ON A MODEL OF MIXTURES WITH INTERNAL VARIABLES: EXTENDED LIU PROCEDURE FOR THE EXPLOITATION OF THE ENTROPY PRINCIPLE

FRANCESCO OLIVERI,[a] [*] ANNUNZIATA PALUMBO,[a] AND PATRIZIA ROGOLINO [a]

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ABSTRACT. The exploitation of second law of thermodynamics for a mixture of two fluids with a scalar internal variable and a first order nonlocal state space is achieved by using the extended Liu approach. This method requires to insert as constraints in the entropy inequality either the field equations or their gradient extensions. Consequently, the thermodynamic restrictions imposed by the entropy principle are derived without introducing extra terms neither in the energy balance equation nor in the entropy inequality.

1. Introduction

In many applications, models of fluid continua need to be treated as *mixtures* (de Groot and Mazur 1962; Müller 1968; Bowen 1976), *i.e.*, as continua microscopically formed by two or more separate components having different specific physical properties. These models are particularly effective when they are used to describe the thermodynamical behaviour of composite materials, *e.g.* polymers, or fluxes through porous media and in presence of liquid Helium, as well as mixtures of granular media (Goodman and Cowin 1972).

Whenever a continuum is composed as two or more *internal phases*, the properties are in general known not as single deterministic components but rather as suitable averages of microlocal phenomena; hence, a convenient modelization technique may pass through the use of so–called *internal variable approach* (Coleman and Gurtin 1967; Maugin and Muschik 1994a,b; Verhás 1997). The internal variables are introduced to describe phenomena occurring at the microscopic or mesoscopic level that can not be controlled in their full detail but only in average over small portions of the continuum. These microlocal phenomena (which are typical of non–equilibrium and dissipation processes) are thus modeled by introducing a set of extra variables, the so–called *internal variables*, which depend on the particular model, and obey a number of phenomenological equations. Usually, the internal variables enter directly the state functions and the constitutive laws, but it is sometimes convenient to adopt more general models in which these averages are non–uniform in space so that the internal variables appear together with their spatial gradients. Moreover, the

constitutive equations may include the gradients of field variables (Ván 2003) to take into account nonlocal effects.

As discussed by Ván, Berezovski, and Engelbrecht (2008), there are two basic methods to generate the evolution equations for internal variables. Several authors have given a distinction between these two methods (Maugin and Muschik 1994a,b) and proposed a large number of applications (Maugin 1990). In this paper, we follow the approach introduced by Coleman and Gurtin (1967), and postulate the existence of internal state variables which influence the free energy and whose rate of change is governed by a (generally nonlinear) function of all the state variables.

In a previous paper Francaviglia, Palumbo, and Rogolino (2006) analyzed a model of a mixture with N different components from a thermodynamical viewpoint with internal variables, both in the presence and absence of viscosity; the general thermodynamical restrictions and residual dissipation inequalities have been obtained by Clausius–Duhem inequality along with the Coleman–Noll procedure (Coleman and Noll 1963). The behaviour of the mixture has been described by a state space W with local coordinates

$$W \equiv (\rho, c_\alpha, \theta, \gamma_A, \nabla\gamma_A), \qquad \alpha = 1, \dots, N-1, \ A = 1, \dots, N, \qquad (1)$$

where ρ is the mass density of the mixture, c_α the concentrations of $N-1$ components, θ the absolute temperature of the mixture, γ_A and $\nabla\gamma_A$ the N internal variables together with their gradients, respectively.

A different procedure for the exploitation of the second law, based on the method of Lagrange multipliers, was introduced by Liu (1972). Lagrange multipliers are used in non–equilibrium thermodynamics in the method proposed by Liu to take into account the restrictions placed on the thermodynamic fields by the balance equations. In recent years, some extensions of these two classical techniques, the Coleman–Noll procedure and the Liu one, have been proposed (see Cimmelli, Oliveri, and Triani 2011; Cimmelli, Sellitto, and Triani 2010; Triani *et al.* 2008, and references therein) in order to include additional restrictions consistent with higher–order nonlocal constitutive equations. Remarkably, these extended procedures (see, for instance, Cimmelli, Oliveri, and Pace 2011, 2013, 2015) for their application in some thermodynamic models), when nonlocal constitutive equations are used, do *not* require the introduction of extra terms or extra fluxes (Dunn 1986; Dunn and Serrin 1985; Gurtin and Vargas 1971; Müller 1967) neither in the balance equation for energy nor in the entropy inequality. In particular, the extended Liu technique requires to add to the entropy inequality a linear combination of the field equations and of the spatial gradients of the latter up to the order of the gradients entering the state space.

In this paper, our aim is to apply the extended Liu method to a model of mixtures composed by two fluid components, in order to obtain the restrictions on the constitutive relations arising from the entropy principle in the case in which nonlocal effects of all variables and not only of the internal variables are considered, so generalizing the results obtained in a previous paper (Francaviglia, Palumbo, and Rogolino 2008).

The plan of the paper is the following. In Sec. **2**, we fix the balance equations of the two–component mixture described by the total mass density, the concentration of one constituent, the barycentric velocity, the total internal energy density and a scalar internal variable. In Sec. **3**, after setting the state space, we exploit the entropy inequality by using the extended Liu procedure and derive a set of thermodynamic restrictions. In Sec. **4**, a suitable

representation of the specific entropy is assumed and some solutions of the thermodynamic restrictions are recovered; in particular, it is shown how the thermodynamic constraints can be integrated in the case of a mixture of perfect fluids in three space dimensions and in the case of a mixture of viscous fluids in one space dimension; in the latter case a complete solution to all thermodynamical constraints is provided.

2. Balance equations for the mixture

Let us consider a mixture made by components whose state variables are labeled with a capital roman letter. The mixture occupies a region $\Omega \subset \mathbb{R}^3$. At any time $t \geq 0$, the thermodynamic state of the mixture is described by N partial mass densities ρ_A, by N partial velocities $\mathbf{v}_A$ of the constituents and by the temperature θ of the mixture.

We can define the total mass density ρ and the barycentric velocity $\mathbf{v}$ of the mixture by the positions

$$\sum_A \rho_A = \rho, \qquad \sum_A \rho_A \mathbf{v}_A = \rho \mathbf{v}. \tag{2}$$

Also, we may introduce the diffusion velocities $\mathbf{d}_A$ and the corresponding diffusional mass fluxes $\mathbf{J}_A$,

$$\mathbf{d}_A = \mathbf{v}_A - \mathbf{v}, \qquad \mathbf{J}_A = \rho_A \mathbf{d}_A, \qquad \sum_A \mathbf{J}_A = \mathbf{0}, \tag{3}$$

as well as the concentrations of the constituent A, $c_A = \rho_A / \rho$.

Mixtures can be modeled at different degrees of detail:

- models where primitive variables are the mass densities of the constituents, the barycentric velocity $\mathbf{v}$ and the temperature θ of the mixture (Class I);
- models where primitive variables are the mass densities and the velocities of the constituents, and the temperature θ of the mixture (Class II);
- models where the primitive variables are the partial mass densities, the velocities and the temperatures of the constituents (Class III).

For models of Class III it is worth of being quoted the paper by Gouin and Ruggeri (2008) where a physically consistent way of defining an average temperature in a multitemperature mixture of fluids is considered.

The total mass of a mixture is a conserved quantity, while the mass of a particular component is not conserved, if chemical reactions occur, *i.e.*,

$$\frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A \mathbf{v}_A) = P_A^{chem}, \tag{4}$$

where P_A^{chem} is a production terms of mass due to chemical reactions.

In this paper, we consider models of Class I, and, in particular, models of mixtures with two components. Instead of the partial mass densities, we use the mass density of the mixture and the concentration c of one arbitrarily chosen constituent.

According to the third metaphysical principle given by Truesdell (1984), let us write the balance equations for the mixture as a whole:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0,$$
$$\frac{\partial}{\partial t}(\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v} - T) = \rho \mathbf{f}, \tag{5}$$
$$\frac{\partial}{\partial t}\left(\rho(\varepsilon + \frac{1}{2}\mathbf{v} \cdot \mathbf{v})\right) + \nabla \cdot \left(\mathbf{q} - T \cdot \mathbf{v} + \rho \mathbf{v}(\varepsilon + \frac{1}{2}\mathbf{v} \cdot \mathbf{v})\right) - \rho(\mathbf{f} \cdot \mathbf{v} + r) = 0,$$

where T denotes the (symmetric) Cauchy stress tensor, $\mathbf{f}$ is the specific density of volume forces, ε the specific internal energy density (internal energy per unit mass), $\mathbf{q}$ the heat flux density, and r the energy supply density. To properly describe the mixture we add to (5) the balance equation for the concentration c of one of the two constituents (say, the first one),

$$\rho \frac{dc}{dt} + \nabla \cdot \mathbf{J} = P_1^{chem} \qquad (\mathbf{J} = \mathbf{J}_1), \tag{6}$$

where $\dfrac{d}{dt} = \dfrac{\partial}{\partial t} + \mathbf{v} \cdot \nabla$ is the material time derivative. In the following, we will set $P_1^{chem} = 0$.

Finally, in order to consider dissipative effects due to thermo–diffusion we introduce a scalar internal variable, which we denote by γ, whose time evolution is governed by an equation of the form:

$$\rho \left(\frac{\partial \gamma}{\partial t} + \mathbf{v} \cdot \nabla \gamma\right) + \nabla \cdot \Phi = \Gamma, \tag{7}$$

where Φ denotes the flux associated to the internal variable γ, and Γ represents a suitable production term.

We postulate a balance law for the internal variable γ even if we are aware that this form can be a consequence of the exploitation procedure of the entropy principle (Ván, Berezovski, and Engelbrecht 2008). A comment is in order regarding the divergence term in the balance equations for concentration and the internal variables, since they imply the need to fix data at boundaries. In fact, along with Maugin and Muschik (1994a), we can say that a clever physicist will always manage to detect the internal variables and to measure them. However, in general, he cannot control them, *i.e.*, to adjust their value on the boundary through a direct action of surface or body forces. On the other hand, a large number of physical phenomena exhibiting a spatial localization or a marked diffusion of dissipative processes, are directly amenable by means of spatially non-uniform internal variables (Maugin 1990), whose evolution is determined by complete balance laws, including both a rate term and a divergence term. If the body occupies a bounded domain, such balance laws require appropriate boundary conditions which, in turn, cannot be assigned if the internal variables are not controllable. In a series of papers (Valanis 1996, 1997, 1998) Valanis derived suitable boundary conditions in particular cases by applying a variational method. A different method introduced by Waldmann (1967) also constitutes a good way to construct boundary conditions associated with a diffusive internal variable. A deep discussion on this topic was given by Cimmelli (2002), who showed how it is possible to force the internal variable or its gradient in some cases to assume given values on the boundary by using the second law of thermodynamics.

3. Thermodynamical restrictions

We assume that the mixture is described by a state space W with local coordinates

$$W \equiv \{\rho, c, \varepsilon, \gamma, \nabla\rho, \nabla c, \nabla\varepsilon, \nabla\gamma, \nabla\mathbf{v}\}, \tag{8}$$

i.e., we put ourselves in the framework of a first order nonlocal theory. Notice that we are using the canonically conjugate variable ε instead of the absolute temperature.

The system above must be closed by a suitable set of constitutive equation for the stress tensor T, for the fluxes $\mathbf{J}$, $\mathbf{q}$, Φ, and for the internal source of energy r and the production Γ of the internal variable; these constitutive relations have to be assigned in such way the local entropy production is nonnegative, *i.e.*,

$$\sigma_s = \rho\left(\frac{\partial s}{\partial t} + \mathbf{v}\cdot\nabla s\right) + \nabla\cdot\mathbf{J}^{(s)} \geq 0, \tag{9}$$

s and $\mathbf{J}^{(s)}$ being the specific entropy and entropy flux, respectively. Also the specific entropy and the entropy flux are thought of as functions of the state variables (8).

Since we are considering a nonlocal theory, we exploit the entropy inequality by means of the Liu's extended procedure (Cimmelli, Oliveri, and Triani 2011; Triani *et al.* 2008); therefore, we need to compute the gradients of the fundamental balance equations.

By neglecting the external body forces and the internal sources of energy, let us rewrite in components the set of field equations:

$$\begin{aligned}
&\rho_{,t} + v_i\rho_{,i} + \rho v_{i,i} = 0,\\
&\rho c_{,t} + \rho v_i c_{,i} + J_{i,i} = 0,\\
&\rho v_{j,t} + \rho v_i v_{j,i} - T_{ji,i} = 0,\\
&\rho \varepsilon_{,t} + \rho v_i \varepsilon_{,i} + q_{i,i} - T_{ij}v_{i,j} = 0,\\
&\rho \gamma_{,t} + \rho v_i \gamma_{,i} + \Phi_{i,i} - \Gamma = 0,
\end{aligned} \tag{10}$$

where the indices $_{,t}$ and $_{,i}$ stand for the partial derivatives with respect to the time t and the coordinate x_i $(i = 1, 2, 3)$ (the Einstein summation convention over repeated indices is used), and compute their first order gradients:

$$\begin{aligned}
&\rho_{,kt} + v_{i,k}\rho_{,i} + v_i\rho_{,ki} + \rho_{,k}v_{i,i} + \rho v_{i,ik} = 0,\\
&\rho_{,k}c_{,t} + \rho c_{,kt} + \rho_{,k}v_i c_{,i} + \rho v_{i,k}c_{,i} + \rho v_i c_{,ki} + J_{i,ki} = 0,\\
&\rho_{,k}v_{j,t} + \rho v_{j,kt} + \rho_{,k}v_i v_{j,i} + \rho v_{i,k}v_{j,i} + \rho v_i v_{j,ki} - T_{ji,ki} = 0,\\
&\rho_{,k}\varepsilon_{,t} + \rho\varepsilon_{,kt} + \rho_{,k}v_i\varepsilon_{,i} + \rho v_{i,k}\varepsilon_{,i}\\
&\quad + \rho v_i\varepsilon_{,ki} + \rho_{i,ki} - T_{ij,k}v_{i,j} - T_{ij}v_{i,kj} = 0,\\
&\rho_{,k}\gamma_{,t} + \rho\gamma_{,kt} + \rho_{,k}v_i\gamma_{,i} + \rho v_{i,k}\gamma_{,i} + \rho v_i\gamma_{,ki} + \Phi_{i,ki} - \Gamma_{,k} = 0.
\end{aligned} \tag{11}$$

Now let us introduce some Lagrange multipliers; we use lower case greek letters for the Lagrange multipliers related to the field equations, and capital greek letters for the Lagrange multipliers related to the gradients of the field equations. Therefore, let us multiply the equations $(10)_{1-5}$, by the Lagrange multipliers $\lambda^{(m)}$, $\lambda^{(c)}$, $\lambda_j^{(mv)}$, $\lambda^{(\varepsilon)}$ and $\lambda^{(\gamma)}$, respectively, and the equations $(11)_{1-5}$ by $\Lambda_k^{(m)}$, $\Lambda_k^{(c)}$, $\Lambda_{jk}^{(mv)}$, $\Lambda_k^{(\varepsilon)}$, $\Lambda_k^{(\gamma)}$, respectively; then, let us subtract the equations so obtained from (9).

After some lengthy but straightforward computations (that can be done automatically by means of the package LiuExt, written by one of the authors, F.O., in the Computer Algebra System Reduce (Hearn 1995)), the entropy inequality (9) can be put in the following form:

$$
\begin{aligned}
&\left(\rho\frac{\partial s}{\partial \rho}-\lambda^{(m)}\right)\rho_{,t}+\left(\rho\frac{\partial s}{\partial c}-\rho\lambda^{(c)}-\Lambda_j^{(c)}\rho_{,j}\right)c_{,t}\\
&\quad+\left(\rho\frac{\partial s}{\partial \varepsilon}-\rho\lambda^{(\varepsilon)}-\rho_{,j}\Lambda_j^{(\varepsilon)}\right)\varepsilon_{,t}+\left(\rho\frac{\partial s}{\partial \gamma}-\rho\lambda^{(\gamma)}-\rho_{,j}\Lambda_j^{(\gamma)}\right)\gamma_{,t}\\
&\quad-\left(\rho_{,j}\Lambda_{ij}^{(mv)}+\rho\lambda_i^{(mv)}\right)v_{i,t}+\left(\rho\frac{\partial s}{\partial \rho_{,i}}-\Lambda_i^{(m)}\right)\rho_{,it}\\
&\quad+\left(\rho\frac{\partial s}{\partial c_{,i}}-\rho\Lambda_i^{(c)}\right)c_{,it}+\left(\rho\frac{\partial s}{\partial \varepsilon_{,i}}-\rho\Lambda_i^{(\varepsilon)}\right)\varepsilon_{,it}\\
&\quad+\left(\rho\frac{\partial s}{\partial \gamma_{,i}}-\rho\Lambda_j^{(\gamma)}\right)\gamma_{,jt}+\left(\rho\frac{\partial s}{\partial v_{i,j}}-\rho\Lambda_{ij}^{(mv)}\right)v_{i,jt}\\
&\quad-\left(\Lambda_j^{(\varepsilon)}\frac{\partial q_k}{\partial \rho_{,m}}+\Lambda_j^{(c)}\frac{\partial J_k}{\partial \rho_{,m}}+\Lambda_j^{(\gamma)}\frac{\partial \Phi_k}{\partial \rho_{,m}}-\Lambda_{ij}^{(mv)}\frac{\partial T_{ik}}{\partial \rho_{,m}}\right)\rho_{,mjk}\\
&\quad-\left(\Lambda_j^{(\varepsilon)}\frac{\partial q_k}{\partial c_{,m}}+\Lambda_j^{(c)}\frac{\partial J_k}{\partial c_{,m}}+\Lambda_j^{(\gamma)}\frac{\partial \Phi_k}{\partial c_{,m}}-\Lambda_{ij}^{(mv)}\frac{\partial T_{ik}}{\partial c_{,m}}\right)c_{,mjk}\\
&\quad-\left(\Lambda_j^{(\varepsilon)}\frac{\partial q_k}{\partial \varepsilon_{,m}}+\Lambda_j^{(c)}\frac{\partial J_k}{\partial \varepsilon_{,m}}+\Lambda_j^{(\gamma)}\frac{\partial \Phi_k}{\partial \varepsilon_{,m}}-\Lambda_{ij}^{(mv)}\frac{\partial T_{ik}}{\partial \varepsilon_{,m}}\right)\varepsilon_{,mjk}\\
&\quad-\left(\Lambda_j^{(\varepsilon)}\frac{\partial q_k}{\partial \gamma_{,m}}+\Lambda_j^{(c)}\frac{\partial J_k}{\partial \gamma_{,m}}+\Lambda_j^{(\gamma)}\frac{\partial \Phi_k}{\partial \gamma_{,m}}-\Lambda_{ij}^{(mv)}\frac{\partial T_{ik}}{\partial \gamma_{,m}}\right)\gamma_{,mjk}\\
&\quad-\left(\Lambda_j^{(\varepsilon)}\frac{\partial q_k}{\partial v_{n,m}}+\Lambda_j^{(c)}\frac{\partial J_k}{\partial v_{n,m}}+\Lambda_j^{(\gamma)}\frac{\partial \Phi_k}{\partial v_{n,m}}-\Lambda_{ij}^{(mv)}\frac{\partial T_{ik}}{\partial v_{n,m}}\right)v_{n,mjk}\\
&\quad+f(\rho,\rho_{,i},\rho_{,ij},c,c_{,i},c_{,ij},\varepsilon,\varepsilon_{,i},\varepsilon_{,ij},v_i,v_{i,j},v_{i,jk},\gamma,\gamma_{,j},\gamma_{,jk})\geq 0.
\end{aligned}
\tag{12}
$$

According to the procedure described by Cimmelli, Oliveri, and Triani (2011), the terms entering the inequality (12) and not included in f are linear combinations of *highest derivatives*, *i.e.*, the first–order time derivatives of ρ, c, v_i, ε, γ, $\rho_{,i}$, $c_{,i}$, $v_{i,j}$, $\varepsilon_{,i}$, $\gamma_{,i}$, and the third–order space derivatives of the fields ρ, c, v_i, ε and γ. The values of the highest derivatives are completely arbitrary and independent of their coefficients, which, in turn, depend only on the state variables. Then, even if only one of the coefficients of the highest derivatives is different from zero, the corresponding highest derivative could assume arbitrary negative values and the entropy inequality violated. As a consequence, all the coefficients of the highest derivatives must vanish, so providing the expression of the

Lagrange multipliers,

$$\lambda^{(m)} = \rho \frac{\partial s}{\partial \rho}, \qquad \lambda^{(c)} = \frac{\partial s}{\partial c} - \frac{1}{\rho} \Lambda_j^{(c)} \rho_{,j}, \qquad \rho \frac{\partial s}{\partial \varepsilon} = \rho \lambda^{(\varepsilon)} + \rho_{,j} \Lambda_j^{(\varepsilon)},$$

$$\rho \frac{\partial s}{\partial \gamma} = \rho \lambda^{(\gamma)} + \Lambda_{1j}^{(\gamma)} \rho_{,j}, \qquad \rho_{,j} \Lambda_{ij}^{(mv)} + \rho \lambda_i^{(mv)} = 0, \qquad \Lambda_i^{(m)} = \rho \frac{\partial s}{\partial \rho_{,i}}, \qquad (13)$$

$$\Lambda_i^{(c)} = \frac{\partial s}{\partial c_{,i}}, \qquad \Lambda_i^{(\varepsilon)} = \frac{\partial s}{\partial \varepsilon_{,i}}, \qquad \Lambda_{ij}^{(mv)} = \frac{\partial s}{\partial v_{i,j}}, \qquad \Lambda_j^{(\gamma)} = \frac{\partial s}{\partial \gamma_{,i}},$$

and the following thermodynamics restrictions:

$$\left\langle \Lambda_j^{(\varepsilon)} \frac{\partial q_k}{\partial \rho_{,m}} + \Lambda_j^{(\gamma)} \frac{\partial \Phi_k}{\partial \rho_{,m}} + \Lambda_j^{(c)} \frac{\partial J_k}{\partial \rho_{,m}} - \Lambda_{ij}^{(mv)} \frac{\partial T_{ik}}{\partial \rho_{,m}} \right\rangle_{(jkm)} = 0,$$

$$\left\langle \Lambda_j^{(\varepsilon)} \frac{\partial q_k}{\partial c_{,m}} + \Lambda_j^{(\gamma)} \frac{\partial \Phi_k}{\partial c_{,m}} + \Lambda_j^{(c)} \frac{\partial J_k}{\partial c_{,m}} - \Lambda_{ij}^{(mv)} \frac{\partial T_{ik}}{\partial c_{,m}} \right\rangle_{(jkm)} = 0,$$

$$\left\langle \Lambda_j^{(\varepsilon)} \frac{\partial q_k}{\partial \varepsilon_{,m}} + \Lambda_j^{(\gamma)} \frac{\partial \Phi_k}{\partial \varepsilon_{,m}} + \Lambda_j^{(c)} \frac{\partial J_k}{\partial \varepsilon_{,m}} - \Lambda_{ij}^{(mv)} \frac{\partial T_{ik}}{\partial \varepsilon_{,m}} \right\rangle_{(jkm)} = 0, \qquad (14)$$

$$\left\langle \Lambda_j^{(\varepsilon)} \frac{\partial q_k}{\partial \gamma_{,m}} + \Lambda_j^{(\gamma)} \frac{\partial \Phi_k}{\partial \gamma_{,m}} + \Lambda_j^{(c)} \frac{\partial J_k}{\partial \gamma_{,m}} - \Lambda_{ij}^{(mv)} \frac{\partial T_{ik}}{\partial \gamma_{,m}} \right\rangle_{(jkm)} = 0,$$

$$\left\langle \Lambda_j^{(\varepsilon)} \frac{\partial q_k}{\partial v_{n,m}} + \Lambda_j^{(\gamma)} \frac{\partial \Phi_k}{\partial v_{n,m}} + \Lambda_j^{(c)} \frac{\partial J_k}{\partial v_{n,m}} - \Lambda_{ij}^{(mv)} \frac{\partial T_{ik}}{\partial v_{n,m}} \right\rangle_{(jkm)} = 0,$$

where the angular parentheses are used to denote the symmetric parts of the included tensorial quantities with respect to the indicated indices; thus, (12) reduces to

$$f(\rho, \rho_{,i}, \rho_{,ij}, c, c_{,i}, c_{,ij}, \varepsilon, \varepsilon_{,i}, \varepsilon_{,ij}, v_i, v_{i,j}, v_{i,jk}, \gamma, \gamma_{,j}, \gamma_{,jk}) \geq 0. \qquad (15)$$

The inequality (15) is not linear in the spatial gradients whose order is higher than that appearing in the state space (the *higher derivatives*). In fact, it contains both quadratic and linear terms in the higher derivatives $\rho_{,ij}$, $c_{,ij}$, $\varepsilon_{,ij}$, $v_{i,jk}$ and $\gamma_{,ij}$; by denoting with

$$\mathbf{Y} = (\rho_{,ij}, c_{,ij}, \varepsilon_{,ij}, v_{i,jk}, \gamma_{,ij})^T$$

the vector of higher derivatives, a direct computation shows that (15) can be written as

$$\mathbf{Y}^T A \mathbf{Y} + \mathbf{B} \cdot \mathbf{Y} + C \geq 0, \qquad (16)$$

where A is a symmetric matrix, $\mathbf{B}$ a vector, C a scalar depending only on the state functions, and the superscript ^{T} stands for transposition.

Because of a theorem proved by Cimmelli, Oliveri, and Triani (2011), the necessary and sufficient conditions in order that the inequality (16) is satisfied are that A is a positive semidefinite matrix, $\mathbf{B} \equiv \mathbf{0}$ and $C \geq 0$. The requirement $\mathbf{B} \equiv \mathbf{0}$ provides the following set of additional thermodynamic restrictions:

$$\left\langle \frac{\partial J_i^{(s)}}{\partial \rho_{,k}} \right\rangle_{(i,k)} = \left\langle \lambda^{(c)} \frac{\partial J_i}{\partial \rho_{,k}} + \lambda^{(\varepsilon)} \frac{\partial q_i}{\partial \rho_{,k}} + \lambda^{(\gamma)} \frac{\partial \Phi_i}{\partial \rho_{,k}} \right.$$

$$- \lambda_j^{(mv)} \frac{\partial T_{ij}}{\partial \rho_{,k}} - \Lambda_i^{(\varepsilon)} \frac{\partial T_{lj}}{\partial \rho_{,k}} v_{l,j} - \Lambda_i^{(\gamma)} \frac{\partial \Gamma}{\partial \rho_{,k}}$$

$$+ \Lambda_i^{(\varepsilon)} \left(\frac{\partial q_k}{\partial \rho} + \frac{\partial^2 q_j}{\partial \rho_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 q_j}{\partial \rho_{,k} \partial c} c_{,j} + \frac{\partial^2 q_j}{\partial \rho_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 q_j}{\partial \rho_{,k} \partial \gamma} \gamma_{,j} \right)$$

$$+ \Lambda_j^{(\varepsilon)} \left(\frac{\partial^2 q_i}{\partial \rho_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 q_i}{\partial \rho_{,k} \partial c} c_{,j} + \frac{\partial^2 q_i}{\partial \rho_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 q_i}{\partial \rho_{,k} \partial \gamma} \gamma_{,j} \right)$$

$$+ \Lambda_i^{(c)} \left(\frac{\partial J_k}{\partial \rho} + \frac{\partial^2 J_j}{\partial \rho_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 J_j}{\partial \rho_{,k} \partial c} c_{,j} + \frac{\partial^2 J_j}{\partial \rho_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 J_j}{\partial \rho_{,k} \partial \gamma} \gamma_{,j} \right)$$

$$+ \Lambda_j^{(\varepsilon)} \left(\frac{\partial^2 J_i}{\partial \rho_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 J_i}{\partial \rho_{,k} \partial c} c_{,j} + \frac{\partial^2 J_i}{\partial \rho_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 J_i}{\partial \rho_{,k} \partial \gamma} \gamma_{,j} \right)$$

$$+ \Lambda_i^{(\gamma)} \left(\frac{\partial \Phi_k}{\partial \rho} + \frac{\partial^2 \Phi_j}{\partial \rho_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 \Phi_j}{\partial \rho_{,k} \partial c} c_{,j} + \frac{\partial^2 \Phi_j}{\partial \rho_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 \Phi_j}{\partial \rho_{,k} \partial \gamma} \gamma_{,j} \right)$$

$$+ \Lambda_j^{(\gamma)} \left(\frac{\partial^2 \Phi_i}{\partial \rho_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 \Phi_i}{\partial \rho_{,k} \partial c} c_{,j} + \frac{\partial^2 \Phi_i}{\partial \rho_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 \Phi_i}{\partial \rho_{,k} \partial \gamma} \gamma_{,j} \right)$$

$$+ \Lambda_{ji}^{(mv)} \left(\frac{\partial T_{jk}}{\partial \rho} + \frac{\partial^2 T_{jl}}{\partial \rho_{,k} \partial \rho} \rho_{,l} + \frac{\partial^2 T_{jl}}{\partial \rho_{,k} \partial c} c_{,l} + \frac{\partial^2 T_{jl}}{\partial \rho_{,k} \partial \varepsilon} \varepsilon_{,l} + \frac{\partial^2 T_{jl}}{\partial \rho_{,k} \partial \gamma} \gamma_{,l} \right)$$

$$\left. + \Lambda_{jl}^{(mv)} \left(\frac{\partial^2 T_{ji}}{\partial \rho_{,k} \partial \rho} \rho_{,l} + \frac{\partial^2 T_{ji}}{\partial \rho_{,k} \partial c} c_{,l} + \frac{\partial^2 T_{ji}}{\partial \rho_{,k} \partial \varepsilon} \varepsilon_{,l} \frac{\partial^2 T_{ji}}{\partial \rho_{,k} \partial \gamma} \gamma_{,l} \right) \right\rangle_{(i,k)},$$

(17)

$$\left\langle \frac{\partial J_i^{(s)}}{\partial c_{,k}} \right\rangle_{(i,k)} = \left\langle \lambda^{(c)} \frac{\partial J_i}{\partial c_{,k}} + \lambda^{(\varepsilon)} \frac{\partial q_i}{\partial c_{,k}} + \lambda^{(\gamma)} \frac{\partial \Phi_i}{\partial c_{,k}} \right.$$

$$- \lambda_j^{(mv)} \frac{\partial T_{ij}}{\partial c_{,k}} - \Lambda_i^{(\varepsilon)} \frac{\partial T_{lj}}{\partial c_{,k}} v_{l,j} - \Lambda_i^{(\gamma)} \frac{\partial \Gamma}{\partial c_{,k}}$$

$$+ \Lambda_i^{(\varepsilon)} \left(\frac{\partial q_k}{\partial \rho} + \frac{\partial^2 q_j}{\partial c_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 q_j}{\partial c_{,k} \partial c} c_{,j} + \frac{\partial^2 q_j}{\partial c_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 q_j}{\partial c_{,k} \partial \gamma} \gamma_{,j} \right)$$

$$+ \Lambda_j^{(\varepsilon)} \left(\frac{\partial^2 q_i}{\partial c_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 q_i}{\partial c_{,k} \partial c} c_{,j} + \frac{\partial^2 q_i}{\partial c_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 q_i}{\partial c_{,k} \partial \gamma} \gamma_{,j} \right)$$

$$+ \Lambda_i^{(c)} \left(\frac{\partial J_k}{\partial \rho} + \frac{\partial^2 J_j}{\partial c_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 J_j}{\partial c_{,k} \partial c} c_{,j} + \frac{\partial^2 J_j}{\partial c_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 J_j}{\partial c_{,k} \partial \gamma} \gamma_{,j} \right)$$

$$+ \Lambda_j^{(\varepsilon)} \left(\frac{\partial^2 J_i}{\partial c_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 J_i}{\partial c_{,k} \partial c} c_{,j} + \frac{\partial^2 J_i}{\partial c_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 J_i}{\partial c_{,k} \partial \gamma} \gamma_{,j} \right)$$

$$+ \Lambda_i^{(\gamma)} \left(\frac{\partial \Phi_k}{\partial \rho} + \frac{\partial^2 \Phi_j}{\partial c_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 \Phi_j}{\partial c_{,k} \partial c} c_{,j} + \frac{\partial^2 \Phi_j}{\partial c_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 \Phi_j}{\partial c_{,k} \partial \gamma} \gamma_{,j} \right)$$

$$+ \Lambda_j^{(\gamma)} \left(\frac{\partial^2 \Phi_i}{\partial c_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 \Phi_i}{\partial c_{,k} \partial c} c_{,j} + \frac{\partial^2 \Phi_i}{\partial c_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 \Phi_i}{\partial c_{,k} \partial \gamma} \gamma_{,j} + \right)$$

$$+ \Lambda_{ji}^{(mv)} \left(\frac{\partial T_{jk}}{\partial \rho} + \frac{\partial^2 T_{jl}}{\partial c_{,k} \partial \rho} \rho_{,l} + \frac{\partial^2 T_{jl}}{\partial c_{,k} \partial c} c_{,l} + \frac{\partial^2 T_{jl}}{\partial c_{,k} \partial \varepsilon} \varepsilon_{,l} + \frac{\partial^2 T_{jl}}{\partial c_{,k} \partial \gamma} \gamma_{,l} \right)$$

$$\left. + \Lambda_{jl}^{(mv)} \left(\frac{\partial^2 T_{ji}}{\partial c_{,k} \partial \rho} \rho_{,l} + \frac{\partial^2 T_{ji}}{\partial c_{,k} \partial c} c_{,l} + \frac{\partial^2 T_{ji}}{\partial c_{,k} \partial \varepsilon} \varepsilon_{,l} + \frac{\partial^2 T_{ji}}{\partial c_{,k} \partial \gamma} \gamma_{,l} \right) \right\rangle_{(i,k)},$$

(18)

$$
\begin{aligned}
\left\langle \frac{\partial J_i^{(s)}}{\partial \varepsilon_{,k}} \right\rangle_{(i,k)} = & \left\langle \lambda^{(c)} \frac{\partial J_i}{\partial \varepsilon_{,k}} + \lambda^{(\varepsilon)} \frac{\partial q_i}{\partial \varepsilon_{,k}} + \lambda^{(\gamma)} \frac{\partial \Phi_i}{\partial \varepsilon_{,k}} \right. \\
& - \lambda_j^{(mv)} \frac{\partial T_{ij}}{\partial \varepsilon_{,k}} - \Lambda_i^{(\varepsilon)} \frac{\partial T_{lj}}{\partial \varepsilon_{,k}} v_{l,j} - \Lambda_i^{(\gamma)} \frac{\partial \Gamma}{\partial \varepsilon_{,k}} \\
& + \Lambda_i^{(\varepsilon)} \left(\frac{\partial q_k}{\partial \rho} + \frac{\partial^2 q_j}{\partial \varepsilon_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 q_j}{\partial \varepsilon_{,k} \partial c} c_{,j} + \frac{\partial^2 q_j}{\partial \varepsilon_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 q_j}{\partial \varepsilon_{,k} \partial \gamma} \gamma_{,j} \right) \\
& + \Lambda_j^{(\varepsilon)} \left(\frac{\partial^2 q_i}{\partial \varepsilon_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 q_i}{\partial \varepsilon_{,k} \partial c} c_{,j} + \frac{\partial^2 q_i}{\partial \varepsilon_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 q_i}{\partial \varepsilon_{,k} \partial \gamma} \gamma_{,j} \right) \\
& + \Lambda_i^{(c)} \left(\frac{\partial J_k}{\partial \rho} + \frac{\partial^2 J_j}{\partial \varepsilon_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 J_j}{\partial \varepsilon_{,k} \partial c} c_{,j} + \frac{\partial^2 J_j}{\partial \varepsilon_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 J_j}{\partial \varepsilon_{,k} \partial \gamma} \gamma_{,j} \right) \\
& + \Lambda_j^{(\varepsilon)} \left(\frac{\partial^2 J_i}{\partial \varepsilon_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 J_i}{\partial \varepsilon_{,k} \partial c} c_{,j} + \frac{\partial^2 J_i}{\partial \varepsilon_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 J_i}{\partial \varepsilon_{,k} \partial \gamma} \gamma_{,j} \right) \\
& + \Lambda_i^{(\gamma)} \left(\frac{\partial \Phi_k}{\partial \rho} + \frac{\partial^2 \Phi_j}{\partial \varepsilon_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 \Phi_j}{\partial \varepsilon_{,k} \partial c} c_{,j} + \frac{\partial^2 \Phi_j}{\partial \varepsilon_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 \Phi_j}{\partial \varepsilon_{,k} \partial \gamma} \gamma_{,j} \right) \\
& + \Lambda_j^{(\gamma)} \left(\frac{\partial^2 \Phi_i}{\partial \varepsilon_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 \Phi_i}{\partial \varepsilon_{,k} \partial c} c_{,j} + \frac{\partial^2 \Phi_i}{\partial \varepsilon_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 \Phi_i}{\partial \varepsilon_{,k} \partial \gamma} \gamma_{,j} \right) \\
& + \Lambda_{ji}^{(mv)} \left(\frac{\partial T_{jk}}{\partial \rho} + \frac{\partial^2 T_{jl}}{\partial \varepsilon_{,k} \partial \rho} \rho_{,l} + \frac{\partial^2 T_{jl}}{\partial \varepsilon_{,k} \partial c} c_{,l} + \frac{\partial^2 T_{jl}}{\partial \varepsilon_{,k} \partial \varepsilon} \varepsilon_{,l} + \frac{\partial^2 T_{jl}}{\partial \varepsilon_{,k} \partial \gamma} \gamma_{,l} \right) \\
& \left. + \Lambda_{jl}^{(mv)} \left(\frac{\partial^2 T_{ji}}{\partial \varepsilon, k \partial \rho} \rho_{,l} + \frac{\partial^2 T_{ji}}{\partial \varepsilon_{,k} \partial c} c_{,l} + \frac{\partial^2 T_{ji}}{\partial \varepsilon_{,k} \partial \varepsilon} \varepsilon_{,l} + \frac{\partial^2 T_{ji}}{\partial \varepsilon_{,k} \partial \gamma} \gamma_{,l} \right) \right\rangle_{(i,k)},
\end{aligned}
\tag{19}
$$

$$
\begin{aligned}
\left\langle \frac{\partial J_i^{(s)}}{\partial \gamma_{,k}} \right\rangle_{(i,k)} = & \left\langle \lambda^{(c)} \frac{\partial J_i}{\partial \gamma_{,k}} + \lambda^{(\varepsilon)} \frac{\partial q_i}{\partial \gamma_{,k}} + \lambda^{(\gamma)} \frac{\partial \Phi_i}{\partial \gamma_{,k}} \right. \\
& - \lambda_j^{(mv)} \frac{\partial T_{ij}}{\partial \gamma_{,k}} - \Lambda_i^{(\varepsilon)} \frac{\partial T_{lj}}{\partial \gamma_{,k}} v_{l,j} - \Lambda_i^{(\gamma)} \frac{\partial \Gamma}{\partial \gamma_{,k}} \\
& + \Lambda_i^{(\varepsilon)} \left(\frac{\partial q_k}{\partial \gamma} + \frac{\partial^2 q_j}{\partial \gamma_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 q_j}{\partial \gamma_{,k} \partial c} c_{,j} + \frac{\partial^2 q_j}{\partial \gamma_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 q_j}{\partial \gamma_{,k} \partial \gamma} \gamma_{,j} \right) \\
& + \Lambda_j^{(\varepsilon)} \left(\frac{\partial^2 q_i}{\partial \gamma_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 q_i}{\partial \gamma_{,k} \partial c} c_{,j} + \frac{\partial^2 q_i}{\partial \gamma_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 q_i}{\partial \gamma_{,k} \partial \gamma} \gamma_{,j} \right) \\
& + \Lambda_i^{(c)} \left(\frac{\partial J_k}{\partial \rho} + \frac{\partial^2 J_j}{\partial \gamma_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 J_j}{\partial \gamma_{,k} \partial c} c_{,j} + \frac{\partial^2 J_j}{\partial \gamma_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 J_j}{\partial \varepsilon_{,k} \partial \gamma} \gamma_{,j} \right) \\
& + \Lambda_j^{(\varepsilon)} \left(\frac{\partial^2 q_i}{\partial \gamma_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 q_i}{\partial \gamma_{,k} \partial c} c_{,j} + \frac{\partial^2 q_i}{\partial \gamma_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 q_i}{\partial \gamma_{,k} \partial \gamma} \gamma_{,j} \right) \\
& + \Lambda_i^{(\gamma)} \left(\frac{\partial \Phi_k}{\partial \gamma} + \frac{\partial^2 \Phi_j}{\partial \gamma_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 \Phi_j}{\partial \gamma_{,k} \partial c} c_{,j} + \frac{\partial^2 \Phi_j}{\partial \gamma_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 \Phi_j}{\partial \gamma_{,k} \partial \gamma} \gamma_{,j} \right) \\
& + \Lambda_j^{(\gamma)} \left(\frac{\partial^2 \Phi_i}{\partial \gamma_{,k} \partial \rho} \rho_{,j} + \frac{\partial^2 \Phi_i}{\partial \gamma_{,k} \partial c} c_{,j} + \frac{\partial^2 \Phi_i}{\partial \gamma_{,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 \Phi_i}{\partial \gamma_{,k} \partial \gamma} \gamma_{,j} \right) \\
& - \Lambda_{ji}^{(mv)} \left(\frac{\partial T_{jk}}{\partial \gamma} + \frac{\partial^2 T_{jl}}{\partial \gamma_{,k} \partial \rho} \rho_{,l} + \frac{\partial^2 T_{jl}}{\partial \gamma_{,k} \partial c} c_{,l} + \frac{\partial^2 T_{jl}}{\partial \gamma_{,k} \partial \varepsilon} \varepsilon_{,l} + \frac{\partial^2 T_{jl}}{\partial \gamma_{,k} \partial \gamma} \gamma_{,l} \right) \\
& \left. - \Lambda_{jl}^{(mv)} \left(\frac{\partial^2 T_{ji}}{\partial \gamma, k \partial \rho} \rho_{,l} + \frac{\partial^2 T_{ji}}{\partial \gamma_{,k} \partial c} c_{,l} + \frac{\partial^2 T_{ji}}{\partial \gamma_{,k} \partial \varepsilon} \varepsilon_{,l} + \frac{\partial^2 T_{ji}}{\partial \gamma_{,k} \partial \gamma} \gamma_{,l} \right) \right\rangle_{(i,k)},
\end{aligned}
\tag{20}
$$

$$
\left\langle \frac{\partial J_i^{(s)}}{\partial v_{m,k}} \right\rangle_{(ik)} = \left\langle \lambda^{(c)} \frac{\partial J_i}{\partial v_{m,k}} + \lambda^{(\varepsilon)} \frac{\partial q_i}{\partial v_{m,k}} + \lambda^{(\gamma)} \frac{\partial \Phi_i}{\partial v_{m,k}} \right.
$$

$$
- \lambda_j^{(mv)} \frac{\partial T_{ij}}{\partial v_{m,k}} - \Lambda_i^{(\varepsilon)} \frac{\partial T_{ij}}{\partial v_{m,k}} v_{l,j} - \Lambda_i^{(\gamma)} \frac{\partial \Gamma}{\partial v_{m,k}}
$$

$$
+ \Lambda_i^{(\varepsilon)} \left(\frac{\partial q_k}{\partial \gamma} + \frac{\partial^2 q_j}{\partial v_{m,k} \partial \rho} \rho_{,j} + \frac{\partial^2 q_j}{\partial v_{m,k} \partial c} c_{,j} + \frac{\partial^2 q_j}{\partial v_{m,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 q_j}{\partial v_{m,k} \partial \gamma} \gamma_{,j} \right)
$$

$$
+ \Lambda_j^{(\varepsilon)} \left(\frac{\partial^2 q_i}{\partial v_{m,k} \partial \rho} \rho_{,j} + \frac{\partial^2 q_i}{\partial v_{m,k} \partial c} c_{,j} + \frac{\partial^2 q_i}{\partial v_{m,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 q_i}{\partial v_{m,k} \partial \gamma} \gamma_{,j} \right)
$$

$$
+ \Lambda_i^{(c)} \left(\frac{\partial J_k}{\partial \rho} + \frac{\partial^2 J_j}{\partial v_{m,k} \partial \rho} \rho_{,j} + \frac{\partial^2 J_j}{\partial v_{m,k} \partial c} c_{,j} + \frac{\partial^2 J_j}{\partial v_{m,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 J_j}{\partial \varepsilon_{,k} \partial \gamma} \gamma_{,j} \right)
$$

$$
+ \Lambda_j^{(\varepsilon)} \left(\frac{\partial^2 q_i}{\partial v_{m,k} \partial \rho} \rho_{,j} + \frac{\partial^2 q_i}{\partial v_{m,k} \partial c} c_{,j} + \frac{\partial^2 q_i}{\partial v_{m,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 q_i}{\partial v_{m,k} \partial \gamma} \gamma_{,j} \right)
$$

$$
+ \Lambda_i^{(\gamma)} \left(\frac{\partial \Phi_k}{\partial \gamma} + \frac{\partial^2 \Phi_j}{\partial v_{m,k} \partial \rho} \rho_{,j} + \frac{\partial^2 \Phi_j}{\partial v_{m,k} \partial c} c_{,j} + \frac{\partial^2 \Phi_j}{\partial v_{m,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 \Phi_j}{\partial v_{m,k} \partial \gamma} \gamma_{,j} \right)
$$

$$
+ \Lambda_j^{(\gamma)} \left(\frac{\partial^2 \Phi_i}{\partial v_{m,k} \partial \rho} \rho_{,j} + \frac{\partial^2 \Phi_i}{\partial v_{m,k} \partial c} c_{,j} + \frac{\partial^2 \Phi_i}{\partial v_{m,k} \partial \varepsilon} \varepsilon_{,j} + \frac{\partial^2 \Phi_i}{\partial v_{m,k} \partial \gamma} \gamma_{,j} \right)
$$

$$
- \Lambda_{ji}^{(mv)} \left(\frac{\partial T_{jk}}{\partial \gamma} + \frac{\partial^2 T_{jl}}{\partial v_{m,k} \partial \rho} \rho_{,l} + \frac{\partial^2 T_{jl}}{\partial \gamma_{2,k} \partial c} c_{,l} + \frac{\partial^2 T_{jl}}{\partial v_{m,k} \partial \varepsilon} \varepsilon_{,l} + \frac{\partial^2 T_{jl}}{\partial v_{m,k} \partial \gamma} \gamma_{,l} \right)
$$

$$
\left. - \Lambda_{jl}^{(mv)} \left(\frac{\partial^2 T_{ji}}{\partial v_{m,k} \partial \rho} \rho_{,l} + \frac{\partial^2 T_{ji}}{\partial v_{m,k} \partial c} c_{,l} + \frac{\partial^2 T_{ji}}{\partial v_{m,k} \partial \varepsilon} \varepsilon_{,l} + \frac{\partial^2 T_{ji}}{\partial v_{m,k} \partial \gamma} \gamma_{,l} \right) \right\rangle_{(i,k)} . \tag{21}
$$

4. Consequences under additional constitutive assumption on the entropy density

Although the relations (13), (14) and (17) – (21) place severe restrictions on the form of the constitutive functions, they are still too much general for practical applications; therefore, a further simplification is necessary according to specific models. This can be achieved by assuming first a representation of the entropy density. The principle of material objectivity tells us that the constitutive functional for s must be an isotropic function of its vectorial (the gradients of ρ, c, ε and γ) and tensorial (the velocity gradient, or, more precisely, its symmetric part) arguments.

In this section we shall consider two simple cases allowing us to provide particular solutions of the thermodynamical restrictions found in the previous section. In both cases the non–equilibrium part of the entropy density will be assumed quadratic in the first order gradients of field variables in such a way the principle of maximum entropy at the equilibrium is satisfied. The first case is concerned with a mixture of perfect fluids (so we do not include the velocity gradient in the expression of the entropy), whereas the second case is concerned with the one–dimensional motion of a mixture of viscous fluids where the velocity gradient enters the representation of the entropy density.

4.1. Mixture of perfect fluids. Let us assume the entropy density in such a way its non–equilibrium part is quadratic in the gradients of the field variables ρ, c, ε and γ:

$$
\begin{aligned}
s = s_E &+ \kappa_1 \rho_{,i} \rho_{,i} + 2\kappa_2 \kappa_4 \rho_{,i} c_{,i} + 2\kappa_2 \kappa_5 \rho_{,i} \varepsilon_{,i} + 2\kappa_2 \rho_{,i} \gamma_{,i} + \kappa_3 \kappa_4^2 c_{,i} c_{,i} \\
&+ 2\kappa_3 \kappa_4 \kappa_5 c_{,i} \varepsilon_{,i} + 2\kappa_3 \kappa_4 c_{,i} \gamma_{,i} + \kappa_3 \kappa_5^2 \varepsilon_{,i} \varepsilon_{,i} + 2\kappa_3 \kappa_5 \varepsilon_{,i} \gamma_{,i} + \kappa_3 \gamma_{,i}^2 ,
\end{aligned} \tag{22}
$$

where $s_E(\rho, \varepsilon, c, \gamma)$ means the equilibrium entropy defined for homogeneous states, and κ_i ($i = 1, \ldots, 5$) are suitable functions depending on ρ, c, ε and γ only. Clearly, this expression is not the most general representation of the entropy density as an isotropic scalar function; nevertheless, it allows us to provide explicitly the integration of the thermodynamic expressions (14). Moreover, the principle of maximum entropy at the equilibrium is fulfilled provided that

$$\kappa_1 \leq 0, \qquad \kappa_1 \kappa_3 - \kappa_2^2 \geq 0. \tag{23}$$

In fact, conditions (23) guarantee that the non–equilibrium part of the entropy density (22) is always negative semidefinite.

By using (22) in (13), we can explicitly compute the Lagrange multipliers, whereas the thermodynamic restrictions (14) provide the relation

$$\Phi_k + \kappa_4 J_k + \kappa_5 q_k = H_k(\rho, c, \varepsilon, \gamma), \tag{24}$$

linking the heat flux, the diffusion flux and the flux of internal variable, where H_k ($k = 1, 2, 3$) are functions of ρ, c, ε and γ. Therefore, if we further assume reasonable constitutive relations for heat flux and the density flux, say

$$\begin{aligned}
q_k &= q_k^{(0)} + q^{(m)} \rho_{,k} + q^{(c)} c_{,k} + q^{(e)} \varepsilon_{,k} + q^{(\gamma)} \gamma_{,k}, \\
J_k &= j_k^{(0)} + j^{(m)} \rho_{,k} + j^{(c)} c_{,k} + j^{(e)} \varepsilon_{,k} + j^{(\gamma)} \gamma_{,k},
\end{aligned} \tag{25}$$

where $q_k^{(0)}$, $q^{(m)}$, $q^{(c)}$, $q^{(e)}$, $q^{(\gamma)}$, $j_k^{(0)}$, $j^{(m)}$, $j^{(c)}$, $j^{(e)}$ and $j^{(\gamma)}$ are suitable material functions depending on ρ, c, ε, and γ, we obtain from (24) the expression for the flux Φ of the internal variable γ.

Finally, if we assign the constitutive relation for the stress tensor, for instance

$$\begin{aligned}
T_{ij} &= (\tau_0 + \tau_1 \rho_{,k} \rho_{,k} + \tau_2 c_{,k} c_{,k} + \tau_3 \varepsilon_{,k} \varepsilon_{,k} + \tau_4 \gamma_{,k} \gamma_{,k}) \delta_{ij} \\
&\quad + \tau_5 \rho_{,i} \rho_{,j} + \tau_6 c_{,i} c_{,j} + \tau_7 \varepsilon_{,i} \varepsilon_{,j} + \tau_8 < \rho_{,i} c_{,j} > + \tau_9 < \rho_{,i} \varepsilon_{,j} > \\
&\quad + \tau_{10} < \rho_{,i} \gamma_{,j} > + \tau_{11} < c_{,i} \varepsilon_{,j} > + \tau_{12} < c_{,i} \gamma_{,j} > \\
&\quad + \tau_{13} < \varepsilon_{,i} \gamma_{,j} > + \tau_{14} \gamma_{,i} \gamma_{,j},
\end{aligned} \tag{26}$$

where τ_i ($i = 0, 1, \ldots, 15$) are suitable functions of ρ, c, ε and γ, the thermodynamic restrictions (17) – (21) allows us to restrict the form of the entropy flux $J_i^{(s)}$ and of the production term Γ of internal variable.

It is worth of being noticed that the constitutive relations so characterized still contain many degrees of freedom; thus, various particular choices of the involved parameters are possible depending on the effects we physically observe and want to model. Moreover, it can be verified that the classical form of the entropy flux proportional to the heat flux is compatible with these thermodynamic restrictions.

4.2. One–dimensional motion of a mixture of viscous fluids.
Here we consider a one–dimensional motion, and include in the expression of the entropy density the velocity gradient. We provide an example of constitutive equations that completely solve all the restrictions imposed by entropy inequality.

Also in this case we choose the non–equilibrium part of the entropy density quadratic in the derivatives of all the field variables with respect to $x \equiv x_1$, say

$$
\begin{aligned}
s = {} & s_E + \kappa_1 \rho_{,x}^2 + 2\kappa_2 \rho_{,x} c_{,x} + 2\kappa_3 \rho_{,x} v_{,x} + 2\kappa_4 \rho_{,x} \varepsilon_{,x} + 2\kappa_5 \rho_{,x} \gamma_{,x} \\
& + \kappa_6 c_{,x}^2 + 2\kappa_7 c_{,x} v_{,x} + 2\kappa_8 c_{,x} \varepsilon_{,x} + 2\kappa_9 c_{,x} \gamma_{,x} + \kappa_{10} v_{,x}^2 \\
& + 2\kappa_{11} v_{,x} \varepsilon_{,x} + 2\kappa_{12} v_{,x} \gamma_{,x} + \kappa_{13} \varepsilon_{,x}^2 + 2\kappa_{14} \varepsilon_{,x} \gamma_{,x} + \kappa_{15} \gamma_{,x}^2,
\end{aligned}
\tag{27}
$$

where $s_E(\rho, \varepsilon, c, \gamma)$ and $\kappa_i(\rho, \varepsilon, c, \gamma)$ $(i = 1, \ldots, 15)$ are suitable functions depending on the indicated arguments; moreover, the constitutive functions κ_i $(i = 1, \ldots, 15)$ must be such that the non–equilibrium part of the entropy density is a semidefinite quadratic form in the derivatives of all the field variables in order to satisfy the principle of maximum entropy at equilibrium. Also, we take the following general though reasonable constitutive equations q, J and T, for instance

$$
\begin{aligned}
q = {} & q^{(0)} + q^{(m)} \rho_{,x} + q^{(c)} c_{,x} + q^{(v)} v_{,x} + q^{(\varepsilon)} \varepsilon_{,x} + q^{(\gamma)} \gamma_{,x}, \\
J = {} & j^{(0)} + j^{(m)} \rho_{,x} + j^{(c)} c_{,x} + j^{(v)} v_{,x} + j^{(\varepsilon)} \varepsilon_{,x} + j^{(\gamma)} \gamma_{,x}, \\
\Phi = {} & \Phi^{(0)} + \Phi^{(m)} \rho_{,x} + \Phi^{(c)} c_{,x} + \Phi^{(v)} v_{,x} + \Phi^{(\varepsilon)} \varepsilon_{,x} + \Phi^{(\gamma)} \gamma_{,x}, \\
T = {} & \tau_0 + \tau_1 v_{,x} + \tau_2 \rho_{,x}^2 + \tau_3 \rho_{,x} c_{,x} + \tau_4 \rho_{,x} \varepsilon_{,x} + \tau_5 \rho_{,x} \gamma_{,x} \\
& + \tau_6 c_{,x}^2 + \tau_7 c_{,x} \varepsilon_{,x} + \tau_8 c_{,x} \gamma_{,x} + \tau_9 \varepsilon_{,x}^2 + \tau_{10} \varepsilon_{,x} \gamma_{,x} + \tau_{11} \gamma_{,x}^2,
\end{aligned}
\tag{28}
$$

where $q^{(0)}$, $q^{(m)}$, $q^{(c)}$, $q^{(v)}$, $q^{(\varepsilon)}$, $q^{(\gamma)}$, $q^{(0)}$, $j^{(m)}$, $j^{(c)}$, $j^{(v)}$, $j^{(\varepsilon)}$, $j^{(\gamma)}$, $\Phi^{(0)}$, $\Phi^{(m)}$, $\Phi^{(c)}$, $\Phi^{(v)}$, $\Phi^{(\varepsilon)}$, $\Phi^{(\gamma)}$ and τ_i $(i = 0, \ldots, 11)$ are suitable functions of ρ, c, ε and γ.

By imposing that all the thermodynamic restrictions are satisfied, and using the Crack package (Wolf 2004) of Reduce Computer Algebra System (Hearn 1995) in order to find automatically explicit solutions of overdetermined system of partial differential equations, we obtain:

$$
\begin{aligned}
s = {} & s_E(\rho, \varepsilon, c + k\gamma) + s_1(\rho, c + k\gamma)(c_{,x} + k\gamma_{,x})^2, \\
q = {} & q^{(m)} \rho_{,x} + q^{(c)} c_{,x} + q^{(v)} v_{,x} + q^{(\varepsilon)} \varepsilon_{,x} + q^{(\gamma)} \gamma_{,x}, \\
J = {} & -k\Phi, \\
\Phi = {} & \Phi^{(0)} + \Phi^{(m)} \rho_{,x} + \Phi^{(c)} c_{,x} + \Phi^{(\varepsilon)} \varepsilon_{,x} + \Phi^{(\gamma)} \gamma_{,x}, \\
T = {} & \left(\frac{\partial s_E}{\partial \varepsilon}\right)^{-1} \left(\rho^2 \frac{\partial s_E}{\partial \rho} - \left(\rho^2 \frac{\partial s_1}{\partial \rho} + 2\rho s_1\right)(c_{,x} + k\gamma_{,x})^2\right) + \tau_1 v_{,x}, \\
\Gamma = {} & \Gamma(\rho, c, \varepsilon, \gamma), \\
J_s = {} & \frac{\partial s_E}{\partial \varepsilon} q,
\end{aligned}
\tag{29}
$$

where k is a constant, s_0 and s_1 functions of the indicated arguments, whereas $q^{(m)}$, $q^{(c)}$, $q^{(v)}$, $q^{(\varepsilon)}$, $q^{(\gamma)}$, $j^{(m)}$, $j^{(c)}$, $j^{(v)}$, $j^{(\varepsilon)}$, $j^{(\gamma)}$, $\Phi^{(0)}$, $\Phi^{(m)}$, $\Phi^{(c)}$, $\Phi^{(v)}$, $\Phi^{(\varepsilon)}$, $\Phi^{(\gamma)}$, τ_1 and Γ are functions of ρ, c, ε and γ; the principle of maximum entropy at the equilibrium is fulfilled provided that

$$
s_1 \leq 0.
\tag{30}
$$

Finally, all the conditions in (16), in order to satisfy the entropy inequality, require

$$kΓ\frac{\partial s_E}{\partial c} \geq 0, \tag{31}$$

and the 5×5 symmetric matrix P with entries

$$P_{11} = q^{(m)} \frac{\partial^2 s_E}{\partial \rho \partial \varepsilon},$$

$$P_{12} = \frac{1}{2}\left(q^{(m)}\frac{\partial^2 s_E}{\partial c \partial \varepsilon} + q^{(c)}\frac{\partial^2 s_E}{\partial \rho \partial \varepsilon}\right) + ks_1\left(\frac{Γ}{\rho} - \frac{\partial Γ}{\partial \rho}\right),$$

$$P_{13} = \frac{1}{2}q^{(v)}\frac{\partial^2 s_E}{\partial \rho \partial \varepsilon},$$

$$P_{14} = \frac{1}{2}\left(q^{(\varepsilon)}\frac{\partial^2 s_E}{\partial \rho \partial \varepsilon} + q^{(m)}\frac{\partial^2 s_E}{\partial \varepsilon^2}\right),$$

$$P_{15} = \frac{1}{2}\left(q^{(m)}\frac{\partial^2 s_E}{\partial \varepsilon \partial \gamma} + q^{(\gamma)}\frac{\partial^2 s_E}{\partial \rho \partial \varepsilon}\right) + k^2 s_1\left(\frac{Γ}{\rho} - \frac{\partial Γ}{\partial \rho}\right),$$

$$P_{22} = q^{(c)}\frac{\partial^2 s_E}{\partial c \partial \varepsilon} - k\left(2s_1\frac{\partial Γ}{\partial c} + Γ\frac{\partial s_1}{\partial c}\right),$$

$$P_{23} = \frac{1}{2}q^{(v)}\frac{\partial^2 s_E}{\partial c \partial \varepsilon},$$

$$P_{24} = \frac{1}{2}\left(q^{(c)}\frac{\partial^2 s_E}{\partial \varepsilon^2} + q^{(\varepsilon)}\frac{\partial^2 s_E}{\partial c \partial \varepsilon}\right) - ks_1\frac{\partial Γ}{\partial \varepsilon}, \tag{32}$$

$$P_{25} = \frac{1}{2}\left(q^{(\gamma)}\frac{\partial^2 s_E}{\partial c \partial \varepsilon} + q^{(c)}\frac{\partial^2 s_E}{\partial \varepsilon \partial \gamma}\right) - k^2\frac{\partial (s_1 Γ)}{\partial c} - ks_1\frac{\partial Γ}{\partial \gamma},$$

$$P_{33} = \tau_1 \frac{\partial s_E}{\partial \varepsilon},$$

$$P_{34} = \frac{1}{2}q^{(v)}\frac{\partial^2 s_E}{\partial \varepsilon^2},$$

$$P_{35} = \frac{1}{2}q^{(v)}\frac{\partial^2 s_E}{\partial \varepsilon \partial \gamma},$$

$$P_{44} = q^{(\varepsilon)}\frac{\partial^2 s_E}{\partial \varepsilon^2}$$

$$P_{45} = \frac{1}{2}\left(q^{(\varepsilon)}\frac{\partial^2 s_E}{\partial \varepsilon \partial \gamma} + q^{(\gamma)}\frac{\partial^2 s_E}{\partial \varepsilon^2}\right) - k^2 s_1 \frac{\partial Γ}{\partial \varepsilon},$$

$$P_{55} = q^{(\gamma)}\frac{\partial^2 s_E}{\partial \varepsilon \partial \gamma} - 2k^2 s_1 \frac{\partial Γ}{\partial \gamma} - k^3 Γ\frac{\partial s_1}{\partial c}$$

be positive semidefinite.

In equilibrium situations, in which the gradients of the unknown functions vanish, s reduces to s_E. Moreover, in such a case, Eq. (7) yields

$$Γ(\rho, c, \varepsilon, \gamma) = 0, \tag{33}$$

and, under suitable hypotheses of invertibility,

$$\gamma = \widetilde{\gamma}(\rho, c, \varepsilon). \tag{34}$$

In such a situation we have

$$s_E = s_{eq}(\rho, c, \varepsilon, \widetilde{\gamma}(\rho, c, \varepsilon)), \tag{35}$$

so that s_E can be interpreted as a natural extension of the classical equilibrium entropy to non-equilibrium states.

In situations close to the equilibrium, with the absolute temperature defined by the classical thermodynamic relation $\dfrac{1}{\theta} = \dfrac{\partial s}{\partial \varepsilon}$, under the hypothesis of invertibility of θ with respect to ε, which is guaranteed by the positivity of the specific heat $c = \dfrac{\partial \varepsilon}{\partial \theta}$, ε can be expressed as function of the arguments ρ, c, θ and γ; therefore, the constitutive relations (28) give the entropy flux in its classical form. Moreover, its worth observing that, taking

$$
\begin{aligned}
q^{(v)} &= 0, & q^{(m)} &= -q^{(\varepsilon)} \frac{\partial \varepsilon}{\partial \rho}, \\
q^{(c)} &= -q^{(\varepsilon)} \frac{\partial \varepsilon}{\partial c}, & q^{(\gamma)} &= -q^{(\varepsilon)} \frac{\partial \varepsilon}{\partial \gamma},
\end{aligned}
\tag{36}
$$

the constitutive equation for heat flux reduces to Fourier law. The solution so recovered contains some degrees of freedom that can be fixed in order to model specific physical situations.

5. Conclusions

In this paper, we considered a model of mixture with two components. Differently from the model studied by Francaviglia, Palumbo, and Rogolino (2006), we assumed a constitutive theory which is nonlocal in all the state variables; thus, special theories can be recovered by restricting the nonlocality to a subset of the field variables. We derived the thermodynamic restrictions imposed by the entropy principle by means of the extended Liu procedure. We provided some particular solutions of the thermodynamic constraints and showed that they are compatible with the classical form of the entropy flux as the ratio between the heat flux and the temperature. In particular, in the one-dimensional case a complete solution of all the conditions arising from the entropy inequality has been given.

As a final remark, we observe that the exploitation of the entropy inequality can be done within the framework of rational thermodynamics by applying the extended Coleman–Noll procedure (Cimmelli, Sellitto, and Triani 2010), where the terms involving time derivatives appearing in the entropy inequality are eliminated by using the governing equations of the unknown fields and their gradient extensions up to the order of the spatial derivatives involved in the constitutive relations. From a methodological point of view, the extended Coleman–Noll procedure and the extended Liu procedure are different; nevertheless, they provide the same set of thermodynamic restrictions.

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^{a} Università degli Studi di Messina
       Dipartimento di Scienze Matematiche e Informatiche, Scienze Fisiche e Scienze della Terra
       Viale F. Stagno d'Alcontres 31, 98166 Messina, Italy

*   To whom correspondence should be addressed | Email: foliveri@unime.it