

## A geometrical model for a fluid flow in porous structures

M.E. Malaspina, L. Restuccia

*Dipartimento di Matematica, Facoltà di Scienze MM.FF.NN.  
Università degli Studi di Messina, Italy  
marileo@tele2.it  
lrest@dipmat.unime.it*

### Abstract

In a previous paper a geometric model for porous media filled by fluid flow was developed, within a thermodynamical model based on the rational extended irreversible thermodynamics with internal variables. The dynamical system for a *simple material element* of these media, the expression of the entropy function and the relevant entropy 1-form were obtained. In this contribution we derive the linear morphism defined on the fibre bundle of the process, the transformation induced by the process and, applying the closure conditions for the entropy 1-form, we give the necessary conditions for the existence of the entropy function. The derivation of the entropy 1-form is the starting point to introduce an extended thermodynamical phase space. Furthermore, considering the necessary conditions for the existence of the entropy function the constitutive laws can be obtained.

*Keywords:* Non-equilibrium Thermodynamics, internal variables, geometrical models, porous structures.

### 1. Introduction

The models describing pore structure filled by fluid flow may have relevance in the description of phenomena accompanying flows of mass. They find applications in several fundamental sectors: in geology, vulcanology, medical science, biology and other science. The porous channels sometime can self propagate because of changed conditions and favorable surrounding conditions. Thus, in metallurgy during a process of fabrication such propagation can provoke a premature fracture. It is well known that the permeability is the the basic property of porous media that allows fluid flow through interconnected pores. There exist several descriptions concerning fluid flow through porous materials (see for instance [1]- [4]). In most papers the volume porosity and the coefficient of permeability, which occur in Darcy's law, are used as macroscopic pore structure parameters. In the

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case of anisotropic pore structure, permeability coefficients are considered as components of a symmetric second order tensor in a generalized Darcy's law, which represents the conductivity of the pore structure regarding the permeation by a fluid flow [1]. In some cases a surface ratio has also been considered as a pore structure parameter. In [4] a macroscopic characterization of a pore structure is given by Kubik accounting for its anisotropic character. In a previous paper [5], in the framework of the rational extended irreversible thermodynamics with internal variables [6], a thermodynamical model for a fluid flow through porous solids was developed by the author, introducing a second order structural permeability tensor à la Kubik and its flux as internal variables. In fact, dissipative fluxes and gradients of the physical fields are included in the state space and additional rate equations for fluxes or internal variables are taken into consideration, so that the balance equations on such extended state space form a hyperbolic system of partial differential equations giving finite speeds of disturbances. Such finite velocity of propagation of physical fields is very important where the signals have transmission velocity very high. In [7], within the same thermodynamical description, a geometrization technique for material elements [8]- [10] was applied to these porous structures and a geometrical model was developed. The dynamical system and the expression for the entropy function were derived. In this contribution, within the same geometrical context the morphism defined on the fibre bundle of the process, the transformation induced by the process, the necessary conditions for the existence of the entropy function and the entropy 1-form, starting point to introduce an extended thermodynamical phase space [14], are obtained as new results within the geometrical model developed in [7] for the description of these media. In [15], [16] and [17] geometrical models for complex media were derived in the same geometrized framework by one of us (L. R.).

## 2. The structural permeability tensor à la Kubik

Now, we recall the thermodynamical model developed [5] for describing a pore structure filled by a fluid flow. The structure of the porous channels resembles a network of infinitesimally capillary tubes in a elastic solid. The fluid and the elastic solid are considered as a two components mixture. To describe a pore structure in [4] Kubik considers a representative elementary sphere volume  $\Omega$  of a porous skeleton filled with fluid (see Fig. 1), large enough to provide a representation of all the statistical properties of the pore space  $\Omega^p$ .  $\Omega = \Omega^s + \Omega^p$ , where  $\Omega^s$  is the solid space. Since all pores are considered to be interconnected the *effective volume porosity* is completely defined as  $f_v = \frac{\Omega^p}{\Omega}$ . The analysis is restricted to media which are homoge-

neous with respect to volume porosity  $f_v$ , i.e.  $f_v$  remains constant in the medium. In Fig. 1 to avoid confusion all microscopic quantities are written with respect to the coordinate system  $\xi_i$ , whereas all the macroscopic quantities are written with respect to the coordinate system  $x_i$ . Let  $\alpha(\xi)$  be any scalar, spatial vector or second order tensor a quantity describing some microscopic property of the fluid flowing through the pore-volume  $\Omega^p$ . We assume that such quantity is zero in the solid-space  $\Omega^s$ . The volume averaging procedures give

$$(2.1) \quad \hat{\alpha}(\mathbf{x}) = \frac{1}{f_v \Omega} \int_{\Omega_p} \alpha(\xi) d\Omega, \quad \bar{\alpha}(\mathbf{x}) = \frac{1}{\Omega} \int_{\Omega_p} \alpha(\xi) d\Omega,$$

where the quantities  $\hat{\alpha}(\mathbf{x})$  and  $\bar{\alpha}(\mathbf{x})$  describe at macroscopic level the same property of the flux of the fluid. They are average quantities on pore-volume and on bulk-volume  $\Omega$ , respectively. Similarly, we define the average quantity of  $\alpha(\xi)$  on pore-area as follows

$$(2.2) \quad \overset{*}{\alpha}(\mathbf{x}, \boldsymbol{\mu}) = \frac{1}{\Gamma^p} \int_{\Gamma} \alpha(\xi) d\Gamma,$$

where  $\Gamma$  is the central sphere section and  $\Gamma^p$  represents the pore-area of  $\Gamma$ . The orientation of  $\Gamma$  in  $\Omega$  is given by the normal vector  $\boldsymbol{\mu}$ . Furthermore,  $\Gamma = \Gamma^s + \Gamma^p$ , where  $\Gamma^s$  is the solid-area. By definition the quantity  $\alpha(\xi)$  is zero in the solid surface  $\Gamma^s$ . In such medium Kubik defines the so called *structural permeability tensor* describing a pore structure, as the following linear mapping

$$(2.3) \quad \bar{v}_i(\mathbf{x}) = \mathcal{R}_{ij}(\mathbf{x}, \boldsymbol{\mu}) \overset{*}{v}_j(\mathbf{x}, \boldsymbol{\mu}),$$

where

$$(2.4) \quad \bar{\mathbf{v}}(\mathbf{x}) = \frac{1}{\Omega} \int_{\Omega^p} \mathbf{v}(\xi) d\Omega, \quad \xi \in \Omega^p, \quad \overset{*}{\mathbf{v}}(\mathbf{x}, \boldsymbol{\mu}) = \frac{1}{\Gamma^p} \int_{\Gamma} \mathbf{v}(\xi) d\Gamma, \quad \xi \in \Omega^p$$

are the average fluid velocity on the bulk-volume and the the average fluid velocity on the pore-area, respectively. In [4] Kubik establishes the geometrical interpretation of  $\mathcal{R}$  considering a fluid flow having the average velocity on a bulk-volume  $\bar{\mathbf{v}}(\mathbf{x})$  as the superposition of three one-dimensional fluid flows (along three mutually perpendicular channels) having average velocities on the orthogonal section areas of these channels  $\overset{*}{v}_i(\mathbf{x}, \boldsymbol{\mu})$ . In fact, equ.(2.3) gives a linear mapping between the average fluid velocity  $\bar{\mathbf{v}}(\mathbf{x})$  on the bulk volume and the area average fluid velocities  $\overset{*}{v}_i(\mathbf{x}, \boldsymbol{\mu})$ . Only part of

the fluid can flow unimpeded while the rest is trapped in the porous structure. Now, following Maruszewski in [18], using the previous definitions, for any flux  $\alpha_i$  of some quantity transported through a cobweb of lines one postulates that

$$(2.5) \quad \bar{\alpha}(\mathbf{x})_i = \mathcal{R}_{ij}(\mathbf{x}, \boldsymbol{\mu}) \alpha_j^*(\mathbf{x}, \boldsymbol{\mu}),$$

where

$$\mathcal{R}_{ij}(\mathbf{x}, \boldsymbol{\mu}) = \Gamma r_{ij}(\mathbf{x}, \boldsymbol{\mu}).$$

In the above equations  $r_{ij}$  is a new tensor called *structural permeability core tensor* that refers  $\mathcal{R}_{ij}$  to the surface  $\Gamma$ . Its unit is  $m^{-2}$ .

### 3. A non conventional model for porous solids filled by a fluid flow

Now, we recall the continuum model developed in [5] in the framework of the extended thermodynamics with internal variables for describing the reciprocal interactions between a fluid flow, a structural permeability field coming from a porous structure in an elastic body and a thermal field. Since during deformation the porous structure evolves in time, the structural permeability field is described by the state tensor  $r_{ij}$  (not necessarily symmetric), which relates to the density of porous, and by the flux of this tensor  $\mathcal{V}_{ijk}$ . The fluid flow is described by two variables: the concentration of the fluid  $c$  and the flux of this fluid  $j_i$ . The mass density of the fluid (transported through the elastic porous body of density  $\rho_2$ ) is called  $\rho_1$ . The fluid and the elastic solid form a two-components mixture of density

$$(3.1) \quad \rho = \rho_1 + \rho_2.$$

The concentration of the fluid  $c$  is defined as follows  $c = \frac{\rho_1}{\rho}$ . For the mixture of continua as a whole and also for each constituent separately the continuity equation is satisfied

$$(3.2) \quad \dot{\rho} + \rho v_{i,i} = 0, \quad \frac{\partial \rho_1}{\partial t} + (\rho_1 v_{1i})_{,i} = r_1, \quad \frac{\partial \rho_2}{\partial t} + (\rho_2 v_{2i})_{,i} = r_2,$$

where a superimposed dot denotes the material derivative,  $v_{1i}$  and  $v_{2i}$  are the velocities of the fluid particles and the particles of the elastic body and  $r_1$  and  $r_2$  denote the sources of mass of the constituents, respectively. In the following  $r_1$  and  $r_2$  will be neglected, because it is assumed that there are not chemical reactions between the constituents or coagulations.

The barycentric velocity of the body and the fluid flux are defined in the following form

$$(3.3) \quad \rho v_i = \rho_1 v_{1i} + \rho_2 v_{2i}, \quad \text{and} \quad j_i = \rho_1 (v_{1i} - v_i).$$

The mechanical properties of the considered system are described by the total stress tensor  $T_{ij}$  (in general non symmetric) related to the whole body considered as a mixture and the small-strain tensor  $\varepsilon_{ij}$  describing the deformation of the elastic solid  $\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i})$  (where  $u_i$  are the components of the displacement vector) so that the gradient of the velocity of the body is given by

$$(3.4) \quad v_{i,j} = w_{ij} + \frac{\partial \varepsilon_{ij}}{\partial t}, \quad \text{where} \quad w_{ij} = \frac{1}{2}(v_{i,j} - v_{j,i})$$

is the antisymmetric part of  $v_{i,j}$ . Finally, the thermal field is governed by the temperature and the heat flux  $q_i$ . Thus, the vector space is chosen as follows

$$(3.5) \quad C = \{\varepsilon_{ij}, c, \theta, r_{ij}, j_i, q_i, \mathcal{V}_{ijk}, c_{,i}, \theta_{,i}, r_{ij,k}\},$$

where we have taken into consideration the gradients  $c_{,i}, \theta_{,i}$  and  $r_{ij,k}$ . We ignore the viscoelastic effects, so that  $T_{ij}$  is not in the set C. All the processes occurring in the considered body are governed by two groups of laws. The first group concerns the classical balance equations: the *balance of mass* resulting from (3.1)-(3.3)

$$(3.6) \quad \rho \dot{c} + j_{i,i} = 0;$$

the *momentum balance*

$$(3.7) \quad \rho \dot{v}_i - T_{j,i,j} - f_i = 0,$$

where denotes a body force. In the following  $f_i$  will be neglected; the *moment of momentum balance*

$$(3.8) \quad \varepsilon_{ijk} T_{jk} + g_i = 0,$$

where  $g_i$  is a couple per unit volume; the *internal energy balance*

$$(3.9) \quad \rho \dot{e} - T_{ji} v_{i,j} + q_{i,i} - \rho r = 0,$$

where  $e$  is the internal energy density and  $r$  is a heat source distribution, that will be neglected in the following. The second group of laws deals with

the rate properties of the structural permeability tensor and the fluxes of the mass, heat and porous field

(3.10)

$$\dot{r}_{ij} + \mathcal{V}_{ijk,k} - R_{ij}(C) = 0, \quad \dot{j}_i - J_i(C) = 0, \quad \dot{q}_i - Q_i(C) = 0, \quad \mathcal{V}_{ijk}^* - V_{ijk}(C) = 0.$$

All processes considered here should be admissible from the thermodynamical point of view and thus they should not contradict the second law of thermodynamics. Thus, all the admissible solutions of the proposed evolution equations should be restricted by the following *entropy inequality*

$$(3.11) \quad \rho \dot{S} + J_{S_{k,k}} - \frac{\rho r}{\theta} \geq 0,$$

where  $S$  denotes the entropy per unit mass and  $\mathbf{J}_S$  is the entropy flux associated with the fields of the set  $C$  given by

$$(3.12) \quad \mathbf{J}_S = \frac{1}{\theta} \mathbf{q} + \mathbf{k}.$$

In equ. (3.12)  $\mathbf{k}$  an additional term called *extra entropy flux density*. Constitutive functions  $W = \tilde{W}(C)$ , with

$$(3.13) \quad W = \{T_{ij}, \mu^c, \nu_{ij}, g_i, e, R_{ij}, J_i, Q_i, V_{ijk}, S, J_{S_i}\},$$

for porous structure filled by a fluid flow were derived in [5] and [19] in order to close the system of balance equations (3.6)-(3.10), by analyzing the entropy inequality by Liu's theorem [20] and using isotropic polynomial representation of proper constitutive functions satisfying the objectivity and material frame indifference principles (see Smith's [21] theorem).  $\mu^c$  and  $\nu_{ij}$  denote the potentials related to the mass and the porous field, respectively.

#### 4. A geometrical model for porous structures

Now, taking into account the results obtained in [5] and [7] and following [9]- [10] and [8], [11]- [13], we derive the linear morphism defined on the fibre bundle of the process, the transformation induced by the process and, applying the closure conditions for the entropy 1-form, we give the necessary conditions for the existence of the entropy function. Then, we consider a material element and we define the state space at time  $t$  as the set  $B_t$  of all state variables which "fit" the configuration of the element at time  $t$ .  $B_t$  is assumed to have the structure of a finite dimensional manifold. The "total state space" is the disjoint union

$$\tilde{B} = \bigcup_t \{t\} \times B_t$$

with a given natural structure of fibre bundle over  $\mathbb{R}$  where time flows (see [9]- [10]). If the instantaneous state space  $B_t$  does not vary in time (i.e. there is an abstract space  $B$  such that  $B_t \simeq B$  for all instant of time  $t$ ), then  $\mathcal{B}$  has the topology of the Cartesian product  $\mathcal{B} \simeq \mathbb{R} \times B$ .

Moreover, we consider an abstract space of *processes*, i.e. a set  $\Pi$  of functions  $P_t^i : [0, t] \rightarrow \mathcal{G}$ , where  $[0, t]$  is any time interval. The space  $\mathcal{G}$  is a suitable target space defined by the problem under consideration,  $i$  a label ranging in an unspecified index set for all allowed processes and  $t \in \mathbb{R}$ , the so called *duration* of the process. For the given state space  $B$  we suppose that the set  $\Pi$  is such that the following hold:

- i)  $\exists D : \Pi \rightarrow \mathcal{P}(B)$ , where  $\mathcal{P}(B)$  is the set of all subsets of  $B$ .  $D$  is the *domain function* and  $D_t^i \equiv D(P_t^i)$  is called the domain of the  $i$ -th process of duration  $t$ ;
- ii)  $\exists R : \Pi \rightarrow \mathcal{P}(B)$ , where  $\mathcal{P}(B)$  is the set of all subsets of  $B$ .  $R$  is the *range function* and  $R_t^i \equiv R(P_t^i)$  is called the range of the  $i$ -th process of duration  $t$ ;
- iii) considering the restrictions

$$(4.1) \quad P_t^i = P_t^i |_{[0, \tau]}, \quad (\tau \leq t)$$

new processes are obtained ('restricted processes') and they satisfy the following statement

$$(4.2) \quad \forall \tau < t \quad D(P_t^i) \subseteq D(P_\tau^i).$$

Incidentally, this implies that

$$(4.3) \quad \bigcap_{\tau=0}^t D(P_\tau^i) = D(P_t^i),$$

where  $t$  is the maximal duration.

Then, a continuous function is defined

$$(4.4) \quad \chi : \mathbb{R} \times \Pi \rightarrow C^0(B, B) \\ (t, P_t^i) \rightarrow \rho_t^i,$$

with  $\rho_t^i : b_0 \in D_t^i \subseteq B \rightarrow \rho_t^i(b_0) = b_t \in R_t^i \subseteq B$ , so that for any instant of time  $t$  and for any process  $P_t^i \in \Pi$  a continuous mapping,  $\rho_t^i$ , called *transformation induced by the process*, is generated.  $\rho_t^i$ , gives point by point a correspondence between the initial state  $b$  and the final state  $\rho_t^i(b) = b_t$ . Now, we can define the following function of time:

$$(4.5) \quad \lambda_b^i(\tau) = \begin{cases} b & \text{if } \tau = 0 \\ \rho_t^i(b) & \text{if } \tau \in ]0, t], \end{cases} \quad \text{with } b \in D_t^i$$

such that the transformation for the medium is given by

$$(4.6) \quad \delta : \mathbb{R} \longrightarrow \mathbb{R} \times B, \quad \tau \longrightarrow \delta(\tau) = (\tau, \lambda_b^i(\tau)).$$

With these positions the transformation is interpreted as a curve  $\delta$  in the union of all state spaces such that it intersects the instantaneous state space just once. Now, we assume that the behaviour of the porous media filled by fluid flow is described by the following state variables

$$\mathbf{C} = \{\mathbf{F}, e, c, \mathbf{r}, \mathbf{j}, \mathbf{q}, \mathcal{V}, \nabla c, \nabla \theta, \nabla \mathbf{r}\}.$$

The full state space is then

$$\mathcal{B} = \text{Lin}(\mathcal{V}) \oplus \mathbb{R} \oplus \mathbb{R} \oplus \mathcal{W}_1 \oplus \mathcal{V} \oplus \mathcal{V} \oplus \mathcal{W}_2 \oplus \mathcal{V} \oplus \mathcal{V} \oplus \text{Lin}(\mathcal{W}_1),$$

where  $\mathcal{V} \simeq \mathbb{R}^3$ ,  $\mathcal{W}_1$  and  $\mathcal{W}_2$  are vector spaces accounting for the internal variables  $\mathbf{r}$  e  $\mathcal{V}$  respectively. The process  $\mathbf{P}_t$  is described by the following functions

$$\mathbf{P}_t^i = [\mathbf{L}, h, \Gamma, \mathbf{R}, \mathbf{J}, \mathbf{Q}, \mathbf{V}, \mathcal{C}, \gamma, \Xi],$$

where  $h(\tau) = -\nabla \cdot \mathbf{q}$ ,  $\Gamma(\tau) = \nabla \cdot \mathbf{j}$  and the space  $\mathcal{G}$  is given by

$$\mathcal{G} = \text{Lin}(\mathcal{V}) \oplus \mathbb{R} \oplus \mathbb{R} \oplus \mathcal{W}_1 \oplus \mathcal{V} \oplus \mathcal{V} \oplus \mathcal{W}_2 \oplus \mathcal{V} \oplus \mathcal{V} \oplus \text{Lin}(\mathcal{W}_1).$$

Moreover, the constitutive functions  $\theta$ ,  $\mathbf{T}$ ,  $\mathbf{R}$ ,  $\mathbf{J}$ ,  $\mathbf{V}$ ,  $\mathbf{Q}$  are defined as follows

$$(4.7) \quad \begin{aligned} \theta &: \mathbb{R} \times B \longrightarrow \mathbb{R}^{++} \\ \mathbf{T} &: \mathbb{R} \times B \longrightarrow \text{Sym}\mathcal{V} \\ \mathbf{R} &: \mathbb{R} \times B \longrightarrow \mathcal{W}_1 \\ \mathbf{J} &: \mathbb{R} \times B \longrightarrow \mathcal{V} \\ \mathbf{V} &: \mathbb{R} \times B \longrightarrow \mathcal{W}_2 \\ \mathbf{Q} &: \mathbb{R} \times B \longrightarrow \mathcal{V} \end{aligned}$$

we assume that for each pair  $(P_t^i, b)$ , the following dynamical system holds

$$(4.8) \quad \begin{cases} \dot{\mathbf{F}} = \mathbf{L}(\tau)\mathbf{F}(\tau) \\ \rho \dot{e} = \mathbf{T}(\tau) \cdot \mathbf{L}(\tau) - h(\tau) \\ \rho \dot{c} = \Gamma(\tau) \\ \dot{\mathbf{r}} = \mathbf{R}(\delta) \\ \dot{\mathbf{j}} = \mathbf{J}(\delta) \\ \dot{\mathbf{q}} = \mathbf{Q}(\delta) \\ \dot{\mathcal{V}} = \mathbf{V}(\delta) \\ \dot{\nabla} c = \mathcal{C}(\tau) \\ \dot{\nabla} \theta = \gamma(\tau) \\ \dot{\nabla} \mathbf{r} = \Xi(\tau). \end{cases}$$

Such a system determines a morphism  $G$  defined on fibre bundle of process in the following way

$$(4.9) \quad \begin{aligned} G : (\mathbf{F}, e, c, \mathbf{r}, \mathbf{j}, \mathbf{q}, \mathcal{V}, \nabla c, \nabla\theta, \nabla\mathbf{r}, \mathbf{L}, h, \Gamma, \mathbf{R}, \mathbf{J}, \mathbf{Q}, \mathbf{V}, \mathcal{C}, \gamma, \Xi) \rightarrow \\ \rightarrow (\mathbf{F}, e, c, \mathbf{r}, \mathbf{j}, \mathbf{q}, \mathcal{V}, \nabla c, \nabla\theta, \nabla\mathbf{r}, \dot{\mathbf{F}}, \dot{e}, \dot{c}, \dot{\mathbf{r}}, \dot{\mathbf{j}}, \dot{\mathbf{q}}, \dot{\mathcal{V}}, \dot{\nabla}c, \dot{\nabla}\theta, \dot{\nabla}\mathbf{r}), \end{aligned}$$

which in matrix form is expressed by

$$(4.10) \quad \begin{aligned} & (\mathbf{F}, e, c, \mathbf{r}, \mathbf{j}, \mathbf{q}, \mathcal{V}, \nabla c, \nabla\theta, \nabla\mathbf{r}, \dot{\mathbf{F}}, \dot{e}, \dot{c}, \dot{\mathbf{r}}, \dot{\mathbf{j}}, \dot{\mathbf{q}}, \dot{\mathcal{V}}, \dot{\nabla}c, \dot{\nabla}\theta, \dot{\nabla}\mathbf{r})^T = \\ & = \begin{pmatrix} \mathbf{I} & \mathbf{o} \\ \mathbf{o} & \mathbf{A} \end{pmatrix} (\mathbf{F}, e, c, \mathbf{r}, \mathbf{j}, \mathbf{q}, \mathcal{V}, \nabla c, \nabla\theta, \nabla\mathbf{r}, \mathbf{L}, h, \Gamma, \mathbf{R}, \mathbf{J}, \mathbf{Q}, \mathbf{V}, \mathcal{C}, \gamma, \Xi)^T, \end{aligned}$$

with

$$(4.11) \quad \mathbf{A} = \begin{pmatrix} \mathbf{F}^T & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{\mathbf{T}}{\rho} & \frac{1}{\rho} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{\rho} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}.$$

Finally,  $\rho_t^i(b)$  is given by

$$(4.12) \quad \rho_t^i(b) = \begin{cases} \mathbf{F} = \int_0^t [\mathbf{L}(\tau)\mathbf{F}(\tau)] dt \\ e = \int_0^t \frac{1}{\rho} [\mathbf{T}(\delta) \cdot \mathbf{L}(\tau) - h(\tau)] dt \\ c = \int_0^t \frac{1}{\rho} [\Gamma(\tau)] dt \\ \mathbf{r} = \int_0^t [\mathbf{R}(\delta)] dt \\ \mathbf{j} = \int_0^t [\mathbf{J}(\delta)] dt \\ \mathbf{q} = \int_0^t [\mathbf{Q}(\delta)] dt \\ \mathcal{V} = \int_0^t [\mathbf{V}(\delta)] dt \\ \nabla c = \int_0^t [\mathcal{C}(\tau)] dt \\ \nabla\theta = \int_0^t [\gamma(\tau)] dt \\ \nabla\mathbf{r} = \int_0^t [\Xi(\tau)] dt. \end{cases}$$

## 5. Entropy Function

Following standard procedures (see [9]- [10] and [13]) in this geometrical framework we are able to introduce an “*entropy function*”, which is related to a transformation between the initial and the final states  $b$  and  $\rho_t^i(b) = b_t$ , respectively, by setting:

$$(5.1) \quad s(\rho_t^i, b, t) = - \int_0^t \frac{1}{\rho} \nabla \cdot \mathbf{J}_S d\tau,$$

where  $\mathbf{J}_S$  is defined according to equation (3.12). Then we get

$$(5.2) \quad s = \int_0^t -\frac{1}{\rho\theta} \nabla \cdot \mathbf{q} d\tau + \int_0^t \frac{1}{\rho\theta^2} \mathbf{q} \cdot \nabla\theta d\tau - \int_0^t \frac{1}{\rho} \nabla \cdot \mathbf{k} d\tau.$$

Moreover, one obtains the following expression for  $\nabla \cdot \mathbf{q}$

$$(5.3) \quad \nabla \cdot \mathbf{q} = -\rho\dot{e} + (\mathbf{T}\mathbf{F}^{-T}) \cdot \dot{\mathbf{F}},$$

so that the final expression for  $s$  is

$$(5.4) \quad s(\rho_t^i, b, t) = \int_\delta \Omega, \quad \text{with } \Omega = -\frac{\mathbf{T}\mathbf{F}^{-T}}{\theta\rho} \cdot d\mathbf{F} + \frac{1}{\theta} de + \left[ \frac{1}{\rho\theta^2} \mathbf{q} \cdot \nabla\theta - \frac{1}{\rho} \nabla \cdot \mathbf{k} \right] d\tau.$$

The expressions for  $\mathbf{T}$ ,  $\mathbf{q}$  and  $\mathbf{k}$  have been calculated in [19].

The relation  $\mathbf{T} \cdot (\dot{\mathbf{F}}\mathbf{F}^{-1}) = (\mathbf{T}\mathbf{F}^{-T}) \cdot \dot{\mathbf{F}}$  has been used, with  $\mathbf{F}^{-T} = (\mathbf{F}^{-1})^T$  ( $T$  denoting matrix transposition). Thus, the entropy function is now calculated as an integral along a path  $\delta$  into the space  $\mathbb{R} \times B$  of all thermodynamic variables together with the independent time variable and  $\Omega$  is a 1-form in  $\mathbb{R} \times B$  called the entropy 1-form. In components the *entropy 1-form*  $\Omega$  becomes:  $\Omega = \omega_\mu dq^\mu + \omega_0 dt = \omega_A dq^A$ , ( $A = 1, 2, \dots, 11$ )

where  $q^A = (\mathbf{F}, e, c, \mathbf{r}, \mathbf{j}, \mathbf{q}, \mathcal{V}, \nabla c, \nabla\theta, \nabla\mathbf{r}, t)$

$$\text{and } \omega_A = \left( -\frac{1}{\rho\theta} \mathbf{T}\mathbf{F}^{-T}, \frac{1}{\theta}, 0, 0, 0, 0, 0, 0, 0, 0, \left[ \frac{1}{\rho\theta^2} \mathbf{q} \cdot \nabla\theta - \frac{1}{\rho} \nabla \cdot \mathbf{k} \right] \right).$$

Thus, by external differentiation, a 2-form is obtained:

$$d\Omega = \frac{1}{2} A_{\rho\lambda} dq^\rho \wedge dq^\lambda + E_\lambda dt \wedge dq^\lambda, \quad \text{with } A_{\rho\lambda} = \partial_\rho \omega_\lambda - \partial_\lambda \omega_\rho$$

$$\text{and } E_\lambda = \partial_0 \omega_\lambda - \partial_\lambda \omega_0.$$

Finally, applying the closure conditions for the 1-form, the necessary conditions for the existence of the entropy function during the processes under consideration are:

$$\begin{aligned}
 (5.5) \quad & \partial_e \left( -\frac{1}{\rho\theta} \mathbf{T}\mathbf{F}^{-T} \right) = \partial_{\mathbf{F}} \left( \frac{1}{\theta} \right), \\
 & \frac{\partial \omega_A}{\partial q^B} = 0 \quad (A = 1, 2, 11; B = 3, \dots, 10), \\
 & \partial_{\mathbf{t}} \left( -\frac{1}{\rho\theta} \mathbf{T}\mathbf{F}^{-T} \right) = \partial_{\mathbf{F}} \left[ \frac{1}{\rho\theta^2} \mathbf{q} \cdot \nabla \theta - \frac{1}{\rho} \nabla \cdot \mathbf{k} \right], \\
 & \partial_{\mathbf{t}} \left( \frac{1}{\theta} \right) = \partial_e \left[ \frac{1}{\rho\theta^2} \mathbf{q} \cdot \nabla \theta - \frac{1}{\rho} \nabla \cdot \mathbf{k} \right].
 \end{aligned}$$

These relations give the necessary conditions characterizing a sort of "irrotationality" of the entropy 1-form during the transformation analyzed. If the entropy 1-form in equ. (5.2) is closed and its coefficient are regular, this form is exact the existence of an upper-potential  $S$  satisfying relation  $S(b_t) - S(b) \geq s$  is ensured (see [13]). Starting from the entropy 1-form it's possible to investigate and to introduce an extended thermodynamical phase space in a suitable way [14], and considering the necessary conditions for the existence of the entropy function we can obtain constitutive laws.

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