

A geometric perspective on Irreversible Thermodynamics. Part I: general concepts

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Abstract

A new geometrical formulation of the thermodynamics of irreversible processes revisiting Coleman-Owen material point model has been proposed by the authors (in collaboration with P. Rogolino) a decade ago and since then applied by different teams of researchers to many different physical models in continuum thermodynamics such as viscoelastic media, deformable dielectrics and magnetically polarizable undeformable media. The geometrical tools of contact/symplectic geometry were applied to introduce the Extended Thermodynamic Phase Space (ETPS) with its contact structure; in this space Legendre surfaces of equilibrium and Gibbs bundle have been constructed and the relations between the constitutive properties of continuum systems and the *class of the entropy form* have been discussed together with the introduction of the Hamiltonian formalism. The basic features of this geometrical formulation is here reviewed leaving the illustrations of relevant applications to part II of the present paper. The review is linked to a critical analysis focused on various open problems.

1. Introduction

The thermodynamics of irreversible processes has had many different mathematical formulations; the differences and equivalences among these formulations usually have important consequences, from both theoretical and practical points of view. As remarked by Callen [1] "Each of these alternative formulations is particularly convenient in particular types of problems, and the art of thermodynamic calculations relies largely in the selection of the particular theoretical formulation that most incisively 'fits' the given problem".

In the case of Homogeneous Thermodynamics several geometrical models in the phase space were suggested and studied, after the pioneering

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work by C. Caratheodory [2]. In the papers by R. Mrugala and his collaborators [3–5], a contact Hamiltonian vector field tangent to the equilibrium surface is introduced to model thermodynamical admissible processes of a fixed physical system. In the paper [6], B. Balian and P. Valentin used contact Hamiltonian systems generated by the homogeneous Hamiltonians in the symplectization $\tilde{\mathcal{P}}$ of the contact manifold (\mathcal{P}, ω) . In the space $\tilde{\mathcal{P}}$ entropy is an additional (gauge) variable whose evolution is "geometrically separated" from the evolution of the other variables.

H. Haslash [7,8] models relaxation processes in thermoelastic media introducing the so called generalized energy function and gradient dynamical systems in the symplectic factor of the contact space by the phase curve of the Reeb vector field.

In the paper by D. Eberard et al. [9], a metriplectic (double bracket) dynamical system in a manifold endowed with the Pseudo-Poisson bracket and a symmetrical (2,0)-tensor were lifted to the Extended Thermodynamical Phase Space (ETPS in the following).

In our geometrical formulation of the thermodynamics of irreversible processes we revisited Coleman-Owen formulation for the material element model [10–12] introducing the *thermodynamical bundle* as the manifold of the state variables fibred over time with a related 1-form called *entropy form* [13–15]. The integral of the entropy form along the transformation curve in the thermodynamical bundle measures the entropy change during the same transformation. Closure conditions for the entropy form provide a set of constitutional relations for the involved fields in each specific case.

Different teams of researchers worked on applications of the proposed geometrical formulations, determining the expressions for the entropy form and the related closure conditions for many different physical systems including magnetic and electric phenomena [16]– [28]. In [16], for example, the model was applied to deformable dielectrics including ferroelectric and piezoelectric crystals. The concrete application to chemical components of polarizable crystals, like e.g. the barium titanate of the Perowskity family [29] is very useful in electronics. In [26], the specific example of extrinsic semiconductor crystals, such as germanium and silicon, was considered. The models for semiconductors are applied in the technology of integrated circuits, in the field of electronic microscopy, in nanotechnology, in computer science and in many other sectors of applied science. In [28], the geometric model here reviewed was applied to deformable ferromagnetic crystals in the framework of quasimagnetostatics in insulators. Examples listed above are only a few, while a more exhaustive review of applications will be given in [30]. Many PhD thesis have been also written on applications of the proposed geometric theory. In further developments [31,32], we adopted

the geometrical tools of contact/symplectic geometry similar to that one employed in the homogeneous case, but introducing an ETPS (with its contact structure) in which non-homogeneous variables are present; in this space Legendre surfaces of equilibrium and the Gibbs bundle have been constructed and the relations between the constitutive properties of continuum systems and the *class of the entropy form* (i.e. degeneration of the entropy 1-form) have been discussed together with the introduction of an Hamiltonian formulation.

A unifying purpose of the various cited contributions of the several teams which worked on the presented geometrical formulation represents the aim of this review.

The plan of the paper is the following.

In Section 2 we present a short resumé of Coleman-Owen geometrical formulation of the thermodynamics of the material element model which will be useful for the remaining work.

In Section 3 the new geometrical formulation of the thermodynamics of irreversible processes is illustrated and its main results are deduced.

A key point of the this theory is represented by the possibility of adopting an Hamiltonian formalism; the basic features of the methodology are presented in Section 4.

In Section 5 an example of constitutive relations derived from the closure conditions of the entropy form in the case of extreme degeneracy is described.

Finally, in Section 6 conclusions are drawn.

2. Resumé of Coleman-Owen geometrical formulation of the material element model

We first review the basic features of the formulation of the thermodynamics of irreversible processes in the material element model as proposed by B. Coleman and D. Owen, [10–12]. We make this in order to have a direct comparison with our formulation which started as a revisitation of Coleman-Owen theory. We remark that we are using some standard notations of continuum thermodynamics instead of those of the work [10].

A **simple material element** is defined by the following set of data:

1. A state space B , characterized by the following variables

$B = \{e, \mathbf{F}, \boldsymbol{\beta}\}$ where e is the internal energy, \mathbf{F} is the deformation gradient and $\boldsymbol{\beta} = -\frac{1}{\rho} \nabla \theta^{-1}$ with ρ specific mass density and θ absolute temperature; finally τ (or also t) is the (Newtonian) time. Elements of the state space will be denoted by \mathbf{c} in the following.

2. A system of dynamical equations for the state variables

$$(1) \quad \begin{cases} \dot{\mathbf{F}} = \mathbf{L}\mathbf{F}, \\ \dot{e} = \mathbf{T}[\mathbf{c}(\tau)] : \mathbf{L}(\tau) + h(\tau), \\ \dot{\boldsymbol{\beta}} = \boldsymbol{\gamma}, \end{cases}$$

where \mathbf{L} is the rate of deformation, \mathbf{T} is the Cauchy stress tensor, $h = -\frac{1}{\rho}\nabla \cdot \mathbf{q}$ is the rate of heat absorption for unit of mass and \mathbf{q} is the heat flux (we have not considered heat supply by radiation for the sake of simplicity). Eq.(1)₁ is the usual relation between the deformation gradient and the rate of deformation, eq.(1)₂ is the *I law of thermodynamics* and eq.(1)₃ is just a position. The "dot" is here the time derivative $\frac{d}{d\tau}$ and the symbol ":" is used for total tensor contraction. The stress tensor \mathbf{T} , the heat flux \mathbf{q} and the absolute temperature θ are constitutive (continuous) functions on the state space

$$(2) \quad \begin{cases} \mathbf{T} : B \rightarrow \text{Sym}_2(V), \\ \theta : B \rightarrow \mathbb{R}^+, \\ \mathbf{q} : B \rightarrow V, \end{cases}$$

where $V = E^3$ is the physical Euclidean 3-dimensional vector space and \mathbb{R}^+ is the set of real positive numbers.

3. The space Π of "Noll's processes", i.e. piecewise continuous functions of time

$$(3) \quad \Pi \ni P_t : \tau \in [0, t] \rightarrow [\mathbf{L}(\tau), h(\tau), \boldsymbol{\gamma}(\tau)]$$

with values in the product of vector spaces $\text{End}(V) \times \mathbb{R} \times V$.

In their paper [10], Coleman-Owen introduced the so-called **entropy action** as a scalar function on the product of spaces $B \times \Pi$, defined as follows

$$(4) \quad s(P_t, \mathbf{c}) = \int_0^t \left\{ \frac{h(\tau)}{\theta[\mathbf{c}(\tau)]} + \mathbf{q}[\mathbf{c}(\tau)] \cdot \boldsymbol{\beta}(\tau) \right\} d\tau.$$

The *II law of thermodynamics* is introduced in the following form: the entropy action functional has the "Clausius property", introduced by W.Day as *cycle inequality* (see [10], Sec. 3, or [11]) at least at one state $\mathbf{c}_0 \in B$.

We refer the reader to the cited works for the explicit definition of Clausius property.

By expliciting \mathbf{L} and h from eqs. (1)₁ and (1)₂ respectively, one can write the entropy action (4) as follows

$$\begin{aligned}
 s(P_t, \mathbf{c}) &= \int_0^t \left\{ \frac{\dot{e}}{\theta[\mathbf{c}(\tau)]} - \frac{\mathbf{T} : (\dot{\mathbf{F}}\mathbf{F}^{-1})}{\theta[\mathbf{c}(\tau)]} + \mathbf{q}[\mathbf{c}(\tau)] \cdot \boldsymbol{\beta}(\tau) \right\} d\tau = \\
 &= \int_{\mathbf{c}(\tau)} \left[\frac{1}{\theta[\mathbf{c}(\tau)]} de - \frac{(\mathbf{T}\mathbf{F}^{-T})}{\theta[\mathbf{c}(\tau)]} : d\mathbf{F} + \mathbf{o} \cdot d\boldsymbol{\beta} \right] + \int_0^t \mathbf{q}[\mathbf{c}(\tau)] \cdot \boldsymbol{\beta}(\tau) d\tau = \\
 (5) \qquad \qquad \qquad &= \int_{\mathbf{c}(\tau)} \eta_{CO} + \int_0^t \mathbf{q}[\mathbf{c}(\tau)] \cdot \boldsymbol{\beta}(\tau) d\tau
 \end{aligned}$$

where $\mathbf{c}(\tau) = P_\tau \mathbf{c}(0)$ (with $0 \leq \tau \leq t$) is a curve connecting the states $\mathbf{c}(0), \mathbf{c}(t)$ in the state space B . Here and in the following we use the notation $(\mathbf{F}^{-1})^T = \mathbf{F}^{-T}$. We have introduced the quantity

$$(6) \qquad \qquad \eta_{CO} = \frac{1}{\theta} de - \frac{(\mathbf{T}\mathbf{F}^{-T})}{\theta} : d\mathbf{F} + \mathbf{o} \cdot d\boldsymbol{\beta}$$

in eq.(5) to characterize the 1-form implicitly admitted by Coleman-Owen.

3. A geometric perspective on Irreversible Thermodynamics

In this Section we review the geometrical formulation of irreversible thermodynamics whose basic features were illustrated in our papers [13–15] and further developed in the papers [31,32]. Many applications were made in the papers [17]- [21] and in others which can be found in the references therein.

The II law of thermodynamics entails that a universal arrow of time should exist along which the entropy can only but grow indefinitely. In a sense, entropy "defines" time in thermodynamics. Our geometrical formulation of irreversible processes in thermodynamics, based mainly on a reformulation of Coleman-Owen material element model and "Noll's processes", follows from the idea that the construction of the time variable should come a step before the introduction of the entropy function; i.e. that time should be regarded as an essential independent variable in thermodynamical transformations and, as such, it should be treated on the same footing as the "spatial" ones (i.e. temperature, other extensive variables and so on). Our first step, then, was to replace the thermodynamic state space (where thermodynamic state variables live) by a suitable *thermodynamical bundle* over

the reals, each fibre of it being the space of "instantaneous" thermodynamical state variables. (For a comparison and analysis of this formulation with the Newtonian four-dimensional formulation [33] of Classical Mechanics, see [13]).

Considering a material element [34], it is supposed that an unambiguous definition of its state space can be given (for details see [13]). We introduce then the state space at time t , denoted as B_t , having the structure of a finite dimensional manifold. We define the *thermodynamical bundle* as given by the disjoint union

$$(7) \quad \mathcal{B} = \bigcup_{t \in \mathbb{R}} B_t$$

with the given natural structure of a fibre bundle over the real line \mathbb{R} where time flows [35,36]. In our treatment we assume, for the sake of simplicity, that the instantaneous state space does not vary in time, such that $B_t \simeq B$ for all instants of time t ; then \mathcal{B} is trivial, in this particular case, i.e. it is given by the Cartesian product

$$(8) \quad \mathcal{B} \simeq \mathbb{R} \times B.$$

We remark that this assumption could be relaxed, allowing for instance for phase transitions in the physical system under consideration. According to [34], the abstract space of processes consists of a set Π of functions

$$(9) \quad P_t^i : [0, t] \rightarrow \mathcal{G},$$

where the space \mathcal{G} is a suitable target space suggested by the model, i is a label ranging in an unspecified index set for all allowed processes and $t \in \mathbb{R}$ is the "duration" of the process P_t^i . For specific properties of the set Π , see [13,14]. Then, a continuous function is defined

$$(10) \quad \sigma : \mathbb{R} \times \Pi \rightarrow C^0(B_0, B_t),$$

so that for any instant of time t and for any process $P_t^i \in \Pi$ a continuous mapping called *transformation* (induced by the process) is generated. For any given initial state in the domain of the process, the transformed final state will be called, by an abuse of notation, the *value* of the process (at time t). We define now a function of time in the following way:

$$(11) \quad \lambda_c^i(\tau) = \begin{cases} \mathbf{c} & \text{if } \tau = 0 \\ \sigma_t^i \mathbf{c} & \text{if } \tau \in]0, t] \end{cases}$$

so that we have

$$(12) \quad \lambda_c^i(t) = \sigma_t^i(\mathbf{c}) = \Phi^i(t, \mathbf{c}),$$

with

$$(13) \quad \Phi^i(t, \mathbf{c}) : \mathbb{R} \times B \rightarrow B.$$

The transformation for the system is then a function

$$(14) \quad c : \mathbb{R} \rightarrow \mathbb{R} \times B$$

such that for every local trivialization of the thermodynamic bundle one has

$$(15) \quad c : t \rightarrow (t, \lambda_c^i(t)).$$

With these positions, the transformation is interpreted as a curve in the union of all the state spaces such that it intersects the instantaneous state space just once, i.e. c is a section of the thermodynamic bundle. For details see [13,14].

3.1. Entropy form and comparisons with Coleman-Owen material element model

In this section we apply the general scheme introduced above, to the particular case of a simple material element in order to elucidate the basic features of the methodology and to allow a simpler comparison with Coleman-Owen formulation.

For simple material elements the state space can be given by $B = \{e, \mathbf{F}, \boldsymbol{\beta}\}$, then $B = \mathbb{R} \oplus Lin(V) \oplus V$. The general process P_t is a piecewise continuous function whose values are defined in (3) (for the sake of simplicity an obvious short notation without index is adopted). Thence, the target space turns out to be

$$(16) \quad \mathcal{G} = Lin(V) \oplus \mathbb{R} \oplus V \simeq B$$

so that $B \times \mathcal{G} \simeq TB$.

We introduce three stationary fields

$$(17) \quad \begin{cases} \theta : \mathcal{B} \rightarrow \mathbb{R}^+, \\ \mathbf{T} : \mathcal{B} \rightarrow Sym_2(V), \\ \mathbf{q} : \mathcal{B} \rightarrow V. \end{cases}$$

With position (17)₂, we obtain a response functional on the thermodynamical bundle

$$(18) \quad \tilde{\mathbf{T}} = \mathbf{T} \circ c_t \rightarrow \text{Sym}_2(V),$$

which is the stress determined by the process starting at \mathbf{c} . In the thermodynamical bundle we introduce, in analogy with the entropy action (4), the following integral

$$(19) \quad \int_{\mathbf{c}} \Omega_{\omega} = \int_0^t \left\{ \frac{h(\tau)}{\theta[\mathbf{c}(\tau)]} + \mathbf{q}[\mathbf{c}(\tau)] \cdot \boldsymbol{\beta}(\tau) \right\} d\tau$$

and we call Ω_{ω} the *entropy 1-form* [13,14]. Looking at eqs.(5) and (19), one can easily see that

$$(20) \quad \Omega_{\omega} = \eta_{CO} + \mathbf{q} \cdot \boldsymbol{\beta} dt = \frac{1}{\theta} de - \frac{(\mathbf{T}\mathbf{F}^{-T})}{\theta} : d\mathbf{F} + \mathbf{0} \cdot d\boldsymbol{\beta} + \mathbf{q} \cdot \boldsymbol{\beta} dt.$$

3.2. Integrability (closure) conditions of the entropy form

In general, the 1-form Ω_{ω} is not closed, i.e. $d\Omega_{\omega} \neq 0$. We stress that it is interesting to look at the meaning of "partial integrability" of the entropy form. In general, closure conditions would lead to the appearance of constraints on the attainable states and admissible processes occurring in the physical system under consideration. So, one can analyze constraints placed by the degeneracy of the entropy form; i.e. one can analyze the rank of the introduced 1-form. Here we will look first at the case of extreme degeneration, i.e. closeness of the entropy form (we kindly refer the reader to a forthcoming paper where cases of entropy form of rank different from one are analyzed [32]). The final goal of this analysis is to see which constitutive relations obtained from the closeness conditions simplify the dynamical system under consideration and which restrict the type of admissible processes.

In components the 1-form Ω_{ω} reads

$$(21) \quad \Omega_{\omega} = \omega_{\mu} dq^{\mu} + \omega_0 dt \equiv \omega_A dq^A, \quad (A = 1, 2, 3, 4)$$

where the q^{μ} are the variables in B and $q^0 = t$. From the entropy 1-form, a 2-form can be derived as

$$(22) \quad d\Omega_{\omega} = (\partial_A \omega_B) dq^A \wedge dq^B, \quad (A, B = 1, 2, 3, 4).$$

By applying the usual properties of the exterior differential, one obtains

$$\begin{aligned} d\Omega_\omega &= d\omega_\lambda \wedge dq^\lambda + \omega_0 \wedge dt = \\ (23) \quad &= (\partial_0\omega_0)dt \wedge dq^\lambda + \partial_\mu\omega_0 dq^\mu \wedge dq^\lambda + \partial_\lambda\omega_0) dq^\lambda \wedge dt, \quad (\lambda, \mu = 1, 2, 3) \end{aligned}$$

which can be written as

$$(24) \quad d\Omega_\omega = (\partial_0\omega_\lambda - \partial_\lambda\omega_0)dt \wedge dq^\lambda + \frac{1}{2}(\partial_\mu\omega_\lambda - \partial_\lambda\omega_\mu)dq^\mu \wedge dq^\lambda, \quad (\lambda, \mu = 1, 2, 3).$$

From relation (24) one can obtain the closure conditions Ω_ω in the case of a simple material element

$$(25) \quad \partial_{\mathbf{F}}\left(\frac{1}{\theta}\right) = -\partial_e\left(\frac{\mathbf{TF}^{-1}}{\theta}\right),$$

$$(26) \quad -\partial_t\left(\frac{\mathbf{TF}^{-1}}{\theta}\right) = \partial_{\mathbf{F}}(\mathbf{q} \cdot \boldsymbol{\beta}),$$

$$(27) \quad \partial_t\left(\frac{1}{\theta}\right) = \partial_{\boldsymbol{\beta}}(\mathbf{q} \cdot \boldsymbol{\beta}),$$

$$(28) \quad \partial_{\boldsymbol{\beta}}\left(\frac{\mathbf{TF}^{-1}}{\theta}\right) = \partial_{\boldsymbol{\beta}}\left(\frac{1}{\theta}\right) = \partial_{\boldsymbol{\beta}}(\mathbf{q} \cdot \boldsymbol{\beta}) = \mathbf{0}.$$

Relations (25)-(28) give necessary conditions for the existence of a potential for the entropy 1-form. The first three equations express a sort of "irrotationality" of the entropy 1-form Ω_ω . The last equation (28) gives three conditions expressing the physical requirements that the involved quantities are independent on the gradient of temperature ($\partial_{\boldsymbol{\beta}}\left(\frac{1}{\theta}\right) = \mathbf{0}$ is trivially satisfied because of the hypothesis). In particular the last condition says that the projection of the heat flux field along the direction of the gradient of temperature is constant with respect to the same gradient.

As already said in the introduction, more complex material media have been considered in many applications of the theory; the most relevant examples will be introduced and discussed in a forthcoming paper [30] companion of the present one.^a

To close the dynamical system for the state variables one has to consider the quantities $\mathbf{L} = \nabla \mathbf{v}, \nabla \cdot \mathbf{q}, \gamma$ (and the radiation heat source r whenever

^aLooking at (5) one can see that closure conditions of the part η_{CO} of the 1-form Ω_ω , i.e. "partial integrability of the entropy form", is the direct consequence of the II law in Coleman-Owen formulation. Viceversa, if the 1-form on the right side of (5) is closed, then the potential S of the closed and, therefore, locally exact form, is the upper potential of the entropy action functional (4).

it is present) as given, or one has to use specific phenomenological equations, additional constitutive relations or additional dynamical equations. In fact, if a process P_t is given, the resolution of the dynamical system (1) is not very difficult: the last equation of the system can be solved by direct integration $\boldsymbol{\beta}(t) = \int_0^t \boldsymbol{\gamma}(\tau) d\tau$, the first equation is a linear system with a time-dependent matrix and, when these two equations are solved, one can substitute \mathbf{F} and $\boldsymbol{\beta}$ into the second equation obtaining a one-dimensional nonlinear equation. Yet, as stressed in the paper [31], this convenience is illusory in practical situations where usually the process P_t is unknown. It is one of the goals of our formulation to analyze which constitutive relations one would add to the material element model in order to close the system of dynamical equations. We will introduce an example in Section 5.

4. Extended Thermodynamical Phase Space

In this Section we introduce the entropy and energy forms obtained by localizing the balance equations of continuum thermodynamics in order to show that the Extended Thermodynamical Phase Space (ETPS) of Caratheodory-Hermann-Mrugala [2-5,37] is the natural space where these forms are defined.

Balance equations of mass, of linear momentum and of total or internal energy represent the total balance system of equations of thermoelasticity provided that constitutive relations are known.

The internal energy balance has the form

$$(29) \quad \rho \dot{e} = p_{(i)} + (r - \nabla \cdot \mathbf{q}) = \mathbf{T} : \mathbf{D} + (r - \nabla \cdot \mathbf{q}),$$

where $p_{(i)} = \mathbf{T} : \mathbf{D}$ is the work power of the stress and $\mathbf{D} = \mathbf{L}_{sym}$ is the symmetrized strain rate tensor. Here we also have used the angular momentum balance equation in the form $\mathbf{T}^T = \mathbf{T}$. Substituting here \mathbf{D} in the form $\mathbf{D} = \mathbf{L}_{sym} = (\dot{\mathbf{F}}\mathbf{F}^{-1})_{sym}$ and using the symmetry property of the stress tensor \mathbf{T} , we can rewrite the energy balance equation in the form of a Pfaff equation as

$$(30) \quad \rho de - (\mathbf{T}\mathbf{F}^{-T}) : d\mathbf{F} - (r - \nabla \cdot \mathbf{q})dt = 0.$$

Further, we can rewrite the energy balance equation (30) in the form

$$(31) \quad de - \frac{1}{\rho} \mathbf{P} : d\mathbf{F} - \frac{1}{\rho} (r - \nabla \cdot \mathbf{q})dt = 0,$$

where $\mathbf{P} = \mathbf{TF}^{-T}$ is the first Piola-Kirchhoff stress tensor. The balance equation of entropy is taken in the standard form

$$(32) \quad \rho \dot{s} + \nabla \cdot \mathbf{J}_s = \dot{\Xi} + \frac{r}{\theta},$$

where s is specific entropy density, \mathbf{J}_s is the entropy flux, $\dot{\Xi}$ is the *entropy production rate* that, due to the II law of thermodynamics and the entropy principle, is a nonnegative function of the dynamical variables.

We also admit the relation between the entropy flux \mathbf{J}_s and the heat flux \mathbf{q} in the usual form

$$(33) \quad \mathbf{J}_s = \theta^{-1} \mathbf{q} + \mathbf{k},$$

where \mathbf{k} is the extra entropy flux [38]. Plugging in the expression (33) for the entropy flux, we rewrite eq.(32) in the form

$$(34) \quad \dot{s} + \frac{1}{\rho} \nabla \cdot (\theta^{-1} \mathbf{q}) + \frac{1}{\rho} \nabla \cdot \mathbf{k} = \dot{s} + \frac{1}{\theta \rho} \nabla \cdot \mathbf{q} + \frac{1}{\rho} \mathbf{q} \cdot \nabla \theta^{-1} + \frac{1}{\rho} \nabla \cdot \mathbf{k} = \frac{1}{\rho} \dot{\Xi} + \frac{r}{\rho \theta}.$$

Expressing $(r - \nabla \cdot \mathbf{q})$ from eq.(29) and using it in (34), we obtain the entropy balance in the form (using also the definition of Piola-Kirchhoff first stress tensor)

$$(35) \quad \dot{s} + \frac{1}{\rho} \mathbf{q} \cdot \nabla \theta^{-1} = \frac{1}{\rho} \dot{\Xi} + \frac{1}{\rho \theta} [\rho \dot{e} - p_{(i)}] - \frac{1}{\rho} \nabla \cdot \mathbf{k}.$$

By using the explicit expression for the work power of stress given by $p_{(i)} = (\mathbf{TF}^{-T}) : \dot{\mathbf{F}} = \mathbf{P} : \dot{\mathbf{F}}$, eq.(35) can be written as

$$(36) \quad \dot{s} - \frac{1}{\theta} \dot{e} + \frac{1}{\theta \rho} \mathbf{P} : \dot{\mathbf{F}} + \frac{1}{\rho} \mathbf{q} \cdot \nabla \theta^{-1} + \frac{1}{\rho} \nabla \cdot \mathbf{k} = \frac{1}{\rho} \dot{\Xi},$$

or in the form of a Pfaff equation as follows

$$(37) \quad ds - \frac{1}{\theta} de + \frac{1}{\theta \rho} \mathbf{P} : d\mathbf{F} + \frac{1}{\rho} (\mathbf{q} \cdot \nabla \theta^{-1} - \dot{\Xi} - \nabla \cdot \mathbf{k}) dt = 0.$$

Eq. (37) can be written also in the form of an energy balance equation as

$$(38) \quad de - \theta ds - \frac{1}{\rho} \mathbf{P} : d\mathbf{F} - \frac{\theta}{\rho} (\mathbf{q} \cdot \nabla \theta^{-1} - \nabla \cdot \mathbf{k} - \dot{\Xi}) dt = 0.$$

By using the Pfaff equation (37) and integrating along the curve $\mathbf{c}(\tau)$ in $\mathbb{R} \times B$ one obtains

$$(39) \quad s[c(t)] - s[c(0)] = \int_{\mathbf{c}(\tau)} \left[\frac{1}{\theta} \dot{e} + \frac{1}{\theta \rho} \mathbf{P} : \dot{\mathbf{F}} - \frac{1}{\rho} (\mathbf{q} \cdot \nabla \theta^{-1} + \nabla \cdot \mathbf{k}) \right] d\tau + \int_{\mathbf{c}(\tau)} \dot{\Xi} d\tau$$

The last term in eq. (39) represents the *internal entropy production*. Comparing this last result with the analogous one obtained by Coleman-Owen, one can notice that the entropy function s obtained by localizing the balance equations of continuum thermodynamics coincides with the entropy function S of Coleman-Owen formulations if the thermodynamical system is at homogeneous temperature ($\nabla \theta^{-1} = \mathbf{0}$) and if the internal entropy production vanishes ($\dot{\Xi} = 0$) (we remind that in Coleman-Owen model the classical relation between the entropy flux and the heat flux $\mathbf{J}_s = \frac{\mathbf{q}}{\theta}$ is assumed so that $\mathbf{k} = \mathbf{0}$, but this fact those not affect the comparison). Moreover, in the same physical conditions, eq. (39) is the Gibbs form used by Mrugala [3–5] to introduce the *contact structure in the thermodynamical phase space* of homogeneous thermodynamical systems. The introduction of fluxes and gradients admits non-homogeneities and allows irreversibility of thermodynamical processes.

The obtained results allow us to introduce the ETPS with the following coordinates

$$(40) \quad \mathcal{P} = \left\{ s, e, \theta, \frac{\mathbf{P}}{\rho}, \mathbf{F}, \frac{\theta}{\rho} (\mathbf{q} \cdot \nabla \theta^{-1} - \dot{\Xi}), t \right\}$$

where we dropped out the extra entropy flux \mathbf{k} for the sake of simplicity.

We use the following notation or the the energy form, introduced in eq. (38)

$$(41) \quad E = de - \theta ds - \frac{1}{\rho} \mathbf{P} : d\mathbf{F} - \frac{\theta}{\rho} (\mathbf{q} \cdot \nabla \theta^{-1} - \nabla \cdot \mathbf{k} - \dot{\Xi}) dt$$

so that the I law of thermodynamics can be expressed by the condition

$$(42) \quad E[\dot{\mathbf{c}}] = 0,$$

for any admissible thermodynamic process. In the space \mathcal{P} , also the entropy form Ω_ω is defined so that the II law of thermodynamics can be expressed as

$$(43) \quad (ds - \Omega_\omega)[\dot{\mathbf{c}}] \geq 0.$$

One can notice that the 1-form given by $\omega = ds - \Omega_\omega$ is written in the standard form

$$(44) \quad ds - \sum_{i=1}^n p_i q^i$$

in the $(2n + 1)$ vector space with coordinates $[s, q^i, p^i (i_1, \dots, n)]$. By using this fact, in the paper [31] we presented our geometrical formalism as a modification of the contact space of Homogeneous Thermodynamics obtained by adding "inhomogeneous variables" (fluxes and gradients) and the time t .

Let $\mathcal{P} = (R^{2n+1}, \omega)$ be the standard contact space with the contact form given by (44), then to any function $K \in C^\infty(R^{2n+1})$, one can associate a vector field ξ_K , called the contact Hamiltonian vector field [33,37]. The vector field ξ_K is defined by the two conditions:

$$(45) \quad \omega(\xi_K) = K$$

$$(46) \quad i_{\xi_K} d\omega = -DK$$

where $Df = df - (\xi \cdot f)\omega$ is the "contact covariant differential" of a function f . More specifically, the Hamiltonian vector field ξ_K is explicitly given by

$$(47) \quad \xi_K = (K - p_l K_{,p_l} \partial_s + (K_{,x^l} + p_l K_{,s}) \partial_{p_l} - K_{,p_l} \partial_{x_l}.$$

The proof of relation (47) can be found in [32].

Examples of applications to physical systems of this Hamiltonian formulation will be given in a forthcoming paper [32].

5. Constitutive relations obtained from closure conditions

In this Section we describe an example of constitutive relations derived from the closure conditions of the entropy form in the case of extreme degeneracy of it (rank of the entropy form equals to 1).

If $d\Omega_\omega = 0$, then locally (and globally in a simply connected space), there exists a potential U , function of the state variables, such that

$$(48) \quad \eta = dU, \quad \int_{\mathbf{c}(\tau)} \eta = U[\mathbf{c}(t)] - U[\mathbf{c}(0)]$$

The function U of the state variables (including time) is defined up to an arbitrary constant. The potential U is defined by the entropy flux

(and the radiation r if it is introduced) and, as a result, coincides with the entropy S of Coleman-Owen formulation (up to a constant) only when the entropy production in an admissible process \mathbf{c} is zero. In the integrable case the potential U and the entropy function S exist as functions in the state space.

We introduce now the notation

$$(49) \quad \kappa[\mathbf{c}(t)] = S[\mathbf{c}(t)] - U[\mathbf{c}(t)]$$

for the difference of the Coleman-Owen upper potential and the potential derived from the closure of Ω_ω . Then, the entropy balance in its integral form (39) and the II law of thermodynamics can be written under the form

$$(50) \quad \kappa[\mathbf{c}(t)] - \kappa[\mathbf{c}(0)] = \int_0^t \frac{1}{\rho} \dot{\Xi}[\mathbf{c}(\tau)] dt \geq 0.$$

Thus, if the entropy form Ω_ω is closed, the II law of thermodynamics has the form:

Along a thermodynamically admissible process $\mathbf{c}(\tau)$, the value of the function $\kappa[\mathbf{c}(\tau)]$ is nondecreasing.

In particular, this excludes cyclic processes except those without entropy production.

It is interesting to see what form does Clausius-Duhem inequality take in the case when the entropy form Ω_ω is closed in the restricted state space $B' = \{e, \mathbf{F}\}$. The function U is the time-dependent entropy form potential defined in the space of the basic variables. From the closure conditions one can easily obtain the following constitutive relations

$$(51) \quad \begin{cases} \theta^{-1} = \partial_e U + c_1(t), \\ \mathbf{P} = \mathbf{T}\mathbf{F}^{-T} = -\rho \frac{\partial_{\mathbf{F}} U + c_2(t)}{\partial_e U + c_1(t)}, \\ (\mathbf{q} \cdot \boldsymbol{\beta}) = \partial_t U + \dot{c}_2(t) : \mathbf{F} + \dot{c}_1 e + c_3(t). \end{cases}$$

Inverting the first two of these relations we obtain the internal energy e as a definite function of the state variables.

To see this we use the constitutive relations (51) in the following local form of the entropy balance

$$\dot{s} \geq \theta^{-1} (-\rho^{-1} \nabla \cdot \mathbf{q}) + \mathbf{q} \cdot \boldsymbol{\beta}$$

to obtain

$$(52) \quad \dot{s} \geq [\partial_e U + c_1(t)] (-\rho^{-1} \nabla \cdot \mathbf{q}) + [\partial_t U + \dot{c}_2(t) : \mathbf{F} + \dot{c}_1 e + c_3(t)].$$

Comparing this form of Clausius-Duhem inequality with the one in [38] Sec. 3, we see that the potential $U(e, \mathbf{F}, t)$ partly plays the role of the dissipative potential $\mathcal{D}(\mathcal{A})$ introduced by G.A. Maugin in treating the dissipative inequality [38].

Using the constitutive relations (51) in the dynamical system of Coleman-Owen (1) we obtain it in the form

$$(53) \quad \begin{cases} \dot{\mathbf{F}} = \mathbf{L}\mathbf{F}, \\ \dot{e} = \frac{\partial_F U + \mathbf{c}_2(t)}{\partial_e U + \mathbf{c}_1(t)} : \dot{\mathbf{F}} - \rho^{-1} \nabla \cdot \mathbf{q}, \\ \dot{\beta} = \gamma. \end{cases}$$

The last condition in (53) states that the time derivative of the temperature vanishes if the gradient of the inverse of temperature (β) is identically zero. This shows that the temperature gradient in a simple material element changes only due to heat conduction. Correspondingly the changes of temperature by other dissipative processes (without heat conduction) are excluded and this represents an example of restrictions on the type of thermodynamical processes induced by the closure conditions.

Closure conditions can be used to rewrite the dynamical system under consideration in term of the entropy form potential and to determine the constitutive relations among the dynamical variables of the model. An example is given in [31] in the case of deformable ferroelectric crystals. Some other interesting examples will be given in [32].

6. Conclusions

We reviewed a new geometrical formulation of the thermodynamics of irreversible processes first introduced a decade ago by the authors and from then on applied to many physical systems. This paper represents the first part of the review where we introduced the general concepts of this geometrical formulation with only few simple examples; a second part, will be devoted to the illustration of the most significative examples and applications of the theory such as deformable dielectrics including ferroelectric and piezoelectric crystals and deformable ferromagnetic crystals in the framework of quasimagnetostatics in insulators.

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