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MATERIAL ELEMENT MODEL AND THE GEOMETRY
OF THE ENTROPY FORM

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In this work we analyze and compare the model of the material (elastic) element and
the entropy form developed by Coleman and Owen with that one obtained by localizing
the balance equations of the continuum thermodynamics. This comparison allows one to
determine the relation between the entropy function S of Coleman–Owen and that one
imported from the continuum thermodynamics. We introduce the Extended Thermody-
namical Phase Space (ETPS) $\mathcal{P}$ and realize the energy and entropy balance expressions
as 1-forms in this space. This allows us to realizes I and II laws of thermodynamics as
conditions on these forms. We study the integrability (closure) conditions of the entropy
form for the model of thermoelastic element and for the deformable ferroelectric crystal
element. In both cases closure conditions are used to rewrite the dynamical system of the
model in term of the entropy form potential and to determine the constitutive relations
among the dynamical variables of the model.

In a related study (to be published) these results will be used for the formulation of
the dynamical model of a material element in the contact thermodynamical phase space
of Caratheodory and Hermann similar to that of homogeneous thermodynamics.

Keywords: Irreversible thermodynamics; contact structure; entropy form.

1. Introduction

The goal of this work is to investigate the material element model (ME-model) and to exploit the geometrical meaning of the "entropy form". This form was implicitly introduced by Coleman and Owen ([1–3]) in their study of the "entropy action" and, subsequently, using a different approach, applied to a variety of physical systems in [4–9].

In their work, Coleman and Owen developed the basic dynamical scheme of thermodynamical systems postulating the basic properties of states and processes (of Noll's type) in a thermodynamical system, introduced the abstract notion of action, Clausius and conservation properties of actions, stagnant and relaxed states, etc. The geometrical structure of their model was later reformulated in terms of the "thermodynamical bundle" (see [5–7]); the second part of their work is devoted to illustrations and applications of their scheme to the theory of "simple material elements", including the "thermoelastic elements". In particular, the authors have introduced the "*entropy form*", defined in the appropriate *state space* (extended by the time variable) that determines the change of entropy produced by the flux along a process represented by a curve in the state space.

Applying the energy balance and some kinematical relations for the rate of change of the involved dynamical variables, Coleman and Owen rewrite the entropy increase due to the flux as the integral of a 1-form in the state space. *The entropy function* is then defined as an *upper potential of the entropy form.* Existence of this upper potential follows from the II law of thermodynamics formulated as the "Clausius property" of the entropy action. This condition leads to the closure (integrability) of a *part of the entropy form.* In addition, closure conditions provide a set of constitutional relations for participating fields, see Sec. 2.

In the works [5–7, 9] another approach to the entropy form was developed. The entropy form appears as the integral of the entropy balance law complemented by the use of the internal energy law. The study of the entropy form and of the corresponding constitutive relations given by the condition of closure of the entropy form for different thermodynamical systems were done in these (and some other) works.

In the present paper we analyze and compare the models of the material (elastic) element and the entropy form developed by Coleman and Owen with that one obtained by localizing the balance equations of continuum thermodynamics. This allows one to determine the relation between the entropy function S of Coleman-Owen and the one induced by the entropy density function s of continuum thermodynamics.

First goal of this study is to determine which part of the constitutive relations for the dynamical system of the ME-model can be obtained from integrability conditions of the entropy form and which additional informations from continuum

thermodynamics should be used in order to get a closed system of dynamical equations for the ME-model. Second goal is to analyze the physical meaning of new (in comparison to those coming from continuum thermodynamics) relations separating *additional constitutive relations* from conditions *restricting the type of the processes* described by the ME-model.

In Sec. 2, we revisit the "basic model" of a (thermoelastic) *material element* of Coleman–Owen including the entropy form and we study the constitutive relations that follow from the II law of thermodynamics in the form of Clausius conditions.

In Sec. 3, we review the approach to the ME-model starting from the entropy and energy balance laws of continuum thermodynamics, we introduce the energy form, the entropy form and we formulate the II law of thermodynamics in terms of the entropy form and (in the integrable case) in terms of its potential. We compare the obtained results with those of the Coleman–Owen model. We introduce the space X of basic fields containing time instead of the field $\boldsymbol{\beta}$ of the Coleman–Owen model. The *extended thermodynamical phase space* (*ETPS*) $\mathcal{P}$ of Caratheodory-Hermann–Mrugala for the "basic model" of a thermoelastic point is then defined as the natural space where the energy and the entropy forms are defined. Energy form is interpreted as a (possibly degenerate) contact structure whose nullity on the physical processes constitutes the fulfillment of the I law of thermodynamics in our ME-model.

In Sec. 4, the integrability conditions of the entropy form in the original state space of Coleman–Owen (with time t added) are studied and compared with the constitutive relations obtained by Coleman and Owen. We determine the dynamical part of the integrability conditions entering the dynamical equations and the part delivering the constitutive relations between the dynamical variables of the model.

In Sec. 5, we work out the same program for a more complex situation of deformable ferroelectric crystals [9] determining the basic state space, the extended thermodynamical state space and analyzing the integrability conditions for the entropy form.

One can readily observe a strong similarity of the model of the material element here with the geometrical formalism of homogeneous thermodynamics ([10, 11], etc.). In fact one can identify the phase space of a material element with the extended (by time and its dual variable as well as some other flux/gradient variables) version of the thermodynamical phase space $\mathcal{P}$ (ETPS). In this approach the entropy form appears as the dynamical part of the canonical contact form in this space. This allows one to formulate the geometrical theory of material elements with the corresponding energy and entropy forms in terms similar to those of homogeneous thermodynamics [11, 12]. These similarities will be exploited in a forthcoming work for the dynamical modeling of processes in the extended thermodynamical phase space satisfying the I and II laws of thermodynamics.

2. Coleman–Owen Model, Entropy Action and the II Law of Thermodynamics

In this section we review the model of the material elastic element which is the basic example in the theory of Coleman and Owen [1]. We are doing this in the form convenient for comparison with the construction of the entropy form obtained by the entropy and the internal energy balances of continuum thermodynamics which will be done in Sec. 3. We remark that we are using some notations standard in continuum thermodynamics instead of those of the work [1].

2.1. *Simple material element model*

Simple material element $(\Sigma, \Pi; \theta, \boldsymbol{\sigma}, \mathbf{q})$ is defined by the following set of data ([1, Secs. 9 and 10]):

(1) Basic state space Σ of dynamical variables $\Sigma = \{\mathbf{F}, \epsilon, \boldsymbol{\beta}\}$; elements of the state space will be denoted by $\mathbf{c}$. Here $\mathbf{F}$ is the deformation gradient tensor of the material element (point), ϵ is the internal energy scalar, $\boldsymbol{\beta} = -\frac{1}{\rho}\nabla\theta^{-1}$ is a vector characterizing the temperature gradient in a material element and ρ is the specific mass density that is considered given. Notice that the temperature θ itself is present in the scheme as function of the basic variables.

(2) Continuous (constitutive) functions on the state space

$$\begin{cases} \text{Temperature scalar } \theta : \Sigma \to R^+, \\ \text{Stress tensor } \boldsymbol{\sigma} : \Sigma \to \mathrm{Sym}_2(V), \\ \text{Heat flux vector } \mathbf{q} : \Sigma \to V, \end{cases} \tag{1}$$

where $V = E^3$ is the physical Euclidean 3-dim vector space and $\boldsymbol{\sigma}$ is the Cauchy stress tensor.

(3) Space Π of "Noll's processes": piecewise continuous functions of time $P_t : [0, t] \ni \tau \to [\mathbf{L}(\tau), h(\tau), \boldsymbol{\gamma}(\tau)]$, with values in the product of vector spaces $\mathrm{End}(V) \times \mathbf{R} \times V$.

Here $\mathbf{L}(\tau)$ is the (1,1)-tensor of *rate of deformation*, $h(\tau) = r - \frac{\mathrm{div}(\mathbf{q})}{\rho}$ is the *rate of heat absorbtion per unit of mass* (r being the supply of heat by radiation) and $\boldsymbol{\gamma}$ is the material time derivative of the vector $\boldsymbol{\beta}(\tau)$,

(4) System of dynamical equations for the basic variables $\mathbf{c}(\tau) = (\epsilon(\tau), \mathbf{F}(\tau), \boldsymbol{\beta}(\tau)), \tau \in [0, t)$ defined by the choice of a process P_t (dot here is the time derivative $\frac{d}{d\tau}$)

$$\begin{cases} \dot{\mathbf{F}} = \mathbf{L}\mathbf{F}, \\ \dot{\epsilon} = \boldsymbol{\sigma}[\mathbf{c}(\tau)] : \mathbf{L}(\tau) + h(\tau), \\ \dot{\boldsymbol{\beta}} = \boldsymbol{\gamma}. \end{cases} \tag{2}$$

Equation $(2)_2$ is the I law of thermodynamics. Equation $(2)_1$ is the usual relation between the deformation gradient and the rate of deformation and $(2)_3$ is just a position. Further the symbol ":" is used for total tensor contraction.

2.2. *Entropy action, Clausius form of II law and the upper potential S*

Entropy action is a scalar function on the product of spaces $\Sigma \times \Pi$ and is defined as follows:

$$s(P_t, \mathbf{c}) = \int_0^t \frac{h(\tau)}{\theta[\mathbf{c}(\tau)]} d\tau + \int_0^t \mathbf{q}[\mathbf{c}(\tau)] \cdot \boldsymbol{\beta}(\tau) d\tau. \tag{3}$$

Data 1.- 4. of the previous subsection are supposed to satisfy the II law of Thermo-dynamics in the following form: the entropy action functional has the "**Clausius property**", introduced by Day under the name of *cycle inequality* (see [1, Sec. 3] or [2]) at least at one state $\mathbf{c}_0 \in \Sigma$. Since in this work we are using only corollaries of this property we refer the reader to the cited works for the explicit definition of Clausius property.

Expliciting h and $\mathbf{L}$ from the system (2) we get

$$\begin{cases} \mathbf{L} = \dot{\mathbf{F}}\mathbf{F}^{-1}, \\ h = \dot{\epsilon} - \boldsymbol{\sigma} : (\dot{\mathbf{F}}\mathbf{F}^{-1}). \end{cases} \tag{4}$$

Using (4) in the formula for the entropy action (3) we rewrite it in the form

$$\begin{aligned} s(P_t, \mathbf{c}) &= \int_0^t \frac{\dot{\epsilon}}{\theta[\mathbf{c}(\tau)]} d\tau - \int_0^t \frac{\boldsymbol{\sigma} : (\dot{\mathbf{F}}\mathbf{F}^{-1})}{\theta[\mathbf{c}(\tau)]} d\tau + \int_0^t \mathbf{q}[\mathbf{c}(\tau)] \cdot \boldsymbol{\beta}(\tau) d\tau \\ &= \int_{\mathbf{c}(\tau)} \left[\frac{1}{\theta[\mathbf{c}(\tau)]} d\epsilon - \frac{(\mathbf{F}^{-T}\boldsymbol{\sigma})}{\theta[\mathbf{c}(\tau)]} : d\mathbf{F} + \mathbf{0} \cdot d\boldsymbol{\beta} \right] + \int_0^t \mathbf{q}[\mathbf{c}(\tau)] \cdot \boldsymbol{\beta}(\tau) d\tau, \end{aligned} \tag{5}$$

where $\mathbf{c}(\tau) = P_\tau \mathbf{c}(0)(0 \leq \tau \leq t)$ is a curve in the state space Σ connecting states $\mathbf{c}(0), \mathbf{c}(t)$ and we have used the notation $(\mathbf{F}^{-1})^T = \mathbf{F}^{-T}$. In this form, the entropy action looks as the exterior 1-form

$$\begin{aligned} \eta' &= \frac{1}{\theta[\mathbf{c}(\tau)]} d\epsilon - \frac{1}{\theta[\mathbf{c}(\tau)]} (\mathbf{F}^{-T}\boldsymbol{\sigma}) : d\mathbf{F} + \mathbf{q}[\mathbf{c}(\tau)] \cdot \boldsymbol{\beta}(\tau) d\tau \\ &= \eta_{CO} + \mathbf{q}[\mathbf{c}(\tau)] \cdot \boldsymbol{\beta}(\tau) d\tau \end{aligned} \tag{6}$$

integrated over the curve in the state space (with time included as an independent variable). Here we have introduced the notation η_{CO} for the sum of the first two terms in the first expression of (6). The 1-form η', explicitly introduced in the works [5, 6], was named there *entropy form*. Below we will introduce a similar form in a different way, starting from the entropy balance of continuum thermodynamics.

From the II law of thermodynamics in this (cyclic) form several important corollaries follow ([1, Sec. 9]).

(1) (Theorem 9.1) If for a state $\mathbf{c}_0 = (\mathbf{F}_0, \epsilon_0, \boldsymbol{\beta}_0)$ there exists a process P_t with $h(\tau) = 0$ such that $P_t \mathbf{c}_0 = \mathbf{c}_0$, then

$$\mathbf{q}(\mathbf{c}_0) \cdot \boldsymbol{\beta}_0 \leq 0, \tag{7}$$

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(2) (Theorem 9.3) A simple material element obeys the II law of Thermodynamics
if and only if the action functional s has an *upper potential*, i.e. a function $S(\mathbf{c})$
on the state space Σ which satisfies the following properties:

(a) Function S is upper semicontinuous,
(b) The domain of the function S is closed under the s-approach [1] and contains
a state $\mathbf{c}_0$ occurring in the II law,
(c) if $\mathbf{c}, \mathbf{c}'$ are in the domain of function S, then, for any process P_t such that
$\mathbf{c}' = P_t \mathbf{c}$,

$$S(\mathbf{c}') - S(\mathbf{c}) \geq \int_0^t \frac{h(\tau)}{\theta[\mathbf{c}(\tau)]} d\tau + \int_0^t \mathbf{q}[\mathbf{c}(\tau)] \cdot \boldsymbol{\beta}(\tau) d\tau. \tag{8}$$

Remark 1. If the function $S(\mathbf{c})$ is differentiable then inequality (8) is equivalent
to the local Clausius–Duhem inequality

$$\dot{S} \geq \frac{h}{\theta} + \mathbf{q} \cdot \boldsymbol{\beta}. \tag{9}$$

A simple material element is called an **elastic element** if, in addition to the
4 conditions listed in the previous subsection some additional requirements are
fulfilled. We require the space of states Σ to be an open subset in the vector space
where $(\mathbf{F}, \epsilon, \boldsymbol{\beta})$ take place, constitutive functions $\theta, \mathbf{q}$ to be continuous and $\boldsymbol{\sigma}$ to
be continuously differentiable functions of their arguments and we state that for a
given process P_t and a given initial state $\mathbf{c}$ the dynamical system (2) has a local
solution $\mathbf{c}(\tau) \in \Sigma$ such that $P_t \mathbf{c} = \mathbf{c}(t)$.

For an elastic material element the upper potential S is differentiable and unique
([1, Sec. 10, p. 50]).

The existence of the upper potential $S(\mathbf{c})$ called the *entropy function* was proved
using very general results of Secs. 3 and 5 of the work [1]. Yet, for the elastic material
element the upper potential $S(\mathbf{c})$ appeared in the proof of Theorem 10.5 in [1] p. 52,
is the potential of the 1-form η_{CO} on the connected state space Σ *determined by
the first two terms of the form η'*, see Eq. (6), in the sense that for an arbitrary
polygonal curve $\mathbf{c}(\tau)$ in Σ started at the state $\mathbf{c}(0)$, one has

$$S[\mathbf{c}(t)] - S[\mathbf{c}(0)] = \int_0^t \eta_{CO}[\mathbf{c}(\tau)]$$
$$= \int_{\mathbf{c}(\tau)} \left[\frac{1}{\theta[\mathbf{c}(\tau)]} d\epsilon - \frac{1}{\theta[\mathbf{c}(\tau)]} (\boldsymbol{\sigma} \mathbf{F}^{-T}) : d\mathbf{F} \right], \tag{10}$$

or, infinitesimally,

$$dS = \frac{1}{\theta[\mathbf{c}(\tau)]} d\epsilon - \frac{1}{\theta[\mathbf{c}(\tau)]} (\boldsymbol{\sigma} \mathbf{F}^{-T}) : d\mathbf{F} + \mathbf{0} \cdot d\boldsymbol{\beta}. \tag{11}$$

As a result, for a curve $\mathbf{c}(\tau) = P_\tau \mathbf{c}$ in the state space Σ obtained from the point
$\mathbf{c}$ by the action of a process P_t, one has for the entropy action s

$$s(P_t, \mathbf{c}) = S[\mathbf{c}(t)] - S[\mathbf{c}(0)] + \int_0^t \mathbf{q} \cdot \boldsymbol{\beta} d\tau. \tag{12}$$

Thus, closure conditions of the part η_{CO} of the 1-form η' — i.e. "*partial integrability of the entropy form η'*" — is the direct consequence of the II law in Coleman–Owen formulation. Viceversa, if the 1-form on the right side of (11) is closed and at the same time, the inequality (7) takes place, then the potential S of the closed and, therefore, locally exact form, is the upper potential of the entropy action functional (3).

2.3. *Constitutive relations obtained as consequences of the partial integrability of the entropy form*

Using these additional properties, the following constitutive relations follow from the proof of the corresponding version of Theorems (9.1) and (9.3) demonstrated in [1]:

(1) (Theorem 10.3) If an elastic element $(\Sigma, \Pi; \theta, \boldsymbol{\sigma}, \mathbf{q})$ satisfies the II law of thermodynamics, then for all states $(\mathbf{F}, \epsilon, \boldsymbol{\beta}) \in \Sigma$,

$$\mathbf{q}(\mathbf{F}, \epsilon, \boldsymbol{\beta}) \cdot \boldsymbol{\beta} \le 0. \tag{13}$$

It follows from this that $\mathbf{q}(\mathbf{F}, \epsilon, \mathbf{0}) = \mathbf{0}$.

(2) (Theorem 10.5) If an elastic element $(\Sigma, \Pi; \theta, \boldsymbol{\sigma}, \mathbf{q})$ satisfies the II law of thermodynamics, then the upper potential S (defined above) is unique, is a continuously differentiable function $S(\mathbf{c}) \in C^1(\Sigma)$ and one has

$$\begin{cases} \partial_\epsilon S(\mathbf{c}(\tau)) = \theta(\mathbf{c}(\tau))^{-1}, \\ \boldsymbol{\sigma}(\mathbf{c}) = -\theta(\mathbf{c})[\partial_{\mathbf{F}} S]\mathbf{F}^T, \\ \partial_{\boldsymbol{\beta}} S = 0. \end{cases} \tag{14}$$

It follows from these properties that temperature θ and Cauchy stress tensor $\boldsymbol{\sigma}$ are functions of the dynamical variables ϵ and $\mathbf{F}$ but do not depend on $\boldsymbol{\beta}$.

The fact that the entropy function exists (and for an elastic element is unique) as a function of state in such a general scheme is the remarkable result.

More than this, *if* a process P_t is given and *if* the constitutive functions (1) are specified, the dynamical system (2) for state variables seems quite elementary: the last equation can be solved simply by integration: $\boldsymbol{\beta}(\tau) = \int_0^\tau \boldsymbol{\gamma}(s)ds$, the first equation is a linear system with time-dependent matrix and its numerical (and in some situations analytical) solution is not difficult. When these two equations are solved, one can substitute $\mathbf{F}(\tau)$ and $\boldsymbol{\beta}(\tau)$ into the second equation which becomes the one-dimensional nonlinear equation $\dot{\epsilon} = f(\epsilon, t)$.

Yet, this convenience is illusory in practical situations where one does not know functions (1) and where the process P_t is also unknown. In order to apply the material element model to practical situations one should be able to determine the dynamical behavior of the state variables (here $\mathbf{F}, \epsilon, \boldsymbol{\beta}$) *from their initial conditions.* Thus, one needs to complete the dynamical system (2) by specifying the quantities $\mathbf{L}, \boldsymbol{\gamma}, \mathbf{F}$ and the constitutive fields as well. It is the goal of the present work to analyze

the material element model in order to determine which constitutive relations one
has to add to the model to close system (2).

3. Localization of the Balance Equations of Continuum Thermodynamics: Energy and Entropy Forms

An approach to the ME-model and an entropy form different from the one present in
the theory of Coleman–Owen was suggested in [6] and applied to different physical
systems in works [5, 7, 9] etc. Starting point of this approach are the balance
equations of continuum thermodynamical systems. More specifically, the entropy
form was constructed starting from the entropy and internal energy balances of
such systems.

Conventionally, the *elastic* material body is considered as a 3-dim material
manifold M^3 with boundary embedded at the time t into the physical (Euclidian)
space $\mathbb{E}^3$ by the diffeomorphism $\phi_t : M^3 \rightarrow \mathbb{E}^3$. A deformation in M^3 is character-
ized by the deformation gradient $F_I^i = \frac{\partial \phi_t^i}{\partial X^I}$. Balance equations of mass (continuity
equation), of linear momentum and of total or internal energy represent the total
balance system of equations of thermoelasticity provided that constitutive relations
are known; after that the entropy balance can be determined with the use of the
entropy principle [9] or in some other way.

The *internal energy balance* for a thermoelastic media has the form

$$\rho \dot{\epsilon} = p_{(i)} + (r - \nabla \cdot \mathbf{q}) = \boldsymbol{\sigma} : \mathbf{D} + (r - \nabla \cdot \mathbf{q}), \tag{15}$$

where ϵ is the internal energy per unit volume and $p_{(i)} = \boldsymbol{\sigma} : \mathbf{D}$ is the work power
of the stress. Here $\mathbf{D} = \mathbf{L}_{\text{sym}}$ is the symmetrized strain rate tensor. Here we also
have used the angular momentum balance equation in the form $\boldsymbol{\sigma}^T = \boldsymbol{\sigma}$.

Substituting here $\mathbf{D}$ in the form $\mathbf{D} = \mathbf{L}_{\text{sym}} = (\dot{\mathbf{F}}\mathbf{F}^{-1})_{\text{sym}}$ and using the symme-
try of the stress tensor $\boldsymbol{\sigma}$, we can rewrite the energy balance equation in the form
of a Pfaff equation as

$$\rho d\epsilon - (\boldsymbol{\sigma}\mathbf{F}^{-T}) : \dot{\mathbf{F}}dt - (r - \nabla \cdot \mathbf{q})dt$$
$$= \rho d\epsilon - (\boldsymbol{\sigma}\mathbf{F}^{-T}) : d\mathbf{F} - (r - \nabla \cdot \mathbf{q})dt = 0. \tag{16}$$

We recall that $\mathbf{P} = \boldsymbol{\sigma}\mathbf{F}^{-T}$ is the first Piola–Kirchhoff stress tensor. Using it and
dividing by ρ we can rewrite the energy balance equation in the form

$$d\epsilon - \frac{1}{\rho}\mathbf{P} : d\mathbf{F} - \frac{1}{\rho}(r - \nabla \cdot \mathbf{q})dt = 0. \tag{17}$$

The *balance of entropy* is taken in the standard form

$$\rho \dot{s} + \nabla \cdot \mathbf{J}_s = \dot{\Xi} + \frac{r}{\theta}, \tag{18}$$

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 [14], and r is the heat absorbtion by radiation.

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

$$\mathbf{J}_s = \theta^{-1}\mathbf{q} + \mathbf{k}. \tag{19}$$

Plugging in the last expression for the entropy flux, we rewrite Eq. (18) in the form

$$\dot{s} + \frac{1}{\rho}\nabla \cdot (\theta^{-1}\mathbf{q}) + \frac{1}{\rho}\nabla \cdot \mathbf{k} = \dot{s} + \frac{1}{\theta\rho}\nabla \cdot \mathbf{q} + \frac{1}{\rho}\mathbf{q} \cdot \nabla\theta^{-1} + \frac{1}{\rho}\nabla \cdot \mathbf{k} = \frac{1}{\rho}\dot{\Xi} + \frac{r}{\rho\theta}. \tag{20}$$

Expressing $(r - \nabla \cdot \mathbf{q})$ from Eq. (15) and using it in (20) we obtain the entropy balance in the form (using also the definition of Piola–Kirchoff first stress tensor)

$$\dot{s} + \frac{1}{\rho}\mathbf{q} \cdot \nabla\theta^{-1} = \frac{1}{\rho}\dot{\Xi} + \frac{1}{\rho\theta}[\rho\dot{\epsilon} - p_{(i)}] - \frac{1}{\rho}\nabla \cdot \mathbf{k}. \tag{21}$$

By using the explicit expression for the work power of stress given by $p_{(i)} = (\boldsymbol{\sigma}\mathbf{F}^{-T}) : \dot{\mathbf{F}} = \mathbf{P} : \dot{\mathbf{F}}$, Eq. (21) can be written as

$$\dot{s} - \frac{1}{\theta}\dot{\epsilon} + \frac{1}{\theta\rho}\mathbf{P} : \dot{\mathbf{F}} + \frac{1}{\rho}\mathbf{q} \cdot \nabla\theta^{-1} + \frac{1}{\rho}\nabla \cdot \mathbf{k} = \frac{1}{\rho}\dot{\Xi}, \tag{22}$$

or

$$ds - \frac{1}{\theta}d\epsilon + \frac{1}{\theta\rho}\mathbf{P} : d\mathbf{F} + \frac{1}{\rho}\mathbf{q} \cdot \nabla\theta^{-1}dt = \frac{1}{\rho}\dot{\Xi}dt + \frac{1}{\rho}\nabla \cdot \mathbf{k}dt. \tag{23}$$

We could reverse the arguments and substitute $\frac{1}{\rho}(r - \nabla \cdot \mathbf{q})$ from (20) into (17) to get the energy balance equation in the form of a Pfaff equation

$$d\epsilon - \theta ds - \frac{1}{\rho}\mathbf{P} : d\mathbf{F} - \frac{\theta}{\rho}(\mathbf{q} \cdot \nabla\theta^{-1} + \nabla \cdot \mathbf{k} - \dot{\Xi})dt = 0. \tag{24}$$

In the next section the term $\mathbf{k}$ will be taken to be zero but will appear in more complex situations below.

3.1. *Material element model*

Now, we refer the relations obtained in the previous subsection to a material element, i.e. a small enough volume of a material to associate with it definite values of the state variables participating in the internal energy and the entropy balance equations, values of stress etc. see [1]. For such an element the Coleman–Owen approach suggests to deliver a local approximation of a thermoelastic behavior that may, in some physical situations, adequately describe the response of the material element to exterior conditions (loading, heating, etc). The evolution of the dynamical variables of a thermoelastic element is described by the collection of scalar, vectorial and tensor *functions of time*

$$(\rho(t), \mathbf{F}(t), \theta(t), \mathbf{q}(t), \epsilon(t), \boldsymbol{\sigma}(t), (\nabla\theta^{-1})(t), s(t), etc.).$$

1   Some of these quantities are assumed to be fixed (density, for instance), others
2   are defined by constitutive relations determined by the properties of the related
3   specific continuum medium. Other quantities can be prescribed by conditions on
4   the specific process (heating, loading, etc.) similar to situations in homogeneous
5   thermodynamics, see [16].

6   Thus, the "real state space" $\mathcal{P}$ [11] of the material element model should include
7   a smaller number of fields then in the list above and implement all the constitutive
8   relations of the continuum model. In addition to this the I and II laws of thermo-
9   dynamics should be true for processes in this space where a process in such a space
10   is a (piecewise smooth) curve $\mathbf{c}(t)$.

11   Looking at the 1-form (24) that is supposed to annulate the velocity vector $\dot{\mathbf{c}}(t)$
12   for all t for which the process is defined, we see that the space $\mathcal{P}$ should include the
13   variables

$$(s, \epsilon, \theta, \mathbf{P}, \mathbf{F}, (\mathbf{q} \cdot \nabla \theta^{-1} - \dot{\Xi}), t). \tag{25}$$

15   If we would like Pfaff form (24) to be in the Darboux canonical form, we take
16    $\frac{\theta}{\rho}(\mathbf{q} \cdot \nabla \theta^{-1} - \dot{\Xi})$ instead of $(\mathbf{q} \cdot \nabla \theta^{-1} - \dot{\Xi})$ in the previous list. Density ρ is considered
17   as a parameter (given or simply constant).

18   In addition to this, we have to be able to rewrite (24) in the form (23) in order
19   to implement the II law — nonnegativity of the entropy production. In order to do
20   it we notice that the entropy production rate $\dot{\Xi}$ is supposed to be given as function
21   of other state variables (and their derivatives entering the constitutive relations
22   of the continuum model). Thus, $\dot{\Xi}$ can be considered as a known function of the
23   variables $(s, \epsilon, \theta, \mathbf{P}, \mathbf{F}, \mathbf{q}, \nabla \theta^{-1}, t)$. Notice that the heat flux $\mathbf{q}$ has his own balance
24   equation.

Therefore, one can rewrite (24) in the form (23) and, integrating the entropy
balance along a curve $\mathbf{c}(t)$ of some process in the space $\mathcal{P}$ one obtains

$$s[\mathbf{c}(t)] - s[\mathbf{c}(0)] = \int_{\mathbf{c}(\tau)} \left\{ \frac{1}{\theta} d\epsilon - \frac{1}{\theta \rho} (\mathbf{P} : d\mathbf{F}) \right\} - \int_{\mathbf{c}(\tau)} \frac{1}{\rho} \mathbf{q} \cdot \nabla(\theta^{-1}) d\tau$$
$$+ \int_{\mathbf{c}(\tau)} \frac{1}{\rho} \dot{\Xi} dt. \tag{26}$$

25   The last term in this expression represents the internal entropy production.

26   Comparing relation (26) with the formula (10) of the Coleman–Owen model
27   we notice that *if* the thermodynamical system is at homogeneous temperature
28   ($\nabla \theta^{-1} = 0$) and *if* the internal entropy production $\dot{\Xi}$ vanishes, then the entropy $s(t)$
29   of a thermoelastic element obtained by localizing the continuum thermodynamical
30   system of equations coincides with the entropy function $S(\mathbf{c})$ of Coleman–Owen
31   theory.

32   More then this, in the same conditions the form (24) represents Gibbs form
33   used by Mrugala ([11]) to introduce the contact structure in the thermodynamical
34   phase space of a homogeneous thermodynamical system. As a result, the model we

present in this paper is a generalization of the geometrical model of Mrugala, introducing fluxes and gradients as dynamical variables and, therefore, admitting non-homogeneity and (a priory) allowing irreversibility of thermodynamical processes.

Time evolution of the dynamical fields has to be determined by a dynamical system of equations. Before choosing a specific dynamical model it is imperative for the construction of a *closed and thermodynamically consistent model* to determine all the constitutive relations coming from the material element model including the II law of thermodynamics. These relations can, in particular, be used for the reduction of the state space to as small one as is reasonable.

Generically, the form (24) is of maximal rank and, therefore, it is contact. Yet, there may be constitutive relations coming from continuum thermodynamics that lead to the degeneration of this 1-form in the state space $\mathcal{P}$.

We introduce now our previous version of the *entropy form* (see also [6])

$$\eta = \frac{1}{\theta}d\epsilon - \frac{1}{\theta\rho}(\boldsymbol{\sigma}\mathbf{F}^{-T}) : d\mathbf{F} - \frac{1}{\rho}\mathbf{q} \cdot \nabla\theta^{-1}dt. \tag{27}$$

As a result, the entropy produced during the process $\mathbf{c}(\tau), 0 \leq \tau \leq T$ is equal to

$$\int_{\mathbf{c}(\tau)} \frac{1}{\rho}\dot{\Xi}dt = \int_{\mathbf{c}(\tau)} (ds - \eta). \tag{28}$$

Thus, the entropy form (6) obtained by Coleman and Owen for a simple material element is a special case of the 1-form (57) that can be obtained from the energy and entropy local balances (plus some kinematical relations of the type $\dot{\mathbf{F}} = \mathbf{LF}$) in much more complicated physical systems (see [5–9], etc.). On the other hand, Coleman and Owen *had proved* the existence of entropy function as consequence of the II law while in the continuum model the existence of an entropy density defining the entropy of the material element is assumed from the beginning.

The II law of thermodynamics here takes the form that for any thermodynamically admissible process $\mathbf{c}(\tau)$, one has

$$\int_{\mathbf{c}(\tau)} (ds - \eta) = s(T) - s(0) - \int_{\mathbf{c}(\tau)} \eta \geq 0. \tag{29}$$

The *entropy action* functional *along a process* $\mathbf{c}(\tau)$ from the time $\tau = 0$ to $\tau = t$ is given (see (5) or, in more details,[1]) by the integral

$$s[\mathbf{c}(t)] - s[\mathbf{c}(0)] \geq \int_{\mathbf{c}(\tau)} \eta = \int_0^t \mathbf{c}^*\eta. \tag{30}$$

Here $\mathbf{c}^*\eta$ is the pullback of 1-form η to the interval $(0, t)$ of time.

In general, the 1-form η is not closed, i.e $d\eta \neq 0$. Yet, if $d\eta = 0$ then locally (and globally in a simply connected space) there exists the potential U-function of the variables $(\epsilon, \mathbf{F}, t))$ such that

$$\eta = dU, \quad \int_{\mathbf{c}(\tau)} \eta = U[\mathbf{c}(end)] - U[\mathbf{c}(start)] \tag{31}$$

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 and, as a result, coincides with the entropy s (up to a constant) only when the entropy production in an admissible process $\mathbf{c}$ is zero (see Eq. (26)). In the integrable case the potential U and the entropy function s exist as functions in the state space. We introduce now the notation

$$\kappa[\mathbf{c}(t)] = s[\mathbf{c}(t)] - U[\mathbf{c}(t)] \tag{32}$$

for the difference of these functions. Then, the entropy balance in its integral form (26) and the II law of thermodynamics can be written in the form

$$\kappa[\mathbf{c}(t)] - \kappa[\mathbf{c}(0)] = \int_0^t \frac{1}{\rho}\dot{\Xi}[\mathbf{c}(\tau)]dt \geq 0. \tag{33}$$

Thus, if the entropy form η 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.*

Remark 2. In the scheme of Coleman and Owen the II law of Thermodynamics eventually takes the form of the inequality (8), which can be rewritten as

$$S[\mathbf{c}(end)] - S[\mathbf{c}(start)] \geq \int_0^t \mathbf{c}^*\eta. \tag{34}$$

This property of upper semi-continuity of the entropy function S (see [1, Sec. 10]) leads to a restriction on the direction of admissible processes. Namely, inequality (34) can be rewritten in the form

$$\int_0^t \mathbf{c}^*(dS - \eta) \geq 0. \tag{35}$$

If one has the equality in this relation, both $\mathbf{c}(t)$ and the inverse curve $\mathbf{c}(-t)$ are thermodynamically admissible. But if the inequality (35) is strict, then the inverse transformation of states is prohibited. Since any segment of a thermodynamically admissible process has to be admissible, this conclusion can be localized, i.e. at each point m in the state space M, there is a cone $C_m \subset T_m(M)$ of thermodynamically admissible directions, being $T_m(M)$ all directions. So, the II law requires the existence of a field of tangent cones in the state space defining directions of admissible processes.

In continuum thermodynamics this is remedied by the "Amendment to the Second Law", see [14, 15]. In the material point model this leads to some interesting geometrical consequences (see below).

Resumé.

We introduced the thermodynamical phase space (TPS) $\mathcal{P}$ with coordinates

$$\mathcal{P} = \left\{ s, \epsilon, \theta, \frac{\mathbf{P}}{\rho}, \mathbf{F}, \frac{\theta}{\rho}(\mathbf{q} \cdot \nabla \theta^{-1} - \dot{\Xi}), t \right\}, \tag{36}$$

where the entropy production rate function $\dot{\Xi}$ is defined by constitutive relations for the original balance system. In this space the energy 1-form is defined as follows

$$\Omega = d\epsilon - \theta ds - \frac{1}{\rho}\mathbf{P} : d\mathbf{F} - \frac{\theta}{\rho}(\mathbf{q} \cdot \nabla \theta^{-1} - \dot{\Xi})dt \tag{37}$$

and the **I law of thermodynamics** in this model is expressed by the condition that along the admissible processes given by piecewise smooth curves $\mathbf{c}(t)$ in the space $\mathcal{P}$, one has

$$\Omega[\dot{\mathbf{c}}(t)] = 0. \tag{38}$$

In addition, in the space $\mathcal{P}$ the entropy form is defined as follows

$$\eta = \frac{1}{\theta}d\epsilon - \frac{1}{\theta\rho}\mathbf{P} : d\mathbf{F} - \frac{1}{\rho}\mathbf{q} \cdot \nabla \theta^{-1}dt, \tag{39}$$

and the **II law of thermodynamics** in this model requires that for any thermodynamically admissible process $\mathbf{c}(t)$,

$$(ds - \eta)(\dot{\mathbf{c}}(t)) \geq 0. \tag{40}$$

As the next step, we would like to notice that the energy 1-form Ω resembles, by virtue of its form, the standard contact 1-form $ds - \sum_{i=1}^{n} p_i dq^i$ defined in the (2n+1)-dim vector space R^{2n+1} with coordinates $s, q^i, p_i (i = 1, \ldots, n)$. The last term in (39) is qualitatively different from the other ones in the fact that it has t as the variable under the differential.

A way to remedy to this is, as suggested in the work [6], to include time as an independent dynamical variable on an equal footing with the temperature, deformation gradient, energy, etc. This approach resembles the use of the duality of time and energy in Mechanics ([17], Ch. 3).

The space $\mathcal{P}$ has dimension $\dim(\mathcal{P}) = 1 + 2(1 + 9 + 1) = 23$ and is similar to the phase space of homogeneous thermodynamics ([16]) or to the thermodynamical phase space of Hermann–Mrugala, see [10, 11].

We also introduce the space with variables

$$B = \{s, \mathbf{F}, t\}. \tag{41}$$

It is clear that the TPS $\mathcal{P}$ is the total space of the bundle $\pi_{\mathcal{P}B} : \mathcal{P} \to B$. Introducing also the intermediate space of variables

$$G = \{\epsilon, s, \mathbf{F}, t\}, \tag{42}$$

we obtain the double bundle $\mathcal{P} \to G \to B$ similar to the bundle picture of homogeneous thermodynamics with the internal energy used as thermodynamical potential, see [16].

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If among the variables in $\mathcal{P}$ there are no constitutive relations, the 1-form Ω determines the contact structure in the space $\mathcal{P}$. Yet, it is easy to see that in real situations there often exist such relations (for instance representing entropy density s as function of $(\epsilon, \theta, \mathbf{F}, \|\nabla\theta^{-1}\|^2)$. This leads to the appearance of constrains on the possible states and processes occurring in the model. The best way to express these conditions is that one in terms of the rank of the 1-form Ω. Similarly, one can consider constrains placed by the degeneracy of the entropy form η. In the extreme case, one of these two forms may be integrable on the physically meaningful processes. This situation is similar to that one in homogeneous thermodynamics where intensive and extensive variables and the entropy s are independent except on the equilibrium surface given by the choice of expressions for s or ϵ as functions of the extensive variables. In a next publication we will study geometrical and dynamical consequences of these degenerations.

Here we look only at the case of extreme degeneration, i.e. closeness of the entropy form η. This condition was the central point in the proof of existence of the entropy function by Coleman and Owen. Constitutive relations for the case of closed η were obtained for different physical situations in a variety of works [4–9]. Our goal is to see which constitutive relations obtained from closeness conditions simplify the dynamical system of the ME-model and which restrict the type of admissible processes the space of this model.

4. Integrability (Closure) Conditions of the Entropy Form η and Constitutive Relations

The entropy s of the material element is one of the dynamical variables and therefore the 1-form $\Omega = ds - \eta$ is closed simultaneously with η. For comparison we remind that the constitutional relations (14) in Coleman–Owen theory [1] were obtained from the requirement that the 1-form $\theta^{-1}d\epsilon - (\theta^{-1}\boldsymbol{\sigma}\mathbf{F}^{-T}) : d\mathbf{F}$ is closed (see Remark 2).

In general one can expect that the closeness conditions of the entropy form limit the possible range of processes occurring in the system. Here, we will look at the closeness conditions of the form η in the space of variables $(\mathbf{F}, \epsilon, t)$.

First, we revisit conditions of integrability for the form (57), i.e.

$$\eta = \frac{1}{\theta}d\epsilon - \frac{1}{\theta\rho}(\boldsymbol{\sigma}\mathbf{F}^{-T}) : d\mathbf{F} + \mathbf{q} \cdot \boldsymbol{\beta}dt.$$

We remind that the basic state space in our situation (differently to that one in [1, 6]) is $B = \{\epsilon, \mathbf{F}, t\}$. We remark that in the works [1, 6] the state space B is extended by $\boldsymbol{\beta} = -\frac{1}{\rho}\nabla\theta^{-1}$. The form η is then replaced by

$$\eta' = -\frac{\boldsymbol{\sigma}\mathbf{F}^{-T}}{\rho\theta} : d\mathbf{F} + \theta^{-1}d\epsilon + \mathbf{0} \cdot d\boldsymbol{\beta} + (\mathbf{q} \cdot \boldsymbol{\beta})dt.$$

Closure conditions of η' have the form

$$
\begin{cases}
\partial_{\mathbf{F}}(\theta^{-1}) = -\partial_\epsilon\left(\dfrac{\boldsymbol{\sigma}\mathbf{F}^{-T}}{\rho\theta}\right), \\[2mm]
\partial_{\boldsymbol{\beta}}(\theta^{-1}) = \mathbf{0}, \\[2mm]
\partial_{\boldsymbol{\beta}}\left(\dfrac{\boldsymbol{\sigma}\mathbf{F}^{-T}}{\rho\theta}\right) = \mathbf{0}, \\[2mm]
\partial_{\boldsymbol{\beta}}(\mathbf{q}\cdot\boldsymbol{\beta}) = \mathbf{0}, \\[2mm]
\partial_t\left(\dfrac{\boldsymbol{\sigma}\mathbf{F}^{-T}}{\rho\theta}\right) = -\partial_{\mathbf{F}}(\mathbf{q}\cdot\boldsymbol{\beta}), \\[2mm]
\partial_t(\theta^{-1}) = \partial_\epsilon(\mathbf{q}\cdot\boldsymbol{\beta}).
\end{cases}
\tag{43}
$$

In our situation, only the following three conditions are present:

$$
\begin{cases}
\partial_{\mathbf{F}}(\theta^{-1}) = -\partial_\epsilon\left(\dfrac{\boldsymbol{\sigma}\mathbf{F}^{-T}}{\rho\theta}\right), \\[2mm]
\partial_t\left(\dfrac{\boldsymbol{\sigma}\mathbf{F}^{-T}}{\rho\theta}\right) = -\partial_{\mathbf{F}}(\mathbf{q}\cdot\boldsymbol{\beta}), \\[2mm]
\partial_t(\theta^{-1}) = \partial_\epsilon(\mathbf{q}\cdot\boldsymbol{\beta}).
\end{cases}
\tag{44}
$$

Last condition in (44) states that *the time derivative $\partial_t(\theta^{-1})$ of the temperature vanishes if the gradient of the inverse of temperature $\boldsymbol{\beta} = -\frac{1}{\rho}\nabla\theta^{-1}$ is identically zero*. This shows that the temperature in the material element changes *only due to the heat conduction*. Correspondingly, *the changes of temperature by the proper dissipative processes* (*without heat conduction*) *are excluded by the last condition* in the list (44) (see, for instance, [7, Sec. 4], where this fact has been explicitly stated). This is an example of restrictions on the type of thermodynamical processes induced by the closure conditions of the entropy form in the ME-model.

The first two equations of system (44) have the general local solution having the form

$$
\begin{cases}
\theta^{-1} = \partial_\epsilon U + c_1(t), \\[2mm]
-\dfrac{\boldsymbol{\sigma}\mathbf{F}^{-T}}{\rho\theta} = -\dfrac{\theta^{-1}}{\rho}\mathbf{P} = \partial_{\mathbf{F}} U + \mathbf{c}_2(t),
\end{cases}
\tag{45}
$$

for a function $U(\epsilon, \mathbf{F}, t)$ and arbitrary functions $c_1(t)$, $\mathbf{c}_2(t)$.

Using these expressions in the second triplet of equations one sees that the last equation in (44) leads to the following presentation of the function $(\mathbf{q}\cdot\boldsymbol{\beta})$:

$$
(\mathbf{q}\cdot\boldsymbol{\beta}) = \partial_t U + \dot{\mathbf{c}}_2(t) : \mathbf{F} + \dot{c}_1\epsilon + c_3(t),
\tag{46}
$$

with an arbitrary function $c_3(t)$.

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The function $U(\epsilon, \mathbf{F}, t)$ is the time-dependent entropy form potential defined in the space of the basic variables. These formulas determine the following constitutive relations

$$
\begin{cases}
\theta^{-1} = \partial_\epsilon U + c_1(t), \\
\mathbf{P} = \boldsymbol{\sigma}\mathbf{F}^{-T} = -\rho\dfrac{\partial_F U + \mathbf{c}_2(t)}{\partial_\epsilon U + \mathbf{c}_1(t))}, \\
(\mathbf{q} \cdot \boldsymbol{\beta}) = \partial_t U + \dot{\mathbf{c}}_2(t) : \mathbf{F} + \dot{c}_1\epsilon + c_3(t).
\end{cases}
\tag{47}
$$

Inverting the first two of these relations we obtain the internal energy ϵ as a definite function of the variables $(\theta, \mathbf{F}, t)$.

It is interesting to see what form does Clausius–Duhem inequality take in the case when the entropy form η is closed. To see this we use the constitutive relations (47) in the following local form of the entropy balance

$$
\dot{s} \geq \theta^{-1}[r - \rho^{-1}\nabla \cdot \mathbf{q}] + \mathbf{q} \cdot \boldsymbol{\beta}
$$

and substituting relation (46) we obtain (compare with (9))

$$
\dot{s} \geq (\partial_\epsilon U + c_1(t))[r - \rho^{-1}\nabla \cdot \mathbf{q}] + (\partial_t U + \dot{\mathbf{c}}_2(t) : \mathbf{F} + \dot{c}_1\epsilon + c_3(t)).
\tag{48}
$$

Comparing this form of Clausius–Duhem inequality with the one in [24, Sec. 3], we see that the potential $U(\mathbf{F}, \epsilon, t)$ partly plays the role of the dissipative potential $\mathcal{D}(\mathcal{A})$, following G. A. Maugin, in the treating of the dissipative inequality.

Using constitutive relations (47) in the following dynamical system of Coleman–Owen

$$
\begin{cases}
\dot{\mathbf{F}} = \mathbf{LF}, \\
\dot{\epsilon} = \rho^{-1}\boldsymbol{\sigma} : \mathbf{L} - \rho^{-1}\nabla \cdot \mathbf{q}, \\
\dot{\boldsymbol{\beta}} = \boldsymbol{\gamma},
\end{cases}
\tag{49}
$$

we obtain it in the form

$$
\begin{cases}
\dot{\mathbf{F}} = \mathbf{LF}, \\
\dot{\epsilon} = \dfrac{\partial_F U + \mathbf{c}_2(t)}{\partial_\epsilon U + \mathbf{c}_1(t))} : \dot{\mathbf{F}} - \rho^{-1}\nabla \cdot \mathbf{q}, \\
\dot{\boldsymbol{\beta}} = \boldsymbol{\gamma}.
\end{cases}
\tag{50}
$$

Resuming the discussion of this section, we state that to close the dynamical system for the variables $(\epsilon, \mathbf{F}, \boldsymbol{\beta})$ in its form (49) one has to determine the quantities $\mathbf{L} = \nabla\mathbf{v}, \nabla \cdot \mathbf{q}, \boldsymbol{\gamma}$ and the radiation heat source r whenever it is present using phenomenological equations or additional constitutive relations or additional dynamical equations, as functions of the dynamical variables (deduced from $\mathcal{P}$). As an example of a possible dynamical system in the space $\mathcal{P}$ "covering" the system (50), in the paper [13] the geometrical framework and the contact Hamiltonian system containing equations (49) has been suggested.

Remark 3. In general, the entropy form η is not closed. This is the reason why it is interesting to look at the meaning of *partial integrability* of this form, the

introduction of potentials coupled to the basic variables $\mathbf{X} = \{\epsilon, \mathbf{F}, t\}$. We leave this study to a future work on examples of thermodynamical systems where it may be important.

5. Entropy Form in Deformable Ferroelectric Crystals

Let us now recall the phenomenological model of an elastic deformable ferroelectric crystal worked out in [20–23] in a suitable Galilean quasi-static approximation. We assume that the total polarization per unit of mass is given by:

$$\boldsymbol{\pi} = \frac{\mathbf{P}_{pol}}{\rho}, \tag{51}$$

where $\mathbf{P}_{pol}$ is the *total polarization* (per unit of volume). The vector $\boldsymbol{\pi}$ is assumed to satisfy the following balance equation

$$I\ddot{\boldsymbol{\pi}} = \boldsymbol{\mathcal{E}} + {}^{L}\mathbf{E} + \rho^{-1}(\nabla \cdot {}^{L}\mathbb{E}), \tag{52}$$

where $I \neq 0$ is an "inertia constant" which, without an essential restriction, will be taken to be equal to 1, $\boldsymbol{\mathcal{E}}$ is an *external electric field* calculated in a comoving frame, ${}^{L}\mathbf{E}$ is a vector field, called *local electric field*, $\nabla \cdot {}^{L}\mathbb{E}$ is the divergence of rank-two tensor, called *local electric field tensor*. ${}^{L}\mathbb{E}$ accounts for the so-called *shell-shell interaction* and is responsible for the typical ferroelectric ordering. The master equation (52) fixes the behavior of the state variable $\boldsymbol{\pi}$ in terms of the electric fields ${}^{L}\mathbf{E}$ and ${}^{L}\mathbb{E}$. Fields ${}^{L}\mathbf{E}$ and ${}^{L}\mathbb{E}$ play the role of internal variables. This equation resembles Newton law of motion equation.

The internal energy balance has the form:

$$\rho\dot{\epsilon} = p_{(i)} - \nabla \cdot (\mathbf{q} - \mathbf{P}_{el}), \tag{53}$$

where $\mathbf{P}_{el}$ is the Poynting vector and the work power of internal forces $p_{(i)}$ is given by

$$p_{(i)} = \mathbf{P} : \dot{\mathbf{F}} - \rho^{L}\mathbf{E} \cdot \dot{\boldsymbol{\pi}} + {}^{L}\mathbb{E} : \nabla\dot{\boldsymbol{\pi}}. \tag{54}$$

The dynamical system, describing the evolution of the dynamical fields for the considered media, was suggested in [9] as:

$$\begin{cases} \dot{\mathbf{F}} = \mathbf{LF}, \\ \dot{\epsilon} = \rho^{-1}\mathbf{P} : \dot{\mathbf{F}} - {}^{L}\mathbf{E} \cdot \dot{\boldsymbol{\pi}} + \rho^{-1L}\mathbb{E} : \nabla\dot{\boldsymbol{\pi}} - \rho^{-1}\nabla \cdot (\mathbf{q} - \mathbf{P}_{el}), \\ \dot{\boldsymbol{\beta}} = \boldsymbol{\gamma}, \\ \dot{\boldsymbol{\pi}} = \mathbf{u}, \\ \dot{\mathbf{u}} = \boldsymbol{\mathcal{E}} + {}^{L}\mathbf{E} + \rho^{-1}(\nabla \cdot {}^{L}\mathbb{E}), \\ \nabla\dot{\boldsymbol{\pi}} = \nabla\mathbf{u}, \\ \nabla\dot{\mathbf{u}} = \nabla \cdot \mathbf{J}_{\nabla\mathbf{u}} + \sigma_{\nabla\mathbf{u}}. \end{cases} \tag{55}$$

Here $\mathbf{J}_{\nabla\mathbf{u}}$ and $\sigma_{\nabla\mathbf{u}}$ are both phenomenological quantities representing, respectively, the current and the source terms associated with $\nabla\mathbf{u}$. We introduced the variable $\mathbf{u} = \dot{\boldsymbol{\pi}}$ in order to obtain a first order dynamical system.

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Using (53) and (54), the entropy balance (22) takes the form:

$$\dot{s} - \theta^{-1}\dot{\epsilon} + (\rho\theta)^{-1}\mathbf{P} : \dot{\mathbf{F}} - \theta^{-1L}\mathbf{E} \cdot \dot{\boldsymbol{\pi}} + (\rho\theta)^{-1L}\mathbb{E}$$
$$: \nabla\dot{\boldsymbol{\pi}} - \mathbf{q} \cdot \boldsymbol{\beta} + (\rho\theta)^{-1}\nabla \cdot \mathbf{P}_{el} + \rho^{-1}\nabla \cdot \mathbf{k} = \frac{1}{\rho}\dot{\Xi} \qquad (56)$$

where the general relation (19) for the entropy flux has been assumed.

The entropy form η is given by

$$\eta = \theta^{-1}d\epsilon + (\rho\theta)^{-1}\mathbf{P} : d\mathbf{F} + \theta^{-1L}\mathbf{E} \cdot d\boldsymbol{\pi} - (\theta\rho)^{-1L}\mathbb{E}$$
$$: d(\nabla\boldsymbol{\pi}) + [\mathbf{q} \cdot \boldsymbol{\beta} - (\rho\theta)^{-1}\nabla \cdot \mathbf{P}_{el} - \rho^{-1}\nabla \cdot \mathbf{k}]dt \qquad (57)$$

Then, the infinitesimal entropy production along a curve in the state space is given by the integral of the following 1-form:

$$\frac{1}{\rho}\dot{\Xi}dt = ds - \eta = ds - \theta^{-1}d\epsilon + (\rho\theta)^{-1}\mathbf{P} : d\mathbf{F} - \theta^{-1L}\mathbf{E} \cdot d\boldsymbol{\pi}$$
$$+ (\rho\theta)^{-1L}\mathbb{E} : d(\nabla\boldsymbol{\pi}) - [\mathbf{q} \cdot \boldsymbol{\beta} - (\rho\theta)^{-1}\nabla \cdot \mathbf{P}_{el} - \rho^{-1}\nabla \cdot \mathbf{k}]dt \qquad (58)$$

The evolution of the material properties is described by time dependent dynamical variables forming the "basic state space"

$$B = (\epsilon, \mathbf{F}, \boldsymbol{\beta}, t; \boldsymbol{\pi}, \nabla\boldsymbol{\pi}, \mathbf{u} = \dot{\boldsymbol{\pi}}, \nabla\mathbf{u}). \qquad (59)$$

Formula (58) can be rewritten as the equality of the **energy 1-form** to zero in admissible processes, i.e.

$$\Omega = d\epsilon - \theta ds - \rho^{-1}\mathbf{P} : d\mathbf{F} + {}^L\mathbf{E} \cdot d\boldsymbol{\pi}$$
$$- \rho^{-1L}\mathbb{E} : d(\nabla\boldsymbol{\pi}) + \theta[\mathbf{q} \cdot \boldsymbol{\beta} - \rho^{-1}(\theta^{-1}\nabla \cdot \mathbf{P}_{el} + \nabla \cdot \mathbf{k}) - \dot{\Xi}]dt \qquad (60)$$

in the space of variables

$$\mathcal{P} = \begin{cases} \epsilon; \\ \mathbf{q^i} : s, \mathbf{F}, \boldsymbol{\pi}, \nabla\boldsymbol{\pi}, t; \\ \mathbf{p_j} : \theta, \rho^{-1}\mathbf{P}, {}^L\mathbf{E}, -\rho^{-1L}\mathbb{E}, \theta[\mathbf{q} \cdot \boldsymbol{\beta} - \rho^{-1}(\theta^{-1}\nabla \cdot \mathbf{P}_{el} + \nabla \cdot \mathbf{k}) - \dot{\Xi}]. \end{cases} \qquad (61)$$

The number of variables in the list $\mathcal{P}$ entering the energy form is **odd** and they are arranged here in the canonical (Darboux) order: (ϵ, q^i, p_j). We notice also that the Poynting vector together with the **k** quantity in the entropy flux determine "outside contributions" to the entropy production. Recall also that the entropy production $\dot{\Xi}$ is function of the other dynamical variables. The variable $\boldsymbol{\beta}$ is a dynamical variable, but does not enter as an independent variable into the energy form. We add also the variables $\mathbf{u} = \dot{\boldsymbol{\pi}}$ and $\nabla\mathbf{u}$. The reason for the appearance of these variables is that for this model the basic equations are of the second order. In order to take into account this second order we add two differential conditions in the space $\mathcal{P}$, (see Eqs. $(55)_4$ and $(55)_6$):

$$\begin{cases} d\boldsymbol{\pi} - \mathbf{u}dt = 0, \\ d\nabla\boldsymbol{\pi} - \nabla\mathbf{u}dt = 0. \end{cases} \qquad (62)$$

These equations together with Eq. (60) form the full set of conditions that has to be fulfilled in the space $\mathcal{P}$ besides the II law.

In general, the 1-form η is not closed. If the form η is closed then, at least locally, and globally in a simply connected domain, $\eta = dU$ for a function $U(\epsilon, \mathbf{F}, \boldsymbol{\pi}, \dot{\boldsymbol{\pi}}, \nabla \boldsymbol{\pi}, \nabla \dot{\boldsymbol{\pi}}, t)$. If closure conditions (see [9] for the explicit expressions) are fulfilled we get the following constitutive relations analogous to the conditions (14) using Eq. (57)

$$\begin{cases} \theta^{-1} = \partial_\epsilon U + c_1(t), \\ \mathbf{P} = \boldsymbol{\sigma} \mathbf{F}^{-T} = -(\rho\theta)\partial_{\mathbf{F}} U + \mathbf{c}_2(t), \\ {}^L\mathbf{E} = \theta\partial_{\boldsymbol{\pi}} U + \mathbf{c}_3(t), \\ {}^L\mathbb{E} = -(\rho\theta)\partial_{\nabla\boldsymbol{\pi}} U + \mathbf{c}_4(t), \\ -\rho\mathbf{q}\cdot\boldsymbol{\beta} + \theta^{-1}\nabla\cdot\mathbf{P}_{el} + \nabla\cdot\mathbf{k} = -\rho\partial_t U, \end{cases} \tag{63}$$

and the following condition due to the presence of the term $\mathbf{0}\cdot d\boldsymbol{\beta}$ in the energy 1-form

$$\partial_\beta U = 0. $$

The last equation of the system (63) can be rewritten as

$$\nabla\cdot\mathbf{P}_{el} = \theta(\rho\mathbf{q}\cdot\boldsymbol{\beta} - \rho\partial_t U - \nabla\cdot\mathbf{k}).$$

Assuming the full integrability of η, we can rewrite the system (55) in terms of the potential U of the entropy form as:

$$\begin{cases} \dot{\mathbf{F}} = \mathbf{L}\mathbf{F}, \\ \dot{\epsilon} = [-\theta\partial_F U + \rho^{-1}\mathbf{c}_2(t)] : \mathbf{L}\mathbf{F} - [\theta\partial_{\boldsymbol{\pi}} U + \mathbf{c}_3(t)]\cdot\dot{\boldsymbol{\pi}} \\ \qquad - [\theta\partial_{\nabla\boldsymbol{\pi}} U + \rho^{-1}\mathbf{c}_4(t)] : \nabla\dot{\boldsymbol{\pi}} - \rho^{-1}\nabla\cdot\mathbf{q} + \theta\mathbf{q}\cdot\boldsymbol{\beta} - \theta\partial_t U - \rho^{-1}\theta\nabla\cdot\mathbf{k}, \\ \dot{\boldsymbol{\beta}} = \boldsymbol{\gamma}, \\ \dot{\boldsymbol{\pi}} = \mathbf{u}, \\ \dot{\mathbf{u}} = \boldsymbol{\mathcal{E}} + \theta\partial_{\boldsymbol{\pi}} U + \mathbf{c}_3(t) + \rho^{-1}\nabla\cdot[-\theta\rho\partial_{\nabla\boldsymbol{\pi}} U) + \mathbf{c}_4(t)], \\ \dot{\overline{\nabla\boldsymbol{\pi}}} = \nabla\mathbf{u}, \\ \dot{\overline{\nabla\mathbf{u}}} = \nabla\cdot\mathbf{J}_{\nabla\mathbf{u}} + \sigma_{\nabla\mathbf{u}}. \end{cases} \tag{64}$$

In order to close this system of equations in the space of basic fields B one would have to specify the following entries in the system:

(1) The terms $\mathbf{L}, \nabla\cdot\mathbf{q}$ as in the simple model [1],
(2) the term $\nabla\cdot\mathbf{k}$ which would be present if mixed dissipative processes would occur in the system (that is usually described by a dissipative potential [24]),
(3) the term $\nabla\cdot(\theta\rho\partial_{\nabla\boldsymbol{\pi}} U)$,
(4) flux and production terms present in the last equation.

It is hardly possible to do this in a simple way. This problem is similar to the problem of closure of systems of equations for momenta in Statistical Mechanics

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or Rational Extended Thermodynamics. The introduction of specific constitutive relations determining some of these quantities as functions of basic variables (on the space B) is possible but may lead to strong limitations on the character of the modelled physical processes.

It seems more reasonable to construct the model introducing a larger space, i.e. the extended thermodynamical phase space $\mathcal{P}$, by which several models of thermodynamical processes were developed [12, 25–27].

6. Conclusions

In this work we analyze and compare the model of the material (elastic) element and the entropy form developed by Coleman and Owen with that one obtained by localizing the balance equations of the continuum thermodynamics. The comparison of the entropy actions and the entropy forms defined in both approaches allows one to determine the relation between the entropy function S of Coleman–Owen and that one imported from continuum thermodynamics.

Considering first the model of thermoelastic material element and then the thermoelastic ferroelectric material element, we showed that the entropy form potential U defined for the closed entropy form determines some more terms in the dynamical system of the corresponding model and produces certain constitutive relations for the fields (for instance $\theta, \boldsymbol{\sigma}$) which depends on the basic fields (called wanted fields, see [28]).

On the other hand, dynamical systems for both above models stayed unclosed and then arguments are presented explaining that in the space of basic fields it is impractical if not impossible to close those dynamical systems. This is the reason why as an alternative to the space of basic fields, we suggest to use extended thermodynamical phase space (ETPS) $(\mathcal{P}, \Omega)$ with the degenerate contact structure Ω defined by the *energy form* and with the entropy form similar to that one studied in homogeneous thermodynamics [11]. We leave this work to a next publication.

Acknowledgment

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