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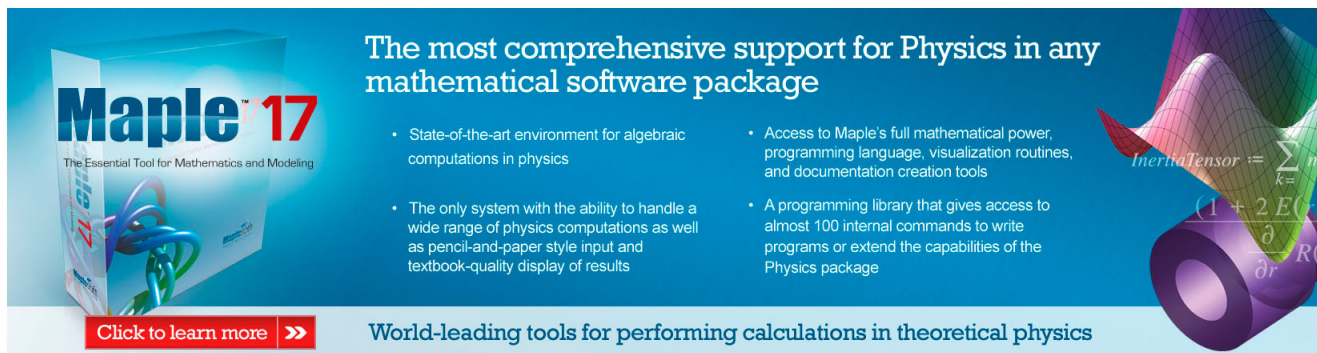
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## On the mathematical structure of thermodynamics

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A mathematically exact dynamical theory of classical thermodynamics of homogeneous bodies is presented in which processes are time-dependent functions, governed by an ordinary differential equation. The fundamental objects of the mathematical structure of a thermodynamical system are the dynamical law, the thermodynamical force, and the constraints; all the other usual notions, too, such as substances, bodies, linear approximation by Onsager, etc. have got a mathematical definition. Equilibria are the constant processes; their stability is investigated by Lyapunov's method. © 2000 American Institute of Physics.  
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### I. INTRODUCTION

Classical mechanics is based on the Newtonian equation and constraints that define the processes unambiguously; then classical mechanics becomes an elegant mathematical theory by the use of contact or symplectic manifolds. Quantum mechanics is based on the Schrödinger equation that defines the processes unambiguously; Hilbert spaces or  $C^*$  algebras offer a complete mathematical formulation of quantum mechanics. Classical electrodynamics is based on the Maxwell equations that define processes unambiguously; differential forms on manifolds admit a nice mathematical formulation of classical electrodynamics. Continuum (irreversible) thermodynamics is based on the balance equations, partial differential equations that define processes unambiguously by boundary conditions and initial values.<sup>1-5</sup>

All these theories are mathematically well defined and have a clear mathematical structure; the physical notions have an exact mathematical definition.

Classical (equilibrium) thermodynamics is a theory to which—at present—no clear mathematical structure is assigned and many physical notions are intuitive ones without a mathematical definition, e.g., equilibrium, processes, reversible, irreversible, quasistatic, trend to equilibrium. It is well known how intuitive notions can mislead us (Richard paradox<sup>6</sup>), which can be demonstrated by an excellent example taken from thermodynamics, too. In usual treatments of thermodynamics one “proves” that the Kelvin–Planck formulation and the Clausius formulation of the second law are equivalent;<sup>7</sup> a rigorous mathematical examination shows, however, that the Kelvin–Planck formulation follows at once if the heating has an integrating factor and thus does not necessarily presume or imply thermodynamic axioms of any kind.<sup>8</sup>

Several attempts have been made for a mathematically correct theory of thermodynamics, starting from different points of view.<sup>9-13</sup> Though some relations have been clarified and obtained an elegant form, the whole theory cannot be treated in those ways satisfactorily. The reason is the following. The physical theories enumerated above—in particular, continuum thermodynamics—are *dynamical theories*: they describe what will happen under given circumstances. On the contrary, in spite of its name, classical thermodynamics—either in its usual treatments or in the mentioned mathematical approaches—does not involve dynamics.

In order to have a satisfactory formulation and to find a convenient mathematical structure of thermodynamics, we must establish a dynamical theory in which processes are described by a differential equation. We know that the Onsager formalism describes nonequilibrium processes

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near equilibria and the relation between forces and fluxes outlines a strong mathematical structure. However, the Onsager formalism is only a linear approximation, and the approximation procedure is not well clarified from a mathematical point of view.

Recently a nonlinear theory has been proposed,<sup>14–19</sup> called *ordinary thermodynamics*, in which the fundamental notion is the process governed by an ordinary differential equation called the dynamical law; thus processes, solutions of the dynamical equation, are functions in time. Equilibria are constant processes. The well-defined linear approximation of the dynamical law gives the usual Onsager formalism in special cases.

To clarify the physical meaning of ordinary thermodynamics, we make the following comments; further details can be found in Ref. 14.

Let us consider a continuous medium consisting of identical, spinless, chargeless particles. A process of such a medium is the field  $(\mathbf{u}, e, v)$ , the velocity, the specific internal energy, and the specific volume as functions defined in space–time. If the body force and the body heating are taken to be zero, then the balances of momentum, energy, and mass yield the partial differential equations,

$$D_u \mathbf{u} = -v \nabla \cdot \mathbf{P},$$

$$D_u e = -v(\nabla \cdot \mathbf{k} + \mathbf{P} : \nabla \mathbf{u}),$$

$$D_u v = v \nabla \cdot \mathbf{u},$$

where  $D_u$  denotes the “substantial time derivative” with respect to the velocity field  $\mathbf{u}$ ,  $\mathbf{k}$  and  $\mathbf{P}$  are the heating flux and the pressure tensor, respectively, given by constitutive relations as functionals of  $(\mathbf{u}, e, v)$ .

The process  $(\mathbf{u}, e, v)$  can be determined, at least in theory, from initial and boundary values by these balance equations that form a complete dynamical law.

In ordinary thermodynamics we consider the bodies as homogeneous i.e., all quantities depend only on time, not on space. Let us insert the conditions  $\nabla \mathbf{u} = 0, \nabla e = 0, \nabla v = 0, \nabla \mathbf{k} = 0, \nabla \mathbf{P} = 0$  into the equations of continuum thermodynamics; we find that the quantities do not depend on time either, that is, nothing happens. There is no nonconstant homogeneous process. *Ordinary thermodynamics cannot be obtained from continuum thermodynamics as a special case.* Perhaps one could even say then that the theory of homogeneous bodies is meaningless, because it is an experimental fact as well that bodies out of equilibrium are never homogeneous; for example, the temperature of a cooling body is always lower on the surface than in the interior of the body. However, we know as well that a rigid body does not exist: all bodies are deformed under forces; still, certain bodies in certain circumstances can be considered as rigid. The rigid body model is simple, much simpler than the model of deformable bodies, and it is suitable for many purposes. Similarly, ordinary thermodynamics offers simpler models than continuum thermodynamics and they are applicable for a large class of phenomena. The theory of ordinary thermodynamics gives a good approximation when the inner motion of the bodies is insignificant, and it has the advantage that we can use ordinary differential equations that are much simpler than partial differential equations. Of course, the homogeneous model is rougher than the continuum model; however, it derives results in several questions where the continuum theory seems useless because of its complexity.

A similar point of view is accepted in the theory of chemical reactions that are mostly described by ordinary differential equations<sup>20,21</sup> as if the materials in chemical reactions were homogeneous though, evidently, they are far from being homogeneous. Nevertheless, a lot of basic features of chemical reactions are well reflected in such a description. Some other properties, of course, can be deduced only from a continuum theory.<sup>22</sup> Then comparing the results we can see clearly where the inhomogeneity plays a fundamental role. In reaction kinetics the differential equations concern only the concentrations, that is, only the concentrations are considered as dynamic variables; thermodynamical properties of reactions are taken into account in another way.

The theory of chemical reactions in ordinary thermodynamics involves the dynamical description of all thermodynamical quantities, so it is an extension of usual reaction kinetics.

Ordinary thermodynamics was formulated and applied in Refs. 14–18 to particular systems of homogeneous bodies (one body in an environment, interacting bodies, phase transitions). Now a general mathematical framework will be given and investigated for systems consisting of single-component bodies. Sections II and III are devoted to the basic notions; Definition 5 includes all the special systems considered in the earlier papers and can be applied for diffusion processes as well that have not yet been treated. The thorough examination of thermodynamic forces leads us to the conclusion that we have to make a clear distinction between nominal forces and effective forces, and suggests how we have to formalize constraints, which is one of the main results of the present paper. In Sec. IV, we present the abstract mathematical structure of ordinary thermodynamics, which can be summarized briefly as follows. There are given an open subset of a vector space (the set of states); a covector field on the set of states (the nominal thermodynamical force); a vector field on the set of states (the dynamical quantities), satisfying some conditions, the most important of which is the dissipative property; and a subspace field on the set of states (the constraint).

The effective thermodynamical force is the restriction of the nominal force onto the constraint subspaces; the dynamical quantities determine the dynamical law, a differential equation whose solutions are the processes. The fundamental properties of this structure are demonstrated in Sec. IV. In Sec. V general theorems on the stability of equilibria are proved.

## II. SUBSTANCES, PHASES, BODIES

Let us recapitulate the most important notions and results indispensable for the mathematical treatment.

To have a mathematically exact and unambiguous formulation, we shall take into account the “physical dimension” of the quantities that will be measured in SI units. For instance, the values of energy are real multiples of  $J = \text{Joule}$ , i.e., they are elements of

$$(J) := \{\alpha J \mid \alpha \in \mathbb{R}\}.$$

Similarly, we shall use the notations  $(m^3)^+$ ,  $(K)^+$  for the (positive) values of volume, temperature, etc. An exact mathematical meaning can be given<sup>23</sup> to the product and quotient of units of measurements (e.g., to  $J/K$ ).

For the sake of perspicuity, here we shall consider the mathematical description of single-component materials. A generalization to multicomponent materials is straightforward from a conceptual point of view (but its composition is more complicated).

The attribute “specific” will mean “per particle” (molecule).

*Definition 1:* A single-component substance is a quintet  $(D, \mathbf{T}, \mathbf{P}, \boldsymbol{\mu}, R)$ , where

(i)  $D$ , called the *constitutive domain*, is a nonvoid subset of  $(J)^+ \times (m^3)^+$ ; the first and second variables in  $D$  (usually denoted by  $e$  and  $v$ , respectively), are the *specific internal energy* and the *specific volume*, respectively; the elements of  $D$  are called *states* of the substance;

(ii)  $\mathbf{T}: D \rightarrow (K)^+$ , the *temperature*,  $\mathbf{P}: D \rightarrow (\text{Pa})$ , the *pressure*,  $\boldsymbol{\mu}: D \rightarrow (J)$ , the *chemical potential*, the *constitutive functions*, are continuous.

(iii)  $R$ , the *regular constitutive domain*, the subset of  $D$  on which the constitutive functions are continuously differentiable and

$$\frac{\partial \mathbf{T}}{\partial e} > 0, \quad \frac{\partial \mathbf{P}}{\partial v} \frac{\partial \mathbf{T}}{\partial e} - \frac{\partial \mathbf{P}}{\partial e} \frac{\partial \mathbf{T}}{\partial v} < 0, \tag{1}$$

holds is an open set dense in  $D$ .

*Definition 2:* Let  $(D, \mathbf{T}, \mathbf{P}, \boldsymbol{\mu}, R)$  be a single-component substance. Then

$$s: D \rightarrow (J/K), \quad (e, v) \mapsto \frac{e + \mathbf{P}(e, v)v - \boldsymbol{\mu}(e, v)}{\mathbf{T}(e, v)} \tag{2}$$

is the *specific entropy*. The substance is called *entropic* if  $Ds = (1/T, P/T)$  on the regular domain. Here and in the following  $D$  denotes the derivative of functions.

Note that if the substance is entropic then the specific entropy is twice continuously differentiable on the regular domain and its second derivative is negative-definite.

*Definition 3:* A *phase* of a single-component substance  $(D, T, P, \mu, R)$  is a connected open subset  $Z$  of  $R$  such that (i)  $(T, P)$  is injective on  $Z$ .

(ii)  $Z$  is maximal with this property (i.e., if  $N$  is a connected open subset of  $R$  containing  $Z$  and  $(T, P)$  is injective on  $N$ , then  $N = Z$ ).

*Proposition 1:* Every point of the regular domain is in a phase.<sup>24</sup>

The injectivity of  $(T, P)$  in a phase implies that there the specific internal energy and the specific volume can be given as functions of temperature and pressure. In particular, to every phase  $Z$  we can define the chemical potential of the phase by

$$\mu_Z := \mu^\circ((T, P)|_Z)^{-1}. \tag{3}$$

The phase connections (“transitions”) have been examined and classified in Ref. 17.

A body means a certain amount of a substance: the triplet of variables  $(e, v, N)$  describes a body where  $(e, v)$  is an element of the constitutive domain and  $N$  is the particle number, an arbitrary positive number.

*Definition 4:* A *body* consisting of a single-component substance  $(D, T, P, \mu, R)$  is  $(D \times \mathbb{R}^+, T, P, \mu, R)$ ; the elements of  $D \times \mathbb{R}^+$  are called the *states* of the body.

It turns out that the description of processes of bodies in which mass varies will be simpler if instead of the variables  $e$  and  $v$  we use the *total internal energy*  $E$  and the *total volume*,  $V$ , respectively. More precisely, we establish the smooth bijection,

$$\begin{aligned} (J)^+ \times (m^3) \times \mathbb{R}^+ &\rightarrow (J)^+ \times (m^3)^+ \times \mathbb{R}^+, \\ (e, v, N) &\mapsto (Ne, Nv, N) =: (E, V, N), \end{aligned}$$

whose inverse,

$$(E, V, N) \mapsto (E/N, V/N, N),$$

is smooth as well.

We find convenient to introduce the notation

$$\mathbb{R}^+ * H := \{(Ne, Nv, N) | (e, v) \in H, N \in \mathbb{R}^+\}, \tag{4}$$

for an arbitrary subset  $H$  of  $D$ .

Using the variables  $(E, V, N)$ , we define

$$\hat{\mathbf{T}}(E, V, N) := \mathbf{T}(E/N, V/N), \tag{5}$$

and similar expressions for  $\hat{\mathbf{P}}$  and  $\hat{\boldsymbol{\mu}}$  as well. For the sake of brevity and perspicuity, an abuse of notations will be applied further on: the simple symbol  $\mathbf{T}$ , etc. will be written instead of  $\hat{\mathbf{T}}$ , etc., i.e., two different functions will be denoted by the same letter. Then we easily derive that

$$\frac{\partial \mathbf{T}}{\partial E} = \frac{1}{N} \frac{\partial \mathbf{T}}{\partial e}, \quad \frac{\partial \mathbf{T}}{\partial V} = \frac{1}{N} \frac{\partial \mathbf{T}}{\partial v}, \tag{6}$$

holds on  $\mathbb{R}^+ * R$ , where, according to the previously accepted abuse of notations, it is understood that the variables on the left-hand side and on the right-hand side are  $(E, V, N)$  and  $(e, v) = (E/N, V/N)$ , respectively. Moreover, we have

$$\frac{\partial \mathbf{T}}{\partial N} = -\frac{E}{N} \frac{\partial \mathbf{T}}{\partial E} - \frac{V}{N} \frac{\partial \mathbf{T}}{\partial V}, \tag{7}$$

and similar formulas for  $\mathbf{P}$  and  $\boldsymbol{\mu}$  as well.

For the *total entropy*,

$$\mathbf{S}(E, V, N) := N\mathbf{s}(E/N, V/N), \tag{8}$$

we get the usual equalities if the substance is entropic:

$$\frac{\partial \mathbf{S}}{\partial E} = \frac{1}{\mathbf{T}}, \quad \frac{\partial \mathbf{S}}{\partial V} = \frac{\mathbf{P}}{\mathbf{T}}, \quad \frac{\partial \mathbf{S}}{\partial N} = -\frac{\boldsymbol{\mu}}{\mathbf{T}}. \tag{9}$$

Then the second derivative of the total entropy is

$$D^2\mathbf{S} = -\frac{1}{\mathbf{T}^2} \begin{pmatrix} \frac{\partial \mathbf{T}}{\partial E} & \frac{\partial \mathbf{T}}{\partial V} & \frac{\partial \mathbf{T}}{\partial N} \\ \mathbf{P} \frac{\partial \mathbf{T}}{\partial E} - \mathbf{T} \frac{\partial \mathbf{P}}{\partial E} & \mathbf{P} \frac{\partial \mathbf{T}}{\partial V} - \mathbf{T} \frac{\partial \mathbf{P}}{\partial V} & \mathbf{P} \frac{\partial \mathbf{T}}{\partial N} - \mathbf{T} \frac{\partial \mathbf{P}}{\partial N} \\ -\boldsymbol{\mu} \frac{\partial \mathbf{T}}{\partial E} + \mathbf{T} \frac{\partial \boldsymbol{\mu}}{\partial E} & -\boldsymbol{\mu} \frac{\partial \mathbf{T}}{\partial V} + \mathbf{T} \frac{\partial \boldsymbol{\mu}}{\partial V} & -\boldsymbol{\mu} \frac{\partial \mathbf{T}}{\partial N} + \mathbf{T} \frac{\partial \boldsymbol{\mu}}{\partial N} \end{pmatrix}. \tag{10}$$

*Proposition 2:*  $D^2\mathbf{S}(E, V, N)$  is negative semidefinite for all  $(E, V, N) \in \mathbb{R}^+ * \mathbb{R}$ , having a one-dimensional kernel spanned by  $(E, V, N)$ .

As usual, we call energy, volume, and mass the *extensive variables*, temperature, pressure, and chemical potential the *intensive variables*.

### III. AN OUTLINE OF ORDINARY THERMODYNAMICS

#### A. Heuristic considerations

In this paragraph we use rather loose notations.

The state of a body is the triplet  $(E, V, N)$ ; a process of a body is a function that assigns states to instants:  $t \mapsto (E(t), V(t), N(t))$ . We assume that the domain of a process is a time interval.

The first law of thermodynamics is expressed in the form

$$\dot{E} = Q + W + L,$$

where  $Q$  is the *heating*,  $W$  is the *working*, and  $L$  is the *transferring*; this last quantity expresses the energy change of the body due to the particle change. The quantities on the right-hand side of the equation are time rates, thus, e.g., the heating is the heat per unit time; working is the work per unit time.

We shall deal with the ideal case only, i.e., when

$$W = -P\dot{V}, \quad L = \mu\dot{N}.$$

The first law is conceived as a differential equation. Of course, this single equation is not sufficient to determine processes consisting of three functions. Therefore we suppose that we have equations for the time change of  $V$  and  $N$  as well:

$$\dot{V} = F, \quad \dot{N} = G,$$

where  $F$  and  $G$  are called the *springing* and the *converting*, respectively. The quantities  $Q$ ,  $W$ ,  $L$ ,  $F$ , and  $G$  are supposed to be given as functions of the state  $(E, V, N)$ ; so we have a complete set of differential equations.

If  $n \geq 2$  bodies interact, then a process of the system of interacting bodies is the joint of the processes of the bodies:  $t \rightarrow ((E_i(t), V_i(t), N_i(t)) | i = 1, \dots, n)$ .

The processes are supposed to be governed by a system of differential equations,

$$\begin{aligned} \dot{E}_i &= Q_i + W_i + L_i, & \dot{V}_i &= F_i & \dot{N}_i &= G_i, \\ (W_i &= -P_i F_i, & L_i &= \mu_i G_i, & i &= 1, \dots, n), \end{aligned}$$

called the *dynamical law*, where the  $i$ th heating  $Q_i$ , etc. are given as functions of the states. Later we examine the properties of these functions.

The bodies can be in contact with an environment, which may be thought as an ‘‘infinitely large’’ body whose process is prefixed (e.g., its temperature and pressure is constant), whose state does not change in the interaction (i.e., the environment acts on the bodies, the bodies do not act on the environment). This means that the environment is always characterized by its given temperature  $T_a$ , pressure  $P_a$ , and chemical potential  $\mu_a$ , which can vary with time.

The heating of a body consists of the heatings from the other bodies and from the environment, so

$$Q_i = \sum_{k=0}^n Q_{ik},$$

where the subscript 0 refers to the environment. Similarly, we have

$$\begin{aligned} F_i &= \sum_{k=0}^n F_{ik}, & G_i &= \sum_{k=0}^n G_{ik}, \\ W_i &= \sum_{k=0}^n W_{ik}, & L_i &= \sum_{k=0}^n L_{ik}. \end{aligned}$$

It is convenient to introduce the notation

$$A_{ik} := Q_{ik} + W_{ik} + L_{ik}, \quad A_i := \sum_{k=0}^n A_{ik}.$$

$Q_{ik}$ , etc. are called the *system constitutive functions* or the *dynamical quantities*.

Evidently, the particle number passed from the  $i$ th body to the  $k$ th body is the opposite to the particle number passed from the  $k$ th body to the  $i$ th body, and a similar statement is true for the energy change and volume change of the  $i$ th body due to the  $k$ th body. Thus we accept—roughly—that  $A_{ik} = -A_{ki}$ ,  $F_{ik} = -F_{ki}$ ,  $G_{ik} = -G_{ki}$ . The exact formulation of these requirements will be given later.

We underline that the heatings need not have the above property, which is a well-known fact in classical thermodynamics: the ‘‘noncompensated heating’’  $Q_{ik} + Q_{ki}$  is not necessarily zero. A similar remark is valid for workings and transferrings.

It is reasonable to suppose (as it is done in mechanics, too) that the interaction of two bodies can be characterized by the properties of the two bodies only, which means that the dynamical quantities between two bodies depend only on the states (i.e., on the extensive variables) of the two bodies. Moreover, according to our experience, we accept that the dynamical quantities depend on the extensive variables through the intensive variables and the particle numbers. Since the intensive variables do not characterize the state (the same intensive values can belong to different states in different phases), the dynamical quantities depend on phases, too, which corre-

sponds to a trivial experimental fact: the heat conduction at a given temperature and pressure between two ice bodies is different from that between two water bodies.

The second law must be reflected in the properties of the dynamical quantities. The dissipative inequality (Clausius–Duhem inequality) in nonequilibrium thermodynamics expresses the second law (positive entropy production); an analogon of this exact relation can be well defined in ordinary thermodynamics, too.<sup>25</sup>

### B. Thermodynamical systems

On the base of the heuristic considerations of the previous paragraph we can formulate an exact definition.

*Definition 5:* Let  $n$  be a given positive integer. A *thermodynamical system* of  $n$  bodies in a given environment consists of the following.

(1) A family of simple substances,  $(D_i, \mathbf{T}_i, \mathbf{P}_i, \boldsymbol{\mu}_i, R_i)$  ( $i=0, \dots, n$ ); the zeroth substance is called the environment; the body corresponding to the  $i$ th substance is called the  $i$ th body of the system.

(2) A given phase  $Z_0$  of the environment, and the given temperature and pressure of the environment, as a continuous function defined on a time interval:  $t \rightarrow (T_a(t), P_a(t)) \in (\mathbf{T}_0, \mathbf{P}_0)$  [ $Z_0$ ].

(3) The *dynamical quantities*, given for all phases  $Z_i$  and  $Z_k$  of the  $i$ th and the  $k$ th body ( $i, k=0, 1, \dots, n$ ), respectively,

$$\mathbf{Q}_{Z_i Z_k}: \Phi_i \times \Phi_k \rightarrow (J/s), \quad \mathbf{F}_{Z_i Z_k}: \Phi_i \times \Phi_k \rightarrow (m^3/s), \quad \mathbf{G}_{Z_i Z_k}: \Phi_i \times \Phi_k \rightarrow (1/s), \quad (11)$$

where

$$\Phi_i := (\mathbf{T}_i, \mathbf{P}_i) [\bar{Z}_i \cap D_i] \times \mathbb{R}^+; \quad (12)$$

these functions are continuous; moreover, they are continuously differentiable on the interior of their domain.

The dynamical quantities satisfy for all  $i, k=0, 1, \dots, n$ .

(i) The *compatibility property*:  $\mathbf{Q}_{Z_i, Z_k}$  and  $\mathbf{Q}_{Z'_i Z'_k}$ , etc. are equal on the intersection of their domain for all phases  $Z_i, Z'_i$  and  $Z_k, Z'_k$ ; furthermore, with the notations

$$\begin{aligned} \mathbf{W}_{Z_i Z_k}(T_i, P_i, N_i, T_k, P_k, N_k) &:= -P_i \mathbf{F}_{Z_i Z_k}(T_i, P_i, N_i, T_k, P_k, N_k), \\ \mathbf{L}_{Z_i Z_k} &:= (T_i, P_i, N_i, T_k, P_k, N_k) := \mu_{Z_i}(T_i, P_i) G_{ik}(T_i, P_i, N_i, T_k, P_k, N_k), \\ \mathbf{A}_{Z_i Z_k} &:= \mathbf{Q}_{Z_i Z_k} + \mathbf{W}_{Z_i Z_k} + \mathbf{L}_{Z_i Z_k}, \end{aligned}$$

and then (for the sake of brevity) with the subscripts  $ik$  instead of  $Z_i Z_k$  and

$$[i, k] := (T_i, P_i, N_i, T_k, P_k, N_k) \in \Phi_i \times \Phi_k,$$

the dynamical quantities satisfy the following.

(ii) The *mutuality property*,

$$\mathbf{A}_{ik}([i, k]) = -\mathbf{A}_{ki}([k, i]), \quad \mathbf{F}_{ik}([i, k]) = -\mathbf{F}_{ki}([k, i]), \quad \mathbf{G}_{ik}([i, k]) = -\mathbf{G}_{ki}([k, i]). \quad (13)$$

(iii) The *dissipative property*:

$$-\frac{\mathbf{Q}_{ik}([i, k])}{T_i} (T_i - T_k) - \frac{\mathbf{W}_{ik}([i, k])}{P_i} (P_i - P_k) - \frac{\mathbf{L}_{ik}([i, k])}{\mu_i(T_i, P_i)} (\mu_i(T_i, P_i) - \mu_k(T_k, P_k)) \geq 0, \quad (14)$$



where equality holds if and only if  $\mathbf{Q}_{ik}([i,k])=0$ ,  $\mathbf{W}_{ik}([i,k])=0$ ,  $\mathbf{L}_{ik}([i,k])=0$ ; this inequality can be rewritten in the form

$$\mathbf{A}_{ik}([i,k])\left(\frac{1}{T_i} - \frac{1}{T_k}\right) + \mathbf{F}_{ik}([i,k])\left(\frac{P_i}{T_i} - \frac{P_k}{T_k}\right) + \mathbf{G}_{ik}([i,k])\left(\frac{-\mu_i(T_i, P_i)}{T_i} + \frac{\mu_k(T_k, P_k)}{T_k}\right) \geq 0, \tag{15}$$

where equality holds if and only if  $\mathbf{A}_{ik}([i,k])=0$ ,  $\mathbf{F}_{ik}([i,k])=0$ ,  $\mathbf{G}_{ik}([i,k])=0$ .

(4) The dynamical law,

$$\dot{E}_i = Q_i + W_i + L_i \quad \dot{V}_i = F_i, \quad \dot{N}_i = G_i \quad (i = 1, \dots, n), \tag{16}$$

where

$$Q_i = \sum_{k=0}^n Q_{ik}, \quad W_i = \sum_{k=0}^n W_{ik}, \quad L_i = \sum_{k=0}^n L_{ik},$$

$$F_i = \sum_{k=0}^n F_{ik}, \quad G_i = \sum_{k=0}^n G_{ik},$$

and

$$Q_{ik} := \mathbf{Q}_{Z_i Z_k}(T_i(E_i, V_i, N_i), \mathbf{P}_i(E_i, V_i, N_i), N_i, \mathbf{T}_k(E_k, V_k, N_k), \mathbf{P}_k(E_k, V_k, N_k), N_k),$$

if  $k \neq 0$  and

$$Q_{i0} := \mathbf{Q}_{Z_i Z_0}(\mathbf{T}_i(E_i, V_i, N_i), \mathbf{P}_i(E_i, V_i, N_i), N_i, T_a, P_a, N_0),$$

etc., where  $Z_i$  and  $Z_k$  are the phases whose closure contains  $(E_i/N_i, V_i/N_i)$  and  $(E_k/N_k, V_k/N_k)$ , respectively.

*Remarks:* The dynamical quantities with subscripts  $0i$  do not appear in the dynamical law, thus they are superfluous; we involved them only for an economic formulation. If the dynamical quantities with subscripts  $i0$  are given, putting  $\mathbf{Q}_{Z_0 Z_i}([0],[i]) := -\mathbf{Q}_{Z_i Z_0}([i],[0])$ , etc. we make all the requirements satisfied.

The particle number  $N_0$  of the environment is irrelevant to the interaction (the environment is ‘‘infinitely large’’), the dynamical quantities do not depend on  $N_0$ ; it is involved as a dummy variable only for an economic formulation.

The dynamical quantities with subscripts  $ii$  are zero by the mutuality property.

The condition imposed on the equality in the dissipative property is a strong requirement for the dynamical quantities, because equality holds evidently if  $T_i = T_k$ ,  $P_i = P_k$ , and  $\mu_i(T_i, P_i) = \mu_k(T_k, P_k)$ , so these relations must imply that the dynamical quantities take the zero value.

Since all the bodies are supposed to be single component, it is understood that if  $\mathbf{G}_{Z_i Z_k} \neq 0$  then the substance of the  $i$ th body coincides with that of the  $k$ th body.

*Definition 6:* A constant solution of the dynamical law—i.e., a state at which the right-hand side of the dynamical law takes a zero value—is called a *standstill*. A standstill is an *equilibrium* if all the dynamical quantities take a zero value at the corresponding state.

*Proposition 3:* If at least one of the dynamical quantities does depend on the process of the environment, then standstill can exist only if the process of the environment is constant.

### C. Thermodynamical forces and the conductivity matrix

For the sake of brevity, in the following the subscripts  $Z_i Z_k$  will be substituted by  $ik$ .

The coefficients of the dynamical quantities in the dissipative inequality (15) are known as the thermodynamical forces; more precisely, we accept the following definition.

Definition 7: The function

$$\left( \frac{1}{\mathbf{T}_i} - \frac{1}{\mathbf{T}_k}, \frac{\mathbf{P}_i}{\mathbf{T}_i} - \frac{\mathbf{P}_k}{\mathbf{T}_k}, -\frac{\boldsymbol{\mu}_i}{\mathbf{T}_i} + \frac{\boldsymbol{\mu}_k}{\mathbf{T}_k} \right) : D_i \times D_k \rightarrow (1/K)^+ \times (Pa/K) \times (J/K),$$

is called the *thermodynamical force* between the *i*th and *k*th body.

Definition 8: The dynamical quantities  $\mathbf{Q}_{ik}, \mathbf{F}_{ik}, \mathbf{G}_{ik}$  are called *quasilinear* if

$$\begin{pmatrix} \mathbf{Q}_{ik} \\ \mathbf{F}_{ik} \\ \mathbf{G}_{ik} \end{pmatrix} = \begin{pmatrix} \lambda_{ik} & \kappa_{ik} & \vartheta_{ik} \\ \alpha_{ik} & \beta_{ik} & \gamma_{ik} \\ \rho_{ik} & \sigma_{ik} & \varphi_{ik} \end{pmatrix} \begin{pmatrix} \frac{1}{T_i} - \frac{1}{T_k} \\ \frac{P_i}{T_i} - \frac{P_k}{T_k} \\ -\frac{\mu_i(T_i, P_i)}{T_i} + \frac{\mu_k(T_k, P_k)}{T_k} \end{pmatrix}, \tag{17}$$

where  $\lambda_{ik}$ , etc. are continuous function defined on  $\Phi_i \times \Phi_k$ . Equivalently,

$$\begin{pmatrix} \mathbf{A}_{ik} \\ \mathbf{F}_{ik} \\ \mathbf{G}_{ik} \end{pmatrix} = \begin{pmatrix} \tilde{\lambda}_{ik} & \tilde{\kappa}_{ik} & \tilde{\vartheta}_{ik} \\ \alpha_{ik} & \beta_{ik} & \gamma_{ik} \\ \rho_{ik} & \sigma_{ik} & \varphi_{ik} \end{pmatrix} \begin{pmatrix} \frac{1}{T_i} - \frac{1}{T_k} \\ \frac{P_i}{T_i} - \frac{P_k}{T_k} \\ -\frac{\mu_i(T_i, P_i)}{T_i} + \frac{\mu_k(T_k, P_k)}{T_k} \end{pmatrix}, \tag{18}$$

where

$$\tilde{\lambda}_{ik} := \lambda_{ik} - P_i \alpha_{ik} + \mu_i \rho_{ik}, \quad \tilde{\kappa}_{ik} := \kappa_{ik} - P_i \beta_{ik} + \mu_i \sigma_{ik}, \quad \tilde{\vartheta}_{ik} := \vartheta_{ik} - P_i \gamma_{ik} + \mu_i \varphi_{ik}.$$

The matrix vector on the right-hand side of equality (18) is called the *conductivity matrix* between the *i*th and the *k*th body.

Note that the conductivity matrix is, in fact, a matrix-valued function. It is a simple fact that the conductivity matrix is not uniquely defined. To see this, it suffices to show that

$$\begin{pmatrix} \tilde{\lambda} & \tilde{\kappa} & \tilde{\vartheta} \\ \alpha & \beta & \gamma \\ \rho & \sigma & \varphi \end{pmatrix} \begin{pmatrix} \frac{1}{T_i} - \frac{1}{T_k} \\ \frac{P_i}{T_i} - \frac{P_k}{T_k} \\ -\frac{\mu_i(T_i, P_i)}{T_i} + \frac{\mu_k(T_k, P_k)}{T_k} \end{pmatrix} = 0, \tag{19}$$

can hold if the matrix above—which represents the difference of two conductivity matrices—is not zero. This is the case, for example, if  $\tilde{\lambda} := P_i/T_i - P_k/T_k$ ,  $\tilde{\kappa} := -1/T_i + 1/T_k$ , and the other entries are zero.

Of course, if the conductivity matrix is constant then it is uniquely determined.

Proposition 4: Suppose (19) holds and the bodies are entropic; if  $\mu_i(T, P) = \mu_k(T, P)$ , then we have

$$\tilde{\lambda}(T, P, N_i, T, P, N_k) + \tilde{\kappa}(T, P, N_i, T, P, N_k)P + \tilde{\vartheta}(T, P, N_i, T, P, N_k)(\mu_i(T, P) + Ts_i(T, P)) = 0,$$

$$\alpha(T, P, N_i, T, P, N_k) + \beta(T, P, N_i, T, P, N_k)P + \gamma(T, P, N_i, T, P, N_k)(\mu_i(T, P) + Ts_i(T, P)) = 0,$$

$$\begin{aligned} \rho(T,P,N_i,T,P,N_k) + \sigma(T,P,N_i,T,P,N_k) + \varphi(T,P,N_i,T,P,N_k)(\mu_i(T,P) + \mathbf{s}_i(T,P)T) &= 0, \\ \tilde{\kappa}(T,P,N_i,T,P,N_k) - \tilde{\vartheta}(T,P,N_i,T,P,N_k)\mathbf{v}_i(T,P) &= 0, \\ \beta(T,P,N_i,T,P,N_k) - \gamma(T,P,N_i,T,P,N_k)\mathbf{v}_i(T,P) &= 0, \\ \sigma(T,P,N_i,T,P,N_k) - \varphi(T,P,N_i,T,P,N_k)\mathbf{v}_i(T,P) &= 0, \end{aligned}$$

where  $\mathbf{s}_i$  and  $\mathbf{v}_i$  are the specific entropy and the specific volume of the  $i$ th body as a function of temperature and pressure in the corresponding phase.

*Proof:* Let  $P := P_i := P_k, T := T_k \neq T_i$ , divide (19) by  $T_i - T$ , and take the limit  $T_i \rightarrow T$ . According to our hypothesis  $\mu_i(T,P) = \mu_k(T,P)$  and to the Gibbs–Duhem relations, we have

$$\lim_{T_i \rightarrow T} \frac{\mu_i(T_i,P) - \mu_k(T,P)}{T_i - T} = -\mathbf{s}_i(T,P),$$

from which we infer the first three equalities. The further ones follow from  $T := T_i := T_k, P := P_k \neq P_i$ , and

$$\lim_{P_i \rightarrow P} \frac{\mu_i(T,P_i) - \mu_k(T,P)}{P_i - P} = \mathbf{v}_i(T,P).$$

□

The elements  $(T,P,N_i,T,P,N_k) \in \Phi_i \times \Phi_k$  for which  $\mu_i(T,P) = \mu_k(T,P)$  holds will be called *central*.

We see that if the bodies cannot change particles—i.e.,  $\tilde{\vartheta} = 0, \gamma = 0, \rho = 0, \sigma = 0, \varphi = 0$ —then the values of the conductivity matrix are uniquely defined at the central values; otherwise they are not.

*Definition 9:* The conductivity matrix between the  $i$ th and  $k$ th body is (1) strictly Onsagerian if it is constant and symmetric, (2) Onsagerian if its every value is symmetric, (3) weakly Onsagerian if its values at central elements are symmetric.

Usually one considers strictly Onsagerian conductivity matrices; however, the Onsagerian formalism is said to be a linear approximation around equilibrium, so the usual Onsager matrix corresponds to a value of our conductivity matrix at a central element. Thus, the usual formalism corresponds, in fact, to the weakly Onsagerian case.

It is a remarkable result<sup>26</sup> that if a twice continuously differentiable conductivity matrix is weakly Onsagerian then—using its nonuniqueness—we can take it to be symmetric in a neighborhood of the central values.

#### IV. GENERAL MATHEMATICAL FORMULAS

##### A. The dynamical law and the nominal thermodynamical force

A state of a system consisting of  $n$  bodies,

$$x := (x_i := (E_i, V_i, N_i) | i = 1, \dots, n), \tag{20}$$

is in

$$X_D := \prod_{i=1}^n (\mathbb{R}^+ * D_i), \tag{21}$$

which is a subset of the vector space,

$$X := ((J) \times (m^3) \times \mathbb{R})^n. \tag{22}$$

Now we find it convenient to consider  $kT$  instead of the temperature  $T$ , where  $k$  is the Boltzmann constant. The physical dimension of  $kT$  is that of energy, i.e.,  $kT \in (J)$ .

The dual of a one-dimensional vector space is its ‘‘reciprocal’’<sup>27</sup> and the duality map is the (tensorial) multiplication that is well reflected in our present notation: an element from  $(1/J)$  multiplied by an element from  $(J)$  results in a real number. The dual of a Cartesian product is identified with the Cartesian product of the duals by the usual rule: take the sum of the products of the components.

Thus we have that the intensive quantities are elements in the dual space of the extensive quantities, namely,

$$y := \left( y_i := \left( \frac{1}{kT_i}, \frac{P_i}{kT_i}, \frac{\mu_i(T_i, P_i)}{kT_i} \right) \middle| i = 1, \dots, n \right) \in X^* = \left( \left( \frac{1}{J} \right) \times \left( \frac{1}{m^3} \right) \times \mathbb{R} \right)^n. \tag{23}$$

Consequently, the constitutive functions map from the state space into its dual:

$$\mathbf{y} := \prod_{i=1}^n \mathbf{y}_i := \prod_{i=1}^n \left( \frac{1}{k\mathbf{T}_i}, \frac{\mathbf{P}_i}{k\mathbf{T}_i}, -\frac{\boldsymbol{\mu}_i}{k\mathbf{T}_i} \right) : X \rightarrow X^*, \tag{24}$$

whose domain is  $X_D$ .

Using the notation

$$y_0 := (1/kT_0, P_0/kT_0, -\mu_0(T_0, P_0)/kT_0) \in Z_0,$$

let us introduce

$$\begin{aligned} R_{ik}(x_i, x_k) &:= (\mathbf{A}_{ik}, \mathbf{F}_{ik}, \mathbf{G}_{ik})(\mathbf{y}_i(x_i), \mathbf{y}_k(x_k)), \\ R_{i0}(x_i, y_0) &:= (\mathbf{A}_{i0}, \mathbf{F}_{i0}, \mathbf{G}_{i0})(\mathbf{y}_i(x_i), y_0), \end{aligned} \tag{25}$$

for  $x \in X_D, i, k = 1, \dots, n$ .

Note that in these notations the mutuality property of the dynamical quantities becomes

$$R_{ik}(x_i, x_k) = -R_{ki}(x_k, x_i) \quad (x \in X_D, i, k = 1, \dots, n). \tag{26}$$

Putting

$$R(x, y_0) := \left( R_i(x) := R_{i0}(x_i, y_0) + \sum_{k=1}^n R_{ik}(x_i, x_k) \middle| i = 1, \dots, n \right), \tag{27}$$

for  $x \in X_D$  and  $y_0 \in Z_0$ , we can rewrite the dynamical law (16) in the form

$$\dot{x} = R(x, y_0). \tag{28}$$

Note that if  $t \mapsto x(t)$  is a function defined in time and having values in  $X$ , then  $\dot{x}$  has values in  $X/s$ , where  $s$  denotes ‘‘second.’’ Thus,  $R(x, y_0) \in X/s$  for all  $x$  and  $y_0$ .

The collection of the thermodynamical forces between the bodies and the environment will play an important role that is why we introduce the following notion.

*Definition 10:* The function

$$F : X_D \times Z_0 \rightarrow X^*, \quad F(x, y_0) := (\mathbf{y}_i(x_i) - y_0 | i = 1, \dots, n), \tag{29}$$

is called the *nominal thermodynamical force* in the system.

**B. The dissipative property and its consequences**

The dissipative property of the dynamical quantities in the previously introduced concise notations reads as follows:

$$\begin{aligned}
 (\mathbf{y}(x_i) - \mathbf{y}_k(x_k)) \cdot R_{ik}(x_i, x_k) &\geq 0 \quad (x \in X_D, i, k = 1, \dots, n), \\
 (\mathbf{y}_i(x_i) - y_0) \cdot R_{i0}(x_i, y_0) &\quad (x \in X_D, y_0 \in Z_0, i = 1, \dots, n),
 \end{aligned}$$

where equality holds if and only if  $R_{ik}(x_i, x_k) = 0$  and  $R_{i0}(x_i, y_0) = 0$ ; the dot denotes the sum of the product of the components.

*Proposition 5: The dissipative property of the dynamical quantities imply*

$$F(x, y_0) \cdot R(x, y_0) \geq 0 \quad (x \in X_D, y_0 \in Z_0), \tag{30}$$

where equality holds if and only  $R_{ik}(x_i, x_k) = 0$  and  $R_{i0}(x_i, y_0) = 0$  for all  $i, k = 1, \dots, n$ .

*Proof:* Let us introduce the formal quantities  $R_{i0}(x_i, x_0) := -R_{0i}(x_0, x_i) := R_{i0}(x_i, y_0)$ , and let us put  $y_k := \mathbf{y}_k(x_k)$  for the sake of brevity. Then we have

$$(y_i - y_k) \cdot R_{ik}(x_i, x_k) \geq 0 \quad (i, k = 0, 1, \dots, n),$$

from which we infer by the mutuality property of the dynamical quantities that

$$\begin{aligned}
 0 &\leq \frac{1}{2} \sum_{i,k=0}^n (y_i - y_k) \cdot R_{ik}(x_i, x_k) \\
 &= \frac{1}{2} \sum_{i,k=0}^n (y_i - y_0) \cdot R_{ik}(x_i, x_k) - \frac{1}{2} \sum_{i,k=0}^n (y_k - y_0) \cdot R_{ik}(x_i, x_k) \\
 &= \sum_{i,k=0}^n (y_i - y_0) \cdot R_{ik}(x_i, x_k) \\
 &= \sum_{i=1}^n (y_i - y_0) \cdot \sum_{k=0}^n R_{ik}(x_i, x_k),
 \end{aligned}$$

where equality holds if and only  $R_{ik}(x_i, x_k) = 0$  for all  $i, k = 0, 1, \dots, n$ . The last formula coincides with the left-hand side of (30).

Of course, equality holds if  $R(x, y_0) = 0$ ; thus we have the following.

*Proposition 6:  $R(x, y_0) = 0$  if and only if  $R_{ik}(x_i, x_k) = 0$  and  $R_{i0}(x_i, y_0) = 0$  for all  $i, k = 1, \dots, n$ .*

This has an interesting and important consequence.

*Proposition 7: Every standstill of the dynamical law (28) is an equilibrium.*

*Proof:* There can be a standstill if and only if either all the dynamical quantities are independent of the environment or  $y_a$  (the process of the environment) is constant. In both cases the state  $x$  is a standstill if and only if  $R(x, y_a) = 0$  that is equivalent by the previous result to the fact that all the dynamical quantities take a zero value at  $x$ , i.e.,  $x$  is an equilibrium.

**C. The quasilinear case**

Let  $C_{ik}$  denote the conductivity matrix between the  $i$ th and  $k$ th body as a function of the extensive variables [i.e., put  $T_i := \mathbf{T}_i(E_i, V_i, N_i)$ , etc. in them]. Then we have for  $x \in X_D$  and  $y_0 \in Z_0$ ,

$$R_{ik}(x_i, x_k) = \mathbf{C}_{ik}(x_i, x_k) \cdot (\mathbf{y}_i(x_i) - \mathbf{y}_k(x_k)), \quad R_{i0}(x_i, y_0) = C_{i0}(x_i, y_0) \cdot (\mathbf{y}_i(x_i) - y_0),$$

for  $i, k = 1, \dots, n$ . It follows from the mutuality property that

$$\mathbf{C}_{ik}(x_i, x_k) \cdot (\mathbf{y}_i(x_i) - \mathbf{y}(x_k)) = -\mathbf{C}_{ki}(x_k, x_i) \cdot (\mathbf{y}_k(x_k) - \mathbf{y}_i(x_i)) = \mathbf{C}_{ki}(x_k, x_i) \cdot (\mathbf{y}_i(x_i) - \mathbf{y}_k(x_k)),$$

which does not imply

$$\mathbf{C}_{ik}(x_i, x_k) = \mathbf{C}_{ki}(x_k, x_i) \quad (x \in X_D, i, k = 1, \dots, n); \tag{31}$$

since these matrices play a role only when multiplied by  $\mathbf{y}_i(x_i) - \mathbf{y}_k(x_k)$ , we do not restrict the generality by requiring equality (31).

Moreover, we have that

$$\mathbf{C}_{i0}(\mathbf{y}_i(x_i), y_0) \cdot (\mathbf{y}_i(x_i) - y_0) + \sum_{i=1}^n \mathbf{C}_{ik}(x_i, x_k) \cdot (\mathbf{y}_i(x_i) - \mathbf{y}_k(x_k)) = \sum_{i=1}^n B_{ik}(x, y_0) \cdot (\mathbf{y}_k(x_k) - y_0),$$

where

$$B_{ik}(x, y_0) := \begin{cases} \mathbf{C}_{ik}(x_i, x_k), & \text{if } i \neq k, \\ \mathbf{C}_{i0}(x_i, y_0) + \sum_{i=1}^n \mathbf{C}_{ik}(x_i, x_k), & \text{if } i = k. \end{cases} \tag{32}$$

Thus, introducing

$$B(x, y_0) := (B_{ik}(x, y_0) | i, k = 1, \dots, n), \tag{33}$$

and using the nominal thermodynamical force defined in (29), we get

$$R(x, y_0) = B(x, y_0) \cdot F(x, y_0), \tag{34}$$

and the dynamical law has the form

$$\dot{x} = B(x, y_a) \cdot F(x, y_a). \tag{35}$$

*Definition 11:* The function  $B: X_D \times Z_0 \rightarrow \text{Lin}(X^*, X/s)$  defined in (33) is called the *nominal conductivity matrix* in the system.

*Proposition 8:* If  $\mathbf{C}_{ik}(x_i, x_k)$  and  $\mathbf{C}_{i0}(x_i, y_0)$  are symmetric for all  $i, k = 1, \dots, n$  for a given  $x$  and  $y_0$ , and (31) holds, then  $B(x, y_0)$  is symmetric as well.

## D. Constraints

### 1. Heuristic considerations

A system of interacting bodies, in general, is subjected to some constraints. As examples let us consider the following systems.

(1) A body with a constant particle number in a given constant environment, the pressure of the body is held constant, equaling the pressure  $P_a$  of the environment; then

$$\dot{N} = 0, \quad \frac{\partial \mathbf{P}(E, V, N)}{\partial E} \dot{E} + \frac{\partial \mathbf{P}(E, V, N)}{\partial V} \dot{V} = 0.$$

(2) A heat insulated body with a constant particle number in a given environment,

$$\dot{N} = 0, \quad \dot{E} = -\mathbf{P}(E, V, N) \dot{V}. \tag{36}$$

(3) A body with constant volume in a given environment,

$$\dot{V} = 0.$$

(4) Two bodies that are totally insulated from the environment,

$$\dot{E}_1 + \dot{E}_2 = 0, \quad \dot{V}_1 + \dot{V}_2 = 0, \quad \dot{N}_1 + \dot{N}_2 = 0. \tag{37}$$

The constraints are not characterized completely by the previous formulas that concern the “fluxes,” i.e., the time derivative of the extensive variables. Constraints are intimately related to forces, too. Namely, the real driving forces in the examples are (1) the temperature difference between the body and the environment; (2) the pressure difference between the body and the environment; (3) the temperature difference between the body and the environment; (4) the temperature difference, the pressure difference, and the chemical potential difference between the two bodies.

Now we shall show how we get these real forces from the nominal one.

The nominal thermodynamical force for the examples (1)–(3), taken at the process of the environment is—in a loose notation—

$$\left( \frac{1}{kT} - \frac{1}{kT_a}, \frac{P}{kT} - \frac{P_a}{kT_a}, -\frac{\mu}{kT} + \frac{\mu_a}{kT_a} \right).$$

(1) Equality (36) and the first law  $\dot{E} = Q - P_a \dot{V}$  result in that the heating is proportional to the springing,  $Q = \alpha F$ , thus the dynamical equation becomes

$$\dot{E} = (\alpha - P_a)F, \quad \dot{V} = F, \quad \dot{N} = 0.$$

The right-hand side of the equation is a multiple of the vector  $(\alpha - P_a, 1, 0)$ .

Let us apply the nominal thermodynamical force (as an element of the dual space) to this vector:

$$\left( \frac{1}{kT} - \frac{1}{kT_a} \right) (\alpha - P_a) + \left( \frac{P_a}{kT} - \frac{P_a}{kT_a} \right) = \alpha \left( \frac{1}{kT} - \frac{1}{kT_a} \right).$$

We have got (a multiple of) the really acting thermodynamical force whose zero value determines the equilibrium if the environment is constant.

(2) In the case of a heat insulated body with a constant particle number, the right-hand side of the dynamical law,

$$\dot{E} = -PF, \quad \dot{V} = F, \quad \dot{N} = 0,$$

is a multiple of the vector  $(-P, 1, 0)$ .

Applying the nominal thermodynamical force to this vector, we get

$$\left( \frac{1}{kT} - \frac{1}{kT_a} \right) (-P_a) + \left( \frac{P_a}{kT} - \frac{P_a}{kT_a} \right) = \frac{1}{kT} (P - P_a),$$

which is (a multiple of) the really acting thermodynamical force whose zero value determines the equilibrium if the environment is constant.

(3) In this example the dynamical law has the form

$$\dot{E} = Q + \mu G, \quad \dot{V} = 0, \quad \dot{N} = G,$$

whose right-hand side is spanned by the multiple of the vectors  $(1, 0, 0)$  and  $(0, 0, 1)$ .

Applying to these vectors the nominal thermodynamical force, we get

$$\left( \frac{1}{kT} - \frac{1}{kT_a}, -\frac{\mu}{kT} + \frac{\mu_a}{kT_a} \right),$$

which is the really acting thermodynamical force whose zero value determines the equilibrium if the environment is constant.

(4) In this example the dynamical law has the form

$$\begin{aligned} \dot{E}_1 &= Q_1 - P_1 F_1 + \mu_1 G_1, & \dot{V}_1 &= F_1, & \dot{N}_1 &= G_1, \\ \dot{E}_2 &= Q_2 - P_2 F_2 + \mu_2 G_2, & \dot{V}_2 &= F_2, & \dot{N}_2 &= G_2, \end{aligned}$$

moreover, relation (37) holds; thus the right-hand side of the dynamical equation is spanned by the multiple of the vectors  $(1, 0, 0, -1, 0, 0)$ ,  $(0, 1, 0, 0, -1, 0)$ , and  $(0, 0, 1, 0, 0, -1)$ . Applying to these vectors the nominal thermodynamical force,

$$\left( \frac{1}{kT_1} - \frac{1}{kT_a}, \frac{P_1}{kT_1} - \frac{P_a}{kT_a}, -\frac{\mu_1}{kT_1} + \frac{\mu_a}{kT_a}, \frac{1}{kT_2} - \frac{1}{kT_a}, \frac{P_2}{kT_2} - \frac{P_a}{kT_a}, -\frac{\mu_2}{kT_2} + \frac{\mu_a}{kT_a} \right),$$

we get

$$\left( \frac{1}{kT_1} - \frac{1}{kT_2}, \frac{P_1}{kT_1} - \frac{P_2}{kT_2}, -\frac{\mu_1}{kT_1} + \frac{\mu_2}{kT_2} \right),$$

which is the really acting thermodynamical force whose zero value determines the equilibrium.

### 2. Mathematical formulation of constraints

*Definition 12:* We say that the dynamical law (28) is subjected to a constraint if there is a set  $\Gamma$  of continuous maps  $X_D \rightarrow X^*$ , such that  $\{p(x) | p \in \Gamma\}$  is linearly independent for all  $x \in X_D$ ;  $p(x)\dot{x} = 0$  holds for all  $p \in \Gamma$  and for all processes  $x$  [solutions of the dynamical law (28)], which is equivalent to

$$R(x, y_a) \in K(x) / s \quad (x \in X_D), \tag{38}$$

where

$$K(x) := \bigcap_{p \in \Gamma} \text{Ker } p(x). \tag{39}$$

is the constraint subspace at  $x$ ;  $R(x, y_a) = 0$  if and only if  $F(x, y_a)|_{K(x)} = 0$ .

The function

$$X_D \rightarrow X^*, \quad x \mapsto F_\Gamma(x, y_a) := F(x, y_a)|_{K(x)}, \tag{40}$$

is called the *effective thermodynamical force* corresponding to the constraint.

Now we apply well-known notions of the theory of manifolds. If  $U$  is a  $u$ -dimensional  $C^r$  submanifold in  $X_D$ , then a parametrization (the inverse of a local coordinatization) of  $U$  around  $x_0 \in U$  is a map  $p: \mathbb{R}^u \rightarrow X$ , such that  $x_0 \in \text{Ran } p \subset U$ ;  $p$  is injective,  $p^{-1}$  is continuous;  $p$  is  $r$  times continuously differentiable;  $Dp(x)$  is injective for all  $x \in \text{Dom } p$ .

One of the most important relations is that  $\text{Ran } Dp(x) = T_x(U)$ , where the last symbol denotes the tangent space of  $U$  at  $x$ .

A submanifold will mean a  $C^1$  submanifold.

A submanifold  $U$  in  $X_D$  is called a *constraint manifold* if  $T_x(U) = K(x)$  for all  $x \in U$ . A constraint manifold  $U$  is invariant for the dynamical law, i.e., every process starting from  $U$  remains in  $U$ .

If the constraint is a foliation i.e., for every  $x$  in the interior of  $X_D$  there is a (maximal) constraint manifold containing  $x$  then the interior of  $X_D$  is the disjoint union of constraint manifolds.



The constraint is called *holonom*, if for all  $p \in \Gamma$  there is a  $\Phi_p : X_D \rightarrow \mathbb{R}$ , continuously differentiable on the interior of  $X_D$ , such that  $p \supset D\Phi_p$ . Then the constraint is a foliation and the constraint manifolds are the subsets that  $\Phi_p$  is constant on for all  $p \in \Gamma$ .

If  $\Gamma = \emptyset$  then there is no constraint, i.e.,  $K(x) = X$  for all  $x \in X_D$ , and there is a single constraint manifold; the interior of  $X_D$ .

In the quasilinear case  $R(x, y_a) = B(x, y_a)F(x, y_a) \in K(x)/s$  does not imply, in general, that  $\text{Ran } B(x, y_a) \subset K(x)/s$  even if  $F(x, y_a) \neq 0$ . Moreover, in general,  $R(x, y_a)$  cannot be given as a quasilinear function of the effective thermodynamical force. That is why we introduce the following notion.

*Definition 13:* The nominal conductivity matrix *fits the constraint* if for all  $x \in X_D$  there is a  $B_\Gamma(x, y_a) \in \text{Lin}(K(x)^*, K(x)/s)$ , such that

$$B(x, y_a)F(x, y_a) = B_\Gamma(x, y_a)F_\Gamma(x, y_a). \tag{41}$$

In this case the map  $x \mapsto B_\Gamma(x, y_a)$  is called the *effective conductivity matrix*.

The relation between the nominal conductivity matrix and the effective conductivity matrix can be expressed by the canonical embedding  $i(x) : K(x) \rightarrow X$  and its transpose  $i(x)^* : X^* \rightarrow K(x)^*$  as follows:

$$i(x)B_\Gamma(x, y_a)i(x)^* = B(x, y_a) \quad (x \in X_D). \tag{42}$$

Then we have the following results.

*Proposition 9:* (i) *The nominal conductivity matrix fits the constraint if and only if for all  $x \in X_D$  we have  $\text{Ran } B(x, y_a) \subset K(x)/s$  and  $\text{Ker } B(x, y_a) \supset (K(x))^\circ$ , which is equivalent to the fact that  $p(x)B(x, y_a) = 0$  and  $B(x, y_a)p(x) = 0$  for all  $p \in \Gamma$ , where  $(K(x))^\circ := \{y \in X^* \mid i(x)^*y = 0\}$  is the annihilator of  $K(x)$ .*

(ii) *The nominal conductivity matrix fits the constraint if  $\text{Ran } B(x, y_a) \subset K(x)$  and  $B(x, y_a)$  is symmetric for all  $x \in X_D$ .*

*Proof:* (i) If the kernel of  $B(x, y_a)$  contains the annihilator of  $K(x)$ , then  $B_\Gamma(x, y_a)$  is well defined by  $B_\Gamma(x, y_a)i(x)^*y := B(x, y_a)y$  ( $y \in X^*$ ); so the stated relations are sufficient. The statement concerning the necessity is trivial.

It is evident that the annihilator of  $K(x)$  is spanned by  $\{p(x) \mid p \in \Gamma\}$ , thus the equivalent statement holds true as well.

(ii) If  $B(x, y_a)$  is symmetric, then its kernel contains the annihilator of its range. Simple arguments prove the following statements, too.

*Proposition 10:* *Let the nominal conductivity matrix fit the constraint and use the previous notations. Then for all  $x \in X_D$ : (i)  $\text{Ker } B_\Gamma(x, y_a) = \{0\}$  if and only if  $\text{Ker } B(x, y_a) = (K(x))^\circ$ ;  $B_\Gamma(x, y_a)$  is symmetric if and only if  $B(x, y_a)$  is symmetric; (iii)  $B_\Gamma(x, y_a)$  is positive semidefinite if and only if  $B(x, y_a)$  is positive semidefinite.*

Since  $R(x, y_a) \in K(x)/s$ , inequality (30) can be rewritten in the form

$$F_\Gamma(x, y_a)R(x, y_a) \geq 0 \quad (x \in X_D), \tag{43}$$

where equality holds if and only if  $R(x, y_a) = 0$ , which is equivalent to  $F_\Gamma(x, y_a) = 0$  by the definition of constraints.

In the quasilinear case if the effective conductivity matrix exists then the above inequality becomes

$$F_\Gamma(x, y_a)B_\Gamma(x, y_a)F_\Gamma(x, y_a) \geq 0 \quad (x \in X_D), \tag{44}$$

where equality holds if and only if  $F_\Gamma(x, y_a) = 0$ .

**E. Onsager formalism**

We call the constraint *affine* if every constraint subspace is the same: there is a linear subspace  $K$  of  $X$  such that  $K(x) = K$  for all  $x \in X_D$ . The constraint is affine in the previous examples 3 and 4 and is not affine in the examples 1 and 2.

Note the important fact that the effective conductivity matrix cannot be constant if the constraint is not affine; indeed,  $B_\Gamma(x, y_a)$  is a linear map from  $K(x)^*$  into  $K(x)/s$ ; thus, if  $K(x) \neq K(x')$  then  $B_\Gamma(x, y_a) \neq B_\Gamma(x', y_a)$ .

If the constraint is affine then the effective conductivity matrix can but evidently need not be constant.

Let us consider an affine constraint with constraint subspace  $K$ . Let  $x_0$  be an equilibrium. Put  $y_0 := \mathbf{y}(x_0)$  and  $y_a^n := (y_a, \dots, y_a)$ . Then

$$0 = F(x_0, y_a)|_K = (y_0 - y_a^n)|_K,$$

consequently,

$$F_\Gamma(x, y_a) = F_\Gamma(x, y_0) := (\mathbf{y}(x) - y_0)|_K,$$

i.e., in this case the effective thermodynamical force can be expressed by the deviation of the intensive quantities from their equilibrium values. In the quasilinear case the effective conductivity matrix  $B_\Gamma(x, y_a)$  maps  $K$  into  $K$  for all  $x$ ; near the equilibrium  $x_0$  it can be approximated by its equilibrium value, which is a linear map  $K \rightarrow K$ , too; thus the dynamical law can be approximated by

$$\dot{x} = B_\Gamma(x_0, y_a) F_\Gamma(x, y_0).$$

This is the usual form of the Onsager formalism: the conductivity matrix is constant, the thermodynamical force is expressed by the difference between the intensive variables and their equilibrium values (and the fluxes correspond to the time derivatives of the extensive quantities).

On the other hand, if the constraint is not affine then  $F_\Gamma(x, y_a) \neq (\mathbf{y}(x) - y_0)|_{K(x)}$ , i.e., the effective thermodynamical force cannot be expressed by the the deviation of the intensive quantities from their equilibrium values. Moreover, any approximation of  $B_\Gamma(x, y_a): K(x) \rightarrow K(x)/s$  must be a map  $K(x) \rightarrow K(x)/s$ ; thus the effective conductivity matrix cannot be approximated by its equilibrium value  $B_\Gamma(x_0, y_a): K(x_0) \rightarrow K(x_0)/s$ . All these mean that the Onsger formalism does not work for nonaffine constraints.

**V. STABILITY**

**A. Some comments**

One of the main problems of thermodynamical systems is the stability of equilibria. The stability investigations of classical thermodynamics are not satisfactory because stability is not defined in a mathematically exact way and, indeed, the results concern only some constitutive properties of the substances (intrinsic stability) and do not take into account dynamical properties (which are formulated here by the dissipative property). In continuum (irreversible) thermodynamics the notion of stability is defined in a mathematically exact way referring to the balance equations; however, the investigations are very hard from a mathematical point of view because the equations describing the processes are partial differential equations.<sup>28–33</sup>

In ordinary thermodynamics stability investigations are based on mathematically correct notions, and are much more easier than in continuum thermodynamics because here ordinary differential equations govern the processes. Trend to equilibrium—a fundamental concept—corresponds to the asymptotic stability of equilibria.

**B. Notions and results from the theory of stability**

For the sake of simplicity, from now on we omit  $y_a$  from the notations of the functions introduced up to now, i.e., we write  $R(x)$ ,  $B(x)$ ,  $F(x)$ , etc. instead of  $R(x, y_a)$ ,  $B(x, y_a)$ ,  $F(x, y_a)$ , etc.; then, in particular, the dynamical law has the form

$$\dot{x} = R(x).$$

Recall that  $x_0$  is an equilibrium if and only if  $R(x_0) = 0$ .

*Definition 14:* Let  $U$  be a subset invariant for the dynamical equation (in particular, a constraint manifold).

- (1) An equilibrium  $x_0 \in U$  is *stable with condition U* if for each neighborhood  $N$  of  $x_0$  there is a neighborhood  $G$  of  $x_0$  such that for every process starting from  $G \cap U$  proceeds in  $N \cap U$ .
- (2) An equilibrium  $x_0 \in U$  is *asymptotically stable with condition U* if it is stable with condition  $U$  and there is a neighborhood  $V$  of  $x_0$  such that for every process  $r$  starting from  $V \cap U$  we have  $\lim_{t \rightarrow \infty} r(t) = x_0$ .
- (3) A set  $E \subset U$  of equilibria is *strictly asymptotically stable<sup>34</sup> with condition U* if every equilibrium in  $E$  is stable with condition  $U$ ; every equilibrium in  $E$  has a neighborhood  $V$  such that if  $r$  is a process starting from  $V \cap U$  then  $\lim_{t \rightarrow \infty} r(t)$  is in the closure of  $E$ .

Besides the well-known and fundamental results of stability theory;<sup>35</sup> we shall apply a less common one,<sup>36</sup> which reads in our formulation as follows.

Consider the differential equation

$$\dot{\xi} = \Phi(\xi),$$

in  $\mathbb{R}^u$ , where  $\Phi$  is continuously differentiable. Let  $\Delta$  be the set of its equilibria and suppose (i) there is a nontrivial linear subspace  $Z \subset \mathbb{R}^u$ , an element  $a$  of  $\mathbb{R}^u$  such that  $\Delta = (a + Z) \cap \text{Dom } \Phi$ ; (ii) for all  $\xi \in \Delta$ :— $\text{Ker } D\Phi(\xi) = Z$ ,—the algebraic multiplicity and the geometric multiplicity of the zero eigenvalue of  $D\Phi(\xi)$  are equal—the real part of the nonzero eigenvalues of  $D\Phi(\xi)$  is negative.

Then  $\Delta$  is strictly asymptotically stable.

If  $L$  is a differentiable scalar-valued function defined in  $X_D$ , then  $\dot{L}(x) := DL(x)R(x)$  is called the *derivative of L along the dynamical equation*.

*Proposition 11:* Let  $U$  be a submanifold in  $X_D$ , invariant for the dynamical law (in particular, a constraint manifold). If  $x_0 \in U$  is an equilibrium and there is a continuously differentiable real-valued function  $L$ , defined in a neighborhood of  $x_0$ , such that (i)  $L$  has a strict local maximum at  $x_0$  with condition  $U$ , i.e.,  $L(x) < L(x_0)$  for all  $x \in U$  in a neighborhood of  $x_0$ ; (ii)  $\dot{L}$  has a (strict) local minimum at  $x_0$  with condition  $U$ , then the equilibrium  $x_0$  is (asymptotically) stable with condition  $U$ .

*Proof:* Let  $u$  be the dimension of  $U$  and take a local parametrization  $p: \mathbb{R}^u \rightarrow U$  around  $x_0$ . Then the restriction of the dynamical law onto the invariant submanifold  $U$  is reduced to the differential equation

$$\dot{\xi} = D_p(\xi)^{-1}R(p(\xi)), \tag{45}$$

for the function  $\xi := p^{-1} \circ x$ .

Then  $\xi_0 := p^{-1}(x_0)$  is an equilibrium of the reduced dynamical equation. It is trivial that  $\Lambda := L \circ p$  is a continuously differentiable function that has a strict maximum at  $\xi_0$ .

Since  $D\Lambda = (DL \circ p)Dp$ , the derivative of  $\Lambda$  along the reduced equation,

$$\dot{\Lambda} = (DL \circ p)(R \circ p) = \dot{L} \circ p, \tag{46}$$

has a (strict) minimum at  $\xi_0$ .

These imply by Lyapunov's theory that  $\xi_0$  is an (asymptotically) stable equilibrium of the reduced equation from which it follows that  $x_0$  is an (asymptotically) stable equilibrium with condition  $U$ .

*Proposition 12:* Let  $U$  be a submanifold, invariant for the dynamical equation (in particular, a constraint manifold) and let  $E$  be the set of equilibria in  $U$ . Suppose that (1)  $E$  is a submanifold; (2) for all  $x \in E$ , the linear map  $DR(x)|_{T_x(U)}: T_x(U) \rightarrow T_x(U)$  has the following properties: (i) its kernel is  $T_x(E)$ ; (ii) the algebraic multiplicity and the geometric multiplicity of its zero eigenvalue coincide; (iii) its nonzero eigenvalues have negative real part.

Then  $E$  is strictly asymptotically stable with condition  $U$ .

*Proof:* Let  $e$  and  $u$  be the dimensions of  $E$  and  $U$ , respectively. There is a local parametrization  $p: \mathbb{R}^e \times \mathbb{R}^{u-e} \rightarrow U$  such that  $p(\cdot, 0): \mathbb{R}^e \rightarrow E$  is a parametrization of  $E$ . Then

$$\text{Ran}(Dp(\eta, 0)|_{\mathbb{R}^e \times \{0\}}) = T_{p(\eta, 0)}(E).$$

The set of equilibria of the reduced dynamical equation (45) is the manifold

$$p^{-1}(E) = \mathbb{R}^e \times \{0\} \cap \text{Dom } p,$$

whose tangent space at  $(\eta, 0)$  equals

$$\mathbb{R}^e \times \{0\} = Dp(\eta, 0)^{-1}[T_{p(\eta, 0)}(E)].$$

The derivative of the right-hand side of the reduced dynamical equation at an equilibrium  $(\eta, 0)$ , is

$$D(\eta, 0) := Dp(\eta, 0)^{-1}DR(p(\eta, 0))Dp(\eta, 0).$$

As a consequence, the spectral properties of  $D(\eta, 0)$  coincide with those of  $DR(p(\eta, 0))$  (i.e., they have the same eigenvalues and multiplicities); moreover,

$$\text{Ker } D(\eta, 0) = (Dp(\eta, 0))^{-1}[\text{Ker } DR(p(\eta, 0))] = \mathbb{R}^e \times \{0\}.$$

Thus, according to the theorem cited above, the set of equilibria of the reduced dynamical equation is strictly asymptotically stable, which implies that our assertion is true.

### C. Stability in ordinary thermodynamics

There are nice stability results for several phenomena, including phase transitions (see Refs. 14–19). It is remarkable that some of them is obtained without the use of entropy. The entropic property, however, admits general results on stability.

The entropy of the environment—in a loose notation—is

$$S_0 = \frac{E_0 + P_0 V_0 - \mu_0 N_0}{T_0}.$$

The total energy, the total volume and the total particle number of the bodies, and the environment together are constant,

$$\sum_{i=0}^n E_i = \text{const}, \quad \sum_{i=0}^n V_i = \text{const}, \quad \sum_{i=0}^n N_i = \text{const}.$$

Let us suppose that the temperature  $T_a$ , the pressure  $P_a$  (thus the chemical potential  $\mu_a$ , too), in the given process of the environment are constant (which is a necessary condition of the existence of equilibrium if at least one of the dynamical quantities is not independent of the environment). Then

$$L := \sum_{i=1}^n \left( S_i - \frac{E_i + P_a V_i - \mu_a N_i}{T_a} \right)$$

is the total entropy of the bodies and the environment together, up to an additive constant.

Using the notations introduced previously, we can write the above function in the form

$$L(x) = \sum_{i=1}^n (\mathbf{S}_i(x_i) - y_a \cdot x_i) \quad (x \in X_D). \tag{47}$$

Further on we refer frequently to the set of states corresponding to the regular domains:

$$X_R := \prod_{i=1}^n (\mathbb{R}^+ * R_i). \tag{48}$$

Suppose the bodies of the thermodynamical system are entropic. Then  $L$  is twice differentiable on  $X_R$ ; the derivative of  $L$  equals the nominal thermodynamical force,

$$DL(x) = F(x), \tag{49}$$

for  $x \in X_R$ . Moreover,

$$D^2L(x) = \sum_{i=1}^n D^2\mathbf{S}_i(x_i) \tag{50}$$

is negative semidefinite; its kernel is spanned by the vectors  $(x_1, 0, 0, \dots, 0)$ ,  $(0, x_2, 0, \dots, 0)$ ,  $\dots$ ,  $(0, 0, 0, \dots, x_n)$ .

*Proposition 13:* Let  $U$  be a constraint manifold and let us apply the previously introduced notations. Let  $x_0$  be an equilibrium in  $U \cap X_R$ . If (i) the bodies are entropic; (ii)  $L$  has a strict local maximum at  $x_0$  with condition  $U$ , then  $x_0$  is asymptotically stable with condition  $U$ .

*Proof:* Condition (ii) implies that  $x_0$  has a neighborhood in which  $F_\Gamma(x) = DL(x)|_{T_{x(U)}} \neq 0$  for  $x_0 \neq x \in U$ . As a consequence, the derivative of  $L$  along the dynamical law,  $\dot{L} = (DL)R = FR = F_\Gamma R$  has a strict local minimum at  $x_0$  by (43); hence we infer the desired result from Proposition 11.  $\square$

Next, we give easily verifiable relations, which imply condition (ii) and will be useful in applications.

*Proposition 14:* Let the constraint manifold  $U$  be a  $C^2$  submanifold. Suppose  $x_0$  is an equilibrium in  $U \cap X_R$  and (i)  $\text{Ker}(D^2L(x_0)) \cap T_{x_0}(U) = 0$ ; (ii) there is a parametrization of  $U$  around  $x_0$  such that  $DL(x_0)D^2p(p^{-1}(x_0))$  is negative semidefinite; then  $L$  has a strict local maximum at  $x_0$  with condition  $U$ .

*Proof:* The function  $\Lambda := L \circ p$  is twice differentiable, and

$$D\Lambda(\xi) = DL(p(\xi))Dp(\xi), \tag{51}$$

$$D^2\Lambda(\xi) = D^2L(p(\xi)) \circ (Dp(\xi) \times Dp(\xi)) + DL(p(\xi))D^2p(\xi), \tag{52}$$

for all  $\xi \in \text{Dom } p$ .

Put  $\xi_0 := p^{-1}(x_0)$ . Since  $x_0$  is an equilibrium, we have  $DL(x_0)|_{T_{x_0}(U)} = 0$ , consequently  $D\Lambda(\xi_0) = 0$ . Moreover, at  $\xi = \xi_0$ , the first term on the right-hand side of (52) is negative definite by (i); the second one is negative semidefinite by (ii), so the sum is negative definite.

As a consequence,  $\Lambda$  has a strict maximum at  $\xi_0$  that is equivalent to that  $L$  has a strict maximum at  $x_0$  with condition  $U$ .  $\square$

Property (ii) in the previous proposition holds if  $U$  is a subset of an affine subspace; then  $p$  can be taken to be affine and its second derivative is zero.

Proposition 13 can be applied when every body has a constant particle number. Indeed, then the third, sixth, ninth, etc. components of the elements in  $K(x)$  are zero, thus only the zero is both in  $K(x)$  and in the kernel of  $D^2L(x)$ . A similar assertion holds when everybody has constant volume.

Asymptotic stability of an equilibrium implies that the equilibrium is locally unique. In general, e.g., in the first-order phase transitions and in diffusions when the particle number and the volume of the bodies changes, equilibria are not locally unique; they constitute a nonzero dimensional submanifold.<sup>37</sup> Then instead of the previous proposition we can apply the following one.

*Proposition 15: Let the constraint manifold  $U$  be a  $C^2$  submanifold and let  $E$  be the set of equilibria in  $U \cap X_R$ . If (i) the bodies are entropic, (ii) the dynamical quantities are quasilinear and the nominal conductivity matrix fits the constraint, (iii)  $E$  is a submanifold; and for all  $x_0 \in E$ , (iv)  $B_\Gamma(x_0)$  is symmetric and positive definite, (v)  $\text{Ker}(D^2L(x_0)) \cap T_{x_0}(U) = T_{x_0}(E)$ , (vi) there is a parametrization  $p$  of  $U$  around  $x_0$  such that  $DL(x_0)D^2p(p^{-1}(x_0))$  is negative semidefinite; then  $E$  is strictly asymptotically stable with condition  $U$ .*

*Proof:* The dynamical equation is of the form

$$\dot{x} = B_\Gamma(x)(DL)_\Gamma(x)$$

and

$$E = \{x \in U \mid (DL)_\Gamma(x) = 0\}.$$

Let  $x_0$  be an arbitrary element of  $E$  and let  $p$  be a parametrization of  $U$  around  $x_0$ . Then for the function  $\Lambda := L \circ p$  and  $\xi_0 := p^{-1}(x_0)$  we have the equalities (51) and (52).

The dynamical equation reduced by the parametrization becomes

$$\dot{\xi} = \Psi(\xi)D\Lambda(\xi), \tag{53}$$

where

$$\Psi(\xi) := Dp(\xi)^{-1}B_\Gamma(p(\xi))(Dp(\xi)^*)^{-1}.$$

The set of equilibria of the reduced dynamical equation is

$$\phi := \{\xi \in \text{Dom } p \mid D\Lambda(\xi) = 0\}. \tag{54}$$

Now we show that

$$T_{\xi_0}(\phi) = \text{Ker } D^2\Lambda(\xi_0).$$

The relation  $\subset$  follows from (54) trivially. The relation  $\supset$  can be verified as follows: if  $p$  has property (vi) and  $v$  is in the kernel of  $D^2\Lambda(\xi_0)$ , then (52) implies that  $Dp(\xi_0)v \in T_{p(\xi_0)}(U)$  is in the kernel of  $D^2L(x_0)$ , thus it is an element of  $T_{x_0}(E)$  according to property (v); this is equivalent to that  $v \in T_{\xi_0}(\phi)$ .

The derivative of the right-hand side of the reduced dynamical equation (53) at  $\xi_0$  equals

$$\Psi(\xi_0)D^2\Lambda(\xi_0).$$

Property (iv) implies that  $\Psi(\xi_0)$  is symmetric and positive definite, and according to (52) and property (vi),  $D^2\Lambda(\xi_0)$  (which is necessarily symmetric) is negative semidefinite. Therefore the kernel of  $\Psi(\xi_0)D^2\Lambda(\xi_0)$  equals the kernel of  $D^2\Lambda(\xi_0)$ , which is the tangent space of  $\phi$  at  $\xi_0$ ; and<sup>38</sup> the geometric multiplicity and the algebraic multiplicity of the zero eigenvalue of  $\Psi(\xi_0)D^2\Lambda(\xi_0)$  coincide, all the nonzero eigenvalues of  $\Psi(\xi_0)D^2\Lambda(\xi_0)$  are negative.

As a consequence of Proposition 12, the set of equilibria of the reduced dynamical equation is strictly asymptotically stable (without a condition), which implies that  $E$  is strictly asymptotically stable with condition  $U$ .

Property (iv) in the previous proposition is equivalent to (see Proposition 10) (iv)  $B(x_0)$  is symmetric, positive semidefinite and  $\text{Ker}B(x_0) = T_{x_0}(U)^\circ$ , which is very useful in practice.

## VI. DISCUSSION

A general mathematical theory of thermodynamical systems consisting of single-component homogenous bodies has been expounded. Substances, phases, bodies, systems, thermodynamical forces, constraints, etc., all the usual notions have got a mathematical definition. The basic object is the dynamical law, a differential equation whose solutions are the processes of the system. Equilibria are the constant processes. The first law is a part of the dynamical law (as in continuum thermodynamics, where the first law is one of the balance equations); the second law is expressed by a condition imposed on the dynamical quantities, called the dissipative property (an analogon of the Gibbs–Duhem relation in continuum thermodynamics); the dissipative property is something like positive entropy production but is formulated without the notion of entropy and can be applied for some systems of nonentropic bodies, too.<sup>39</sup> Constraints can be treated by the notions of manifolds. The Onsager formalism is a well-defined linear approximation of the dynamical law around equilibrium if and only if the constraint is affine. General results on (strict) asymptotic stability (trend to equilibrium) are obtained for a system of entropic bodies.

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