation introduced in classical irreversible

thermodynamics [31].

Following Sec. II C, thermodynamics in N_{ET} implied by (22), i.e., the fundamental thermodynamic relation

$$P = P(m_2^*, \ldots, m_k^*) , \tag{28}$$

is obtained by evaluating (21) at thermodynamic equilibrium states [i.e., solutions to (7)],

$$\frac{\partial \phi^{(N)}}{\partial n_i} = -\nu_1 m_i^* , \quad i = 2, \ldots, k$$

$$\frac{\partial \phi^{(N)}}{\partial n_1} = \sum_{i=2}^{k} \nu_i m_2^* . \tag{29}$$

We see from (23) that if (29) holds then the chemical affinity $a^{(n)} = 0$. It is important to note that the fundamental thermodynamic relation (28) in N_{ET} depends on the stoichiometric coefficients but is independent of the parameters entering the dissipative potential $\Psi^{(N)}$.

Until now, we have analyzed the system in the setting of classical chemical kinetics (i.e., we used the state space N). We have succeeded to recast the mass-action-law time-evolution equation into the NOC equation. We have thus provided an example of Eq. (13). We note that the sign $\approx$ signifies in this example a complete equivalence. Now we turn our attention to a more microscopic analysis in the state space M. The adoption of the reaction rate (more precisely a quantity related to the reaction rate) as an extra state variable [32–34] follows the spirit of extended irreversible thermodynamics [35]. The reaction rate is the odd (i.e., velocity-type) variable that will allow us to introduce the inertia into the time evolution (analogous to the situation in particle dynamics where the adoption of velocity as an independent state variable allows the introduction inertia into the particle dynamics). In the state space N, we know the time evolution equation from classical chemical kinetics (mass action law). In the state space M we do not know the time evolution. We shall therefore use Eq. (13) to introduce it. This means that we look for a NOC equation in M that is required to reduce to (17) and (18) [or equivalently to (22)] if the time evolution of $\mathscr{J}$ is much faster than the time evolution of $n_1, \ldots, n_k$.

We begin by introducing the bundle structure into M, $M = (M, N_{\text{ET}}, \Pi_{\text{ET}}^M)$,

$$(n_1, \ldots, n_k, \mathscr{J}) \xrightarrow[\Pi_{\text{ET}}^M]{} (m_2, \ldots, m_k) , \tag{30}$$

where $m_2, \ldots, m_k$ are the same as in (20). Next, we introduce the generating function

$$\Phi^{(M)}(n_1, \ldots, n_k, \mathscr{J}, m_2^*, \ldots, m_k^*)$$

$$= \phi^{(M)}(n_1, \ldots, n_k, \mathscr{J}) - \sum_{i=2}^{k} m_i^* (\nu_1 n_i - \nu_i n_1) . \tag{31}$$

The free energy $\phi^{(M)}$ is left at this point unspecified. Using the experience collected in extended irreversible thermodynamics [35], we introduce the dissipation only into the equation governing the time evolution of the new state variable $\mathscr{J}$. This means that we let $\Psi^{(M)}$ depend only on $\partial \Phi^{(M)} / \partial \mathscr{J}$.

Next we introduce the Poisson structure into M. We note that in order that the equations governing the time evolution of $n_1, \ldots, n_k$ have the form (17) we have to require

$$\frac{\partial \Phi^{(M)}}{\partial \mathscr{J}} = J \tag{32}$$

and introduce a $(k+1) \times (k+1)$ Poisson matrix $L^{(M)}$ in such a way that its ith row, $i = 1, \ldots, k$, is $(0, \ldots 0, -\nu_i)$. Then, of course, the skew symmetry of $L^{(M)}$ indicates that the last row of $L^{(M)}$ is $(\nu_1, \ldots, \nu_k, 0)$, i.e.,

$$L^{(M)} = \begin{bmatrix} 0 & \cdots & 0 & -\nu_1 \\ 0 & \cdots & 0 & -\nu_2 \\ \vdots & & & \\ \nu_1 & \nu_2 \cdots & \nu_k & 0 \end{bmatrix} \tag{33}$$

and the bracket

$$\{A, B\}^{(M)} = \begin{bmatrix} \dfrac{\partial A}{\partial n_1}, \ldots, \dfrac{\partial A}{\partial n_k}, \dfrac{\partial A}{\partial \mathscr{J}} \end{bmatrix} L^{(M)} \begin{bmatrix} \partial B / \partial n_1 \\ \vdots \\ \partial B / \partial n_k \\ \partial B / \partial \mathscr{J} \end{bmatrix} , \tag{34}$$

where A and B, are sufficiently regular functions of $(n_1, \ldots, n_k, \mathscr{J})$. Since $L^{(M)}$ is a constant matrix, the skew symmetry of $L^{(M)}$ implies immediately the Jacobi identity for the bracket (34). The bracket (34) is thus indeed a Poisson bracket. It is interesting to note that the stoichiometric coefficients enter the Poisson structure.

Having specified the structure in M we can write now the NOC equation

$$\begin{bmatrix} \dfrac{\partial n_1}{\partial t} \\ \vdots \\ \dfrac{\partial n_k}{\partial t} \\ \dfrac{\partial \mathscr{J}}{\partial t} \end{bmatrix} = L^{(M)} \begin{bmatrix} \dfrac{\partial \Phi^{(M)}}{\partial n_1} \\ \vdots \\ \dfrac{\partial \Phi^{(M)}}{\partial n_k} \\ \dfrac{\partial \Phi^{(M)}}{\partial \mathscr{J}} \end{bmatrix} - \begin{bmatrix} 0 \\ \vdots \\ \dfrac{\partial \Psi^{(M)}}{\partial \left[\dfrac{\partial \Phi^{(M)}}{\partial \mathscr{J}} \right]} \end{bmatrix} . \tag{35}$$

The equation governing the time evolution of $\mathscr{J}$ is thus

$$\frac{\partial \mathscr{J}}{\partial t} = a^{(M)} - \frac{\partial \Psi^{(M)}}{\partial \left[\dfrac{\partial \Phi^{(M)}}{\partial \mathscr{J}} \right]} . \tag{36}$$

where $a^{(M)}$ is the chemical affinity (23) with $\Phi^{(M)}$ replacing $\Phi^{(N)}$. If $\mathscr{J}$ evolves in time much faster than $n_1, \ldots, n_k$, we can put $\partial \mathscr{J} / \partial t = 0$ in (36) and thus we have

$$a^{(M)} = \frac{\partial \Psi^{(M)}}{\partial \left[\dfrac{\partial \Phi^{(M)}}{\partial \mathscr{J}} \right]} . \tag{37}$$

In order that (37) and (32) imply (24) we have to choose

appropriately $\Psi^{(M)}$. For example, we can easily verify that if

$$\Psi^{(M)}=W(n_1,\ldots,n_k)\left[1-\frac{1}{W}\frac{\partial\Phi^{(M)}}{\partial\mathscr{J}}\right]$$

$$\times\ln\left[1-\frac{1}{W}\frac{\partial\Phi^{(M)}}{\partial\mathscr{J}}\right]+\frac{\partial\Phi^{(M)}}{\partial\mathscr{J}} \tag{38}$$

and $\Psi^{(N)}$ is given in (27), then indeed (37) is equivalent to (24) and (32). Note that the dissipative potential (38) satisfies the requirement ($M5$) (see Sec. II A).

Now we turn our attention to thermodynamics in M, N, and N_{ET}. First, we note that in the state space N, it is Gibbs's equilibrium statistical mechanics that provides us with a basis for discussing the association between systems and free energies $\phi^{(N)}$. In M the situation is more complicated since $\mathscr{J}$ is an odd (i.e., velocity-type) variable that, from the microscopic (molecular) point of view, relates to both velocities and interactions among the molecules. We shall not enter into a detailed microscopic analysis of $\phi^{(M)}$. We limit ourselves only to a few remarks.

Keeping $\phi^{(M)}$ still undetermined, we use the general discussion in Sec. II C and pass from thermodynamics in M to thermodynamics in N and subsequently to thermodynamics in N_{ET}. In order to pass from $\Phi^{(M)}$ to $\Phi^{(N)}$ we introduce a new generating function

$$\hat{\Phi}^{(M)}(n_1,\ldots,n_k,\mathscr{J},J,m_2^*,\ldots,m_k^*)$$

$$=\Phi^{(M)}(n_1,\ldots,n_k,\mathscr{J},m_2^*,\ldots,m_k^*)-J\mathscr{J} \tag{39}$$

and look for solutions (denoted $\mathscr{J}_{\mathrm{T}}$) of $\partial\hat{\Phi}^{(M)}/\partial\mathscr{J}=0$ [i.e., solutions of (32)]. The resulting Legendre transformation $\tilde{\Phi}^{(M)}(n_1,\ldots,n_k,J,m_2^*,\ldots,m_k^*)$ of $\Phi^{(M)}(n_1,\ldots,n_k,\mathscr{J},m_2^*,\ldots,m_k^*)$,

$$\tilde{\Phi}^{(M)}(n_1,\ldots,n_k,J,m_2^*,\ldots,m_k^*)$$

$$=\hat{\Phi}^{(M)}(n_1,\ldots,n_k,\mathscr{J}_{\mathrm{T}},J,m_2^*,\ldots,m_k^*) \tag{40}$$

then leads to $\Phi^{(N)}$ by setting $J=0$, i.e.,

$$\Phi^{(N)}=[\tilde{\Phi}^{(M)}]_{J=0} . \tag{41}$$

This passage from $\Phi^{(M)}$ to $\Phi^{(N)}$ can also be interpreted differently. The state variable $\mathscr{J}$ in $\Phi^{(M)}$ is regarded as being an order parameter. The passage from $\Phi^{(M)}$ to $\Phi^{(N)}$ is realized by eliminating the order parameter. The elimination consists of evaluating $\Phi^{(M)}$ at the value of the order parameter at which $\Phi^{(M)}$ reaches its minimum (as a function of $\mathscr{J}$). The passage from $\Phi^{(M)}$ to $\Phi^{(N_{\mathrm{ET}})}$ is realized similarly. We look for solutions of $\partial\Phi^{(M)}/\partial n_2=0_1,\ldots,\partial\Phi^{(M)}/\partial n_k=0$, $\partial\Phi^{(M)}/\partial\mathscr{J}=0$ (i.e., we look for thermodynamic equilibrium states) and evaluate $\Phi^{(M)}$ at these states. We note that $\Phi^{(M)}$ and $\Phi^{(N)}$ imply the same thermodynamics in N_{ET} if $[\Phi^{(M)}]_{\mathscr{J}=0}=\Phi^{(N)}$. As an example of $\Phi^{(M)}$ satisfying this requirement, we introduce

$$\Phi^{(M)}=\Phi^{(N)}+\frac{1}{2b(n_1,\ldots,n_k)}\mathscr{J}^2 , \tag{42}$$

where $b(n_1,\ldots,n_k)$ remains an unspecified quantity. From the physical point of view, we can interpret the term $(1/2b)\mathscr{J}^2$ as an analog of kinetic energy with $\mathscr{J}$ playing the role of momentum and b playing the role of mass measuring the inertial of the chemical reaction (16).

B. Driven system: Imposed chemical affinity [Eq. (14)]

In this subsection, we shall submit the system to an external force. We assume that the mole number of some components and thus also the chemical affinity can be controlled from outside of the system. Experience collected in classical chemical kinetics indicates that also under these circumstances the behavior of the system can be well described in the state space N. We are interested to see how the driving force changes thermodynamics. First, we note that there is now no thermodynamics in N_{ET} since the system does not approach states in N_{ET}. Following Sec. III, we shall derive thermodynamics in N from an analysis of the time evolution in M. In terms of Eq. (14) we formulate our problem as

$$\mathrm{Equation}\ (35)\approx\begin{cases}\mathrm{NOC\ equation}\\ \mathrm{Equation}\ (22) .\end{cases} \tag{43}$$

Our objective is to identify the NOC equation in (43).

We begin, as always, by introducing the structure into M. The structure will be different from the one introduced in Sec. IV A 1 since the NOC equation on the right-hand side of Eq. (43) represents a different time evolution than the NOC equation (35). The bundle structure of M is $M=(M,N,\Pi_N^M)$,

$$(n_1,\ldots,n_k,\mathscr{J})\xrightarrow[\Pi_N^M]{}(n_1,\ldots,n_k) . \tag{44}$$

As a first approximation, the NOC equation on the right-hand side of Eq. (43) is chosen to be only a dissipative equation

$$\frac{\partial\mathscr{J}}{\partial t}=-\frac{\partial\Psi^{(M,N)}}{\partial\left[\dfrac{\partial\Phi^{(M,N)}}{\partial\mathscr{J}}\right]} . \tag{45}$$

This means that the Poisson structure is absent in M, $\Psi^{(M,N)}$ is the dissipative potential, and $\Phi^{(M,N)}$ is the generating function. In order to specify $\Phi^{(M,N)}$ we make the following observation. The necessary condition for $\approx$ in (43) to signify a good approximation is that the following is true. The first k equations in (35) with their right-hand sides evaluated at thermodynamic states corresponding to $\Phi^{(M,N)}$ [i.e., states approached as $t\to\infty$ by following the fast time evolution governed by (45)] are equivalent to Eq. (22). In other words, we require that

$$\frac{\partial\Phi^{(M,N)}}{\partial\mathscr{J}}=0\Longrightarrow\frac{\partial\Phi^{(M)}}{\partial\mathscr{J}}=\frac{\partial\Psi^{(N)}}{\partial a^{(N)}} . \tag{46}$$

To find $\Phi^{(M,N)}$ satisfying (46) we turn to $\hat{\Phi}^{(M)}$ introduced in (39). We have seen in the preceding section that $\hat{\Phi}^{(M)}$ becomes, after evaluating it at the states satisfying $\partial\hat{\Phi}^{(M)}/\partial\mathscr{J}=0$, the thermodynamic potential $\Phi^{(N)}$. Now, we look for $J=\mathscr{J}^*(n_1,\ldots,n_k)$ such that

$$\Phi^{(N,N)} = [\hat{\Phi}^{(M)}]_{J = \mathscr{J}^*(n_1, \ldots, n_k)} \tag{47}$$

satisfies (46). From (39) we have

$$\frac{\partial \Phi^{(M,N)}}{\partial \mathscr{J}} = 0 \Longrightarrow \frac{\partial \Phi^{(M)}}{\partial \mathscr{J}} = \mathscr{J}^* . \tag{48}$$

In order that (48) is equivalent to (46) we have to set

$$\frac{\partial \Phi^{(N)}}{\partial \mathscr{J}} = \mathscr{J}^* = \frac{\partial \Psi^{(N)}}{\partial a^{(N)}} . \tag{49}$$

If, in particular, we choose Φ^M as in (42); then (49) implies

$$\frac{1}{b(n_1, \ldots, n_k)} \mathscr{J} = \frac{\partial \Psi^{(N)}}{\partial a^{(N)}} . \tag{50}$$

Having specified $\Phi^{(M,N)}$, it is only the dissipative potential $\Psi^{(M,N)}$ that remains unspecified in (45). To specify it, we have to enter into a detailed analysis of the closeness of solutions of the equations appearing on the left- and right-hand sides of (43). Our main objective in this subsection is to derive thermodynamics in N. To achieve this we need only $\Phi^{(M,N)}$. Hence we can leave the dissipative potential $\Psi^{(M,N)}$ unspecified.

The thermodynamics in N implied by $\Phi^{(M,N)}$ is derived by following Sec. II C. We look for thermodynamic states [i.e., solutions of (7)] and evaluate $\Phi^{(M,N)}$ at these states. From (47)–(49) we have (we use the symbol $\Phi^{(N_{\mathrm{driv}})}$ to denote the resulting potential)

$$\Phi^{(N_{\mathrm{driv}})}(n_1, \ldots, n_k, m_2^*, \ldots, m_k^*)$$
$$= \Phi^{(M)}(n_1, \ldots, n_k, \mathscr{J}_{\mathrm{T}}(n_1, \ldots, n_k), m_2^*, \ldots, m_k^*)$$
$$- \mathscr{J}^*(n_1, \ldots, n_k) \mathscr{J}_{\mathrm{T}}(n_1, \ldots, n_k) , \tag{51}$$

where $\mathscr{J}_{\mathrm{T}}$ is a solution of (49). In the particular case in which $\Phi^{(M)}$ is given by (42) we obtain

$$\Phi^{(N_{\mathrm{driv}})}(n_1, \ldots, n_k, m_2^*, \ldots, m_k^*)$$
$$= \Phi^{(N)}(n_1, \ldots, n_k, m_2^*, \ldots, m_k^*)$$
$$- \tfrac{1}{2} b(n_1, \ldots, n_k) \left[\frac{\partial \Psi^{(N)}}{\partial a^{(N)}} \right]^2 . \tag{52}$$

We end this subsection by making a few observations about the thermodynamic potentials $\Phi^{(N)}$ and $\Phi^{(N_{\mathrm{driv}})}$. First, we emphasize that both $\Phi^{(N)}$ and $\Phi^{(N_{\mathrm{driv}})}$ are thermodynamic potentials introduced in the same state space N. The thermodynamic potential $\Phi^{(N_{\mathrm{driv}})}$ contains more information than $\Phi^{(N)}$ since $\Phi^{(N_{\mathrm{driv}})}$ has been obtained as a result of an analysis made in a more microscopic state space M. The quantities that appear in $\Phi^{(N_{\mathrm{driv}})}$ and are absent in $\Phi^{(N)}$ are b and $\Psi^{(N)}$. The former is introduced in the thermodynamic potential $\Phi^{(M)}$ and the latter in the dissipative slow time evolution in N.

Let the system under consideration be externally unforced. In this case the time evolution in N carries states in N to states in N_{ET}. We note that both $\Phi^{(N)}$ and $\Phi^{(N_{\mathrm{driv}})}$ imply the same thermodynamics in N_{ET}. The time evolu-

tion equation (22) with $\Phi^{(N)}$ replaced by $\Phi^{(N_{\mathrm{driv}})}$ is, however, different. We can regard it as a first approximation in N of the time evolution (35) introduced in M (analogously the Navier-Stokes-Fourier hydrodynamic equations can be regarded as a first approximation in the hydrodynamic state space of the Boltzmann kinetic equation—see [15]).

Let the system under consideration now be subjected to external forces (imposed chemical activity). In this case there is no more macroscopic state space approached as $t \to \infty$. The most macroscopic state space in which thermodynamics can be introduced is the state space N. The thermodynamics in N can be introduced only by analyzing the time evolution in a more macroscopic state space M. By following this route we have arrived at $\Phi^{(N_{\mathrm{driv}})}$, which specifies thermodynamics in N. What prevents us, at this point, from a detailed analysis of thermodynamics in N defined by $\Phi^{(N_{\mathrm{driv}})}$ and from a study of its relation to the slow time evolution in N [generated by Eq. (22)] is the lack of knowledge of $\Phi^{(M)}$. As we have noted in remark 1 of Sec. III, a particularly interesting problem would be a study the relationship between criticality of slow dynamics (e.g., an appearance of bifurcations or transition to chaos) and criticality of the geometric (thermodynamical) structure of N defined by $\Phi^{(N_{\mathrm{driv}})}$.

V. CONCLUSION

Let the starting point of our investigation of physical systems be an analysis of their time evolution in a state space M. Experimental observations of the time evolution in M are assumed to show that (i) there exists a subspace N of M to which the trajectories in M tend to settle as the time-evolution progresses and (ii) the approach of trajectories in M to trajectories in N is "regular" (i.e., it obeys the nonlinear Onsager-Casimir equation—see Sec. II). Thermodynamics is introduced as a geometry of N determined by the dynamics in M. This general formulation of thermodynamics includes as a special case the classical equilibrium thermodynamics (in this case N is the state space composed of time independent equilibrium states) and thermodynamics of driven systems (in this case N is composed of states that evolve in time in a slower pace).

We shall now comment about the experimental evidence for properties (i) and (ii) of the time evolution in M and about the usefulness of the above formulation of thermodynamics. In the case of externally unforced systems property (i) is the fundamental experimental observation on which equilibrium thermodynamics is based. Property (i) is verified both experimentally and theoretically for many particular cases. Moreover, if property (ii) is considered only in a small neighborhood of N, then it becomes equivalent to the result of Onsager [17]. In the case of driven systems, property (i) is also a well-known experimental observation. We recall that the time evolution of many, if not all, driven systems have been found to be well described in a state space (we call it N) that is not the state space used in completely microscopic analysis in which the systems are regarded as composed of atoms or molecules. It means that dynamics formulat-

ed in a state space that is more microscopic than N has to show an approach to N. Property (ii) has been shown to be verified for the case of Boltzmann kinetic equation (i.e., M is the state space composed of one-particle distribution functions) with N being the state space of hydrodynamics [15]. Due to the lack of detailed studies of particular cases of the approach of the fast to the slow time evolution, property (ii) remains, in the context of driven systems, a hypothesis (analogous, for example, to the Gibbs recipe remaining a hypothesis in the context of equilibrium statistical mechanics).

Regarding the usefulness (applications) of the general formulation of the thermodynamics introduced in this paper, we mention the use of the NOC equation in the formulation of dynamical theories (e.g., dynamical theories of complex fluids [12–15]) and in the analysis of driven systems. First, we explain the use of the NOC equation in the search for a dynamical theory. Let results of experimental observations of the time evolution of a class of physical systems (e.g., polymeric fluids—see [14,15]) be collected. We look for a dynamical theory whose predictions agree with the collected results. Since the structure of the NOC equation has been found to be common to a large class of divers dynamical theories, we begin our search by the hypothesis that the dynamical theory that we search will also possess the structure of the NOC equation. In other words, we look for a particular realization of the abstract NOC equation. This

means that we look for the Poisson operator L, the thermodynamic potential Φ, and the dissipative potential Ψ representing the particular physical systems and the particular situations under consideration. Since we can look for these three basic blocks of a dynamical theory separately, the range of available physical insights at our disposal is larger than if other methods of introducing theories are followed. Many worked out examples manifestly exhibiting advantages of the use of the NOC equation can be found in [12–16].

Finally, we comment about the use of the results of this paper in the analysis of driven systems. The classical analysis of driven systems is based on the analysis of dynamics in the state space N (i.e., on the analysis of the slow dynamics). In view of the results of this paper, the classical analysis can be supplemented by a thermodynamic analysis. The thermodynamic analysis is essentially an analysis of the driven system in a more microscopic state space M. The comparison of the time evolution in N and in M results in the introduction of the geometrical (thermodynamic) structure into the slow state space N.

ACKNOWLEDGMENT

[1] R. E. Sonntag and G. J. van Wylen, *Introduction to Thermodynamics* (Wiley, New York, 1991).

[2] *New Perspectives in Thermodynamics,* edited by J. Serrin (Springer, Berlin, 1986).

[3] D. Ruelle, *Thermodynamic Formalism: The Mathematical Structure of Classical Statistical Mechanics,* Encyclopedia of Mathematics and its Applications Vol. 5 (Cambridge University Press, Cambridge, 1984).

[4] J. W. Gibbs, *Collected Works* (Longmans Green, New York, 1978).

[5] L. Tisza, *Generalized Thermodynamics* (MIT Press, Cambridge, MA, 1966).

[6] H. B. Callen, *Thermodynamics* (Wiley, New York, 1960).

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

[8] P. Salamon, E. Ihring, and R. S. Berry, J. Math. Phys. **24**, 2515 (1983).

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

[10] P. Liberman and C. M. Marle, *Symplectic Geometry and Analytical Mechanics* (Reidel, Dordrecht, 1987).

[11] V. I. Arnold, *Les Méthodes Mathématiques de la Mécanique Classique* (MIR, Moscow, 1976).

[12] M. Grmela, Physica D **21**, 179 (1986).

[13] M. Grmela, J. Phys. A **22**, 4375 (1989).

[14] M. Grmela, in *Rheological Modeling: Thermodynamic and Statistical Approaches,* edited by J. Casas-Vazquez and D. Jou, Lecture Notes in Physics Vol. 381 (Springer, Berlin, 191), p. 99.

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

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

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

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

[19] J. E. Marsden and A. Weinstein, Physica D **4**, 394 (1982).

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

[21] J. W. Cahn, Acta Metall. **9**, 795 (1961).

[22] M. Grmela, R. Rosen, and L. S. Garcia-Colin, J. Chem. Phys. **75**, 5474 (1981).

[23] K. O. Friedrichs and P. D. Lax, Proc. Natl. Acad. Sci. U.S.A. **68**, 1686 (1971).

[24] M. S. Green, in *Cargese Lecture in Theoretical Physics,* edited by B. Jancovici (Gordon and Breach, London, 1966).

[25] M. Grmela, in *Hamiltonian Systems, Transformation Groups and Spectral Transform Methods,* edited by J. Harnad and J. E. Mardden (University of Montreal Press, Montreal, 1990).

[26] P. Bak, C. Tang, and K. Wiesenfeld, Phys. Rev. Lett. **59**, 381 (1987); Phys. Rev. A **38**, 264 (1988).

[27] D. N. Zubarev, *Nonequilibrium Statistical Mechanics* (Consultant Bureau, New York, 1974).

[28] *Maximum Entropy Formalism,* edited by R. D. Levin and M. Tribus (MIT Press, Cambridge, MA, 1979).

[29] J. L. del Rio-Correa and L. S. Garcia-Colin, Phys. Rev. A **43**, 6657 (1991).

[30] S. Lengyel, in *Flow, Diffusion and Rate Processes,* edited by S. Sieniutycz and P. Salamon (Taylor and Francis, London, 1992).

[31] S. R. de Groot and P. Mazur, *Non Equilibrium Thermo-*

dynamics (North-Holland, Amsterdam, 1962).

[32] L. S. Garcia-Colin, S. M. T. de la Selva, and E. Pina, Phys. Lett. A **110**, 363 (1985).

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

[34] G. Lebon, M. Torrisi, and A. Valenti, J. Phys. Chem. **91**, 5103 (1987).

[35] D. Jou, J. Casas-Vazquez, and G. Lebon, Rep. Prog. Phys. **51**, 105 (1988).