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DOCTORAL THESIS

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**Non-Equilibrium Thermodynamics
of porous media filled by a fluid flow and
of rigid bodies with an internal tensorial field
influencing the thermal phenomena**

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CONTENTS

Introduction vi

I NON-EQUILIBRIUM THERMODYNAMICS OF POROUS MEDIA FILLED BY A FLUID FLOW

1 A DESCRIPTION OF ANISOTROPIC POROUS NANOCRYSTALS FILLED BY A FLUID FLOW 1

- 1.1 A model for porous nanocrystals 2
- 1.2 Analysis of entropy production 5
- 1.3 Constitutive relations and generalized affinities 8
- 1.4 Rate equations 10
- 1.5 Linearised temperature equation and internal energy equation 13
- 1.6 Closure of system of governing equations 14

Bibliography of the Introduction and the first Chapter 15

2 NON-EQUILIBRIUM THERMODYNAMICS OF ISOTROPIC POROUS NANOCRYSTALS FILLED BY A FLUID FLOW 20

- 2.1 Isotropic porous media with respect to all rotations of axes frame 22
 - 2.1.1 Constitutive relations, generalized affinities and rate equations in the isotropic case 22
 - 2.1.2 Closure of the governing system of equations in the isotropic case 26

- 2.2 Perfect isotropic porous media 27
 - 2.2.1 Constitutive relations, generalized affinities, rate, temperature and energy equations in perfect isotropic case 27
 - 2.2.2 Closure of the governing system of equations in the perfect isotropic case 27

Bibliography of the second Chapter 28

3 A SIMPLE MODEL OF POROUS MEDIA WITH ELASTIC DEFORMATIONS AND EROSION OR DEPOSITION 32

- 3.1 A model for porous media 33
- 3.2 Elastic porous matrix with erosion/deposition 37
 - 3.2.1 Specific illustration: elastic effects 39
- 3.3 Porous metamaterials 42
- 3.4 Theoretical model, including temperature variations 44
- 3.5 Second-law restrictions 46
- 3.6 Constitutive relations and rate equations 49

- 3.6.1 Objective representations of S , P_{ij} , \mathcal{M}_{ij} , $\mathcal{R}_{ij}^{(i)}$ and q_i 49

Bibliography of the third Chapter 51

| | | | |
|-------|---|-----|--|
| 4 | PROPAGATION OF COUPLED POROSITY AND FLUID-CONCENTRATION WAVES IN ISOTROPIC POROUS MEDIA | 55 | |
| 4.1 | Equations for porosity, fluid-concentration fields and fluxes | 56 | |
| 4.1.1 | Propagation of coupled porosity and fluid-concentration waves | 58 | |
| | Bibliography of the fourth Chapter | 63 | |
| 5 | WEAK DISCONTINUITY WAVES IN ISOTROPIC POROUS MEDIA FILLED BY A FLUID FLOW | 66 | |
| 5.1 | Weak discontinuity waves in isotropic porous structures | 67 | |
| 5.1.1 | Wave front and first approximation of U | 71 | |
| 5.1.2 | One-dimensional case | 73 | |
| 5.1.3 | Eigenvalues and eigenvectors of the matrix A | 74 | |
| 5.1.4 | Determination of the approximated solution of the PDEs system | 76 | |
| | Bibliography of the fifth Chapter | 79 | |
| 6 | ASYMPTOTIC WAVES IN POROUS ISOTROPIC MEDIA FILLED BY A FLUID FLOW | 82 | |
| 6.1 | Asymptotic waves in isotropic porous structures | 82 | |
| 6.1.1 | Asymptotic wave propagation into a uniform unperturbed state | 83 | |
| 6.1.2 | The growth equation for the first perturbation term | 85 | |
| | Bibliography of the sixth Chapter | 86 | |
| | | | |
| II | NON-EQUILIBRIUM THERMODYNAMICS OF RIGID BODIES WITH AN INTERNAL TENSORIAL FIELD INFLUENCING THE THERMAL PHENOMENA | | |
| 7 | GENERALIZED BALLISTIC-CONDUCTIVE HEAT TRANSPORT LAWS IN THREE-DIMENSIONAL ISOTROPIC MATERIALS | 90 | |
| 7.1 | Basic equations of heat transport | 92 | |
| 7.2 | Onsager reciprocity relations | 94 | |
| 7.2.1 | Onsager reciprocity relations | 94 | |
| 7.3 | General isotropic case without assumption on the parity of Q_{ij} | 95 | |
| 7.3.1 | Onsager symmetry | 96 | |
| 7.3.2 | Entropy production | 98 | |
| 7.4 | Rate equations for q and Q without assumption on the parity of Q | 100 | |
| 7.5 | The rate equations with Onsager reciprocity when Q has odd parity | 102 | |
| 7.5.1 | One-dimensional heat transport in the case where Q_{ij} has odd parity | 105 | |
| 7.5.2 | Special cases of heat transport equation in the assumption that Q_{ij} has odd parity | 107 | |
| 7.6 | Rate equations in the isotropic case where Q has even parity | 109 | |
| 7.6.1 | One-dimensional isotropic heat transport in the assumption that Q_{ij} has even parity | 110 | |
| 7.6.2 | Special cases of heat transport equation in the assumption that Q_{ij} has even parity | 111 | |
| | Bibliography of the seventh Chapter | 112 | |

| | | |
|-------|--|-----|
| | Conclusions regarding the first and second Part of this thesis | 117 |
| | Bibliography of the conclusions | 121 |
| A | PARTICULAR CASES OF ISOTROPIC AND PERFECT ISOTROPIC TENSORS | 123 |
| A.1 | Special form for isotropic tensors of order three | 123 |
| A.2 | Special form for isotropic tensors of order five | 123 |
| A.2.1 | Case where a fifth order isotropic tensor L_{ijklm} has one particular symmetry | 124 |
| A.2.2 | Case where a fifth order isotropic tensor L_{ijklm} presents two symmetries | 124 |
| A.3 | Special form for fourth order isotropic and perfect isotropic tensors | 124 |
| A.3.1 | Case where a fourth order isotropic tensor L_{ijkl} has one particular type of symmetry | 125 |
| A.3.2 | Case where a fourth order isotropic tensor L_{ijkl} has three symmetries | 125 |
| A.3.3 | Case where a fourth order isotropic tensor L_{ijkl} has one particular symmetry of another type | 125 |
| A.3.4 | Case where a fourth order isotropic tensor L_{ijkl} has the symmetry $L_{ijkl} = L_{ikjl}$ | 126 |
| A.3.5 | Case where a fourth order isotropic tensor L_{ijkl} has two symmetries | 126 |
| A.4 | Special form for isotropic and perfect isotropic tensors of order six | 126 |
| A.4.1 | Case where a sixth order isotropic tensor L_{ijklmn} has one particular symmetry | 127 |
| A.4.2 | Case where a sixth order isotropic tensor L_{ijklmn} has one particular symmetry of another type | 127 |
| A.4.3 | Case where a sixth order isotropic tensor L_{ijklmn} has two particular symmetries | 128 |
| B | OBJECTIVE REPRESENTATION OF FUNCTIONS | 130 |
| B.1 | Objective representation of scalar functions | 130 |
| B.2 | Objective representation of symmetric tensor functions | 131 |
| B.3 | Objective representation of vector functions | 133 |
| | Bibliography of the Appendix B | 134 |
| C | MATRIX REPRESENTATION | 135 |

LIST OF FIGURES

| | | |
|-----------|--|----|
| Figure 1 | The averaging scheme of a porous structure, following [25]. | 2 |
| Figure 2 | The permeability tensor relates the pressure gradient to the flow of fluid in the material. | 34 |
| Figure 3 | Total flux in parallel and equal channels. | 35 |
| Figure 4 | Average flow rate in curved channels. | 36 |
| Figure 5 | Poiseuille flow in a cylindrical channel with rigid walls. | 40 |
| Figure 6 | Poiseuille flow in a cylindrical channel with elastic walls. | 40 |
| Figure 7 | The dilatation of the wall is counteracted by the elasticity of the wall. | 40 |
| Figure 8 | An illustration of elastic force. | 41 |
| Figure 9 | Thickness of the wall. | 41 |
| Figure 10 | An illustration of thermal cloaking and of fluid flow cloaking. | 42 |
| Figure 11 | An illustration of flow concentration. | 43 |
| Figure 12 | Representation of the three wave propagation speeds $v_{(1)}$, $v_{(2)}$ and $v_{(4)}$ as functions of k , for a given numerical set of coefficients. | 63 |

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INTRODUCTION

This thesis consists of two Parts, every one dedicated, in the framework of non-equilibrium thermodynamics, to the study of the behaviour of fluid-saturated porous media and of rigid bodies with an internal tensorial field influencing the thermal phenomena, respectively. Furthermore, three Appendices are present, that clarify some aspects of the arguments presented in the second, third, fourth and seventh Chapter. Regarding the first Part, the description of phenomena accompanying flows of mass in porous structures finds applications in several fields, such as materials sciences, medical sciences, biology and geology, miniaturized systems with porosity defects. Here, we use thermodynamic approaches based on the non-equilibrium thermodynamics (see [2], [4], [18], [19], [20], [23], [24], [26], [28], [30], [33], [34], [45]). The influence of porous channels filled by fluid on the other fields occurring inside the media is illustrated by the introduction of a structural permeability tensor à la Kubik, giving a macroscopic characterization of a porous structure and coming from the use of volume and area averaging procedures. Models for porous media, with some applications, were developed in [1], [5], [6], [7], [8], [9], [10], [36], [37], [43], [49]. Porous channels modify the thermal conductivity. Understanding the influence of porous tubes on mechanical and transport properties in miniaturized systems is an interesting topic, because by experimental and theoretical studies it was found that the porous density has a minor effect on the thermal conductivity for porous defects densities smaller than a characteristic value dependent on the material and temperature but for higher values than this value, the thermal conductivity decreases, and this situation influences the nanodevices performances. Nanostructures can present metallurgical defects (for example porous channels, inclusions, cavities, microfissures, dislocations), that sometimes can self propagate because of some conditions and surrounding conditions that are favourable. A relatively high temperature gradient could produce, for instance, a migration of defects inside the system. In [7], [8], [10], [13], [14], [15], [16], [21], [22], [29], [35], [36], [37], [38], [39] and [40] models, with some applications for media with defects such as piezoelectric, elastic, semiconductor and superlattice structures, were also formulated using the methods of non-equilibrium thermodynamics. Regarding the second Part of this thesis, the deepening knowledge of mechanical, thermal and transport properties in rigid bodies with an internal variable influencing thermal phenomena is very interesting in several technological sectors, such as in material sciences and nanotechnology. The results, obtained in this thesis, may have applications in describing nanostructures, where the rate of variation of the properties of the system is faster than the time scale characterizing the relaxation of the fluxes towards their respective local-equilibrium value. In these nanosystems, there are situations of high-frequency waves propagation. Then, in extended thermodynamics it is essential

to incorporate the fluxes among the state variables. Furthermore, the volume element size L of these nanosystems along some directions is so small that it becomes comparable (or smaller than) the free mean path l of the heat carriers ($L \leq l$, i.e. the Knudsen number $\frac{l}{L}$ is such that $\frac{l}{L} \geq 1$). Other different approaches for porous structures saturated by fluid flows are in [5], [10] and [43].

The organization of this thesis is the following. In the Chapter 1, using a model for porous media filled by a fluid flow [36], in the anisotropic and linear case the constitutive relations, the temperature and energy equations and the rate equations for the porosity field, its flux, the fluid-concentration flux and the heat flux are derived to close the system of equations describing the media under consideration (see [41] and [42]).

In the Chapter 2 the case of porous media isotropic with respect to rotations and inversions of frame axes is treated and symmetry properties of phenomenological tensors of higher order than two (until six) are derived. In Appendix A special forms of isotropic tensors up to six order are deduced (see [7]).

In Chapter 3 a simple model for solids with porous channels, filled by an incompressible isotropic fluid and presenting erosion/deposition phenomena is given. The Darcy-Brinkman-Stokes law is obtained, that represents a rate equation for the local mass flux of the fluid, with a relaxation time in which this flux evolves towards its local-equilibrium value. In Appendix B the objective representations of scalar, vectorial and tensorial functions are presented, clarifying some equations deduced in this Chapter (see [10]).

In Chapters 4, 5 and 6 applications of the theories developed in the first and second Chapters are done. In particular, in Chapter 4 a study of a problem of propagation of coupled porosity and fluid-concentration waves in isotropic porous media is worked out, deducing the wave propagation velocities as functions of the wave number. Also in this Chapter some expressions of isotropic tensors with special symmetries are deduced in Appendix A (see the article [8]). In Chapter 5 following a Boillat's methodology for quasi-linear and hyperbolic systems of the first order, we obtain Bernoulli's equation governing the propagation of weak discontinuities in isotropic porous media filled by a fluid (see the article [9]). In Chapter 6 a general method to construct approximate smooth solutions for nonlinear hyperbolic partial differential equations is illustrated and applied in the case where interactions between the fluid-concentration field, the porosity field and their fluxes in porous isotropic media are considered (see the article [6]).

Finally, in Chapter 7 general constitutive equations of heat transport with second sound and ballistic propagation in isotropic rigid heat conductors are given using non-equilibrium thermodynamics with internal variables. The Appendix C is addressed to a two-dimensional symmetric explicit representation of the conductivity matrix, that appears in the expression of entropy production deduced in this Chapter (see [11]).

Part I

NON-EQUILIBRIUM THERMODYNAMICS OF POROUS
MEDIA FILLED BY A FLUID FLOW

1 | A DESCRIPTION OF ANISOTROPIC POROUS NANOCRYSTALS FILLED BY A FLUID FLOW

In the papers [36] and [37] a non conventional model for fluid-saturated porous crystals was derived in the framework of non-equilibrium thermodynamics introducing in the thermodynamic state vector, as internal variables describing the porous defects, a structural permeability tensor à la Kubik, r_{ij} , its gradient, $r_{ij,k}$, and its flux, \mathcal{V}_{ijk} . In this Chapter, a model is worked out for nanocrystals with porous channels filled by a fluid flow. In the anisotropic and linear case, the constitutive relations for the stress tensor, the entropy density, the chemical potentials for the fluid-concentration and the porosity field, and the rate equations for r_{ij} , \mathcal{V}_{ijk} , the fluid-concentration and the heat fluxes, representing disturbances propagating with finite velocity are derived. Also, the closure of the system of equations describing the behaviour of these nanosystems is discussed, containing the linearized temperature and internal energy equations. The obtained results may have relevance in important advanced studies on nanostructures, where their porous defects have a direct influence on mechanical and transport properties, in particular on thermal conductivity. Inside these nanomaterials there are situations of high-frequency waves propagation and the phenomena are fast. They find applications in materials science, in particular in miniaturized systems with defects, and other applied sciences as medical sciences, biology and geology.

In particular, in Sections 1.1 and 1.2, in the framework of rational extended irreversible thermodynamics with internal variables, a model is presented [36] for porous media filled by a fluid flow, where the internal structure is described by a structural permeability tensor, its gradient and its flux. The very thin porous tubes can self propagate and influence mechanical properties and transport properties of these porous media.

In Sections 1.3 and 1.4 the anisotropic and linear case is treated. The constitutive theory is derived, developing the free energy around a particular thermodynamic equilibrium state, and the rate equations for the structural permeability tensor, its flux, the heat flux and the fluid flux are worked out. According the extended thermodynamics generalized Maxwell-Cattaneo-Vernotte and Fick-Nonnenmacher transport equations for the heat and fluid fluxes, respectively, are derived, from which it is seen the influence of the defects on the transport properties of the medium.

In Section 1.5 a generalized telegraph heat equation, with finite velocity for the thermal disturbances, is derived in the anisotropic case.

Finally, in Section 1.6 the closure of the system of equations describing the behaviour of these media with defects is discussed.

The obtained results have a technological interest in the production of very miniaturized systems (nanotechnology) and the study of high-frequency processes.

The studies presented in this Chapter are contained in the articles [41] and [42]:

L. Restuccia, L. Palese, M. T. Caccamo and A. Famà. A description of anisotropic porous nanocrystals filled by a fluid flow in the framework of Extended Thermodynamics with internal variables. *The Publishing House Proceedings of the Romanian Academy, Series A* 21(2), pp. 123-130, 2020.

L. Restuccia, L. Palese, M. T. Caccamo and A. Famà. Heat equation for porous nanostructures filled by a fluid flow. *Atti della Accademia Peloritana dei Pericolanti* 97(S2), pp. A-16 1-16, 2019.

1.1 A MODEL FOR POROUS NANOCRYSTALS

In this Section, we present a model for fluid-saturated porous crystals, developed in [36], in the framework of extended irreversible thermodynamics with internal variables, where, among the various descriptions of porous structures, that one based on the consideration of a structural permeability tensor r_{ij} à la Kubik [25] is used, and the tensor r_{ij} , its gradient and its flux are introduced in the thermodynamic state vector. A representative elementary sphere volume Ω of a porous skeleton filled by a fluid flow is considered, large enough to give a representation of its statistical properties and such that $\Omega = \Omega^s + \Omega^p$, being Ω^s and Ω^p the solid space and the pore space of Ω , respectively. All pores are considered interconnected and having effective volume porosity $f_v = \frac{\Omega^p}{\Omega}$ constant. The sphere central section Γ (with normal vector $\boldsymbol{\mu}$) is introduced, being $\Gamma = \Gamma^s + \Gamma^p$, with Γ^s and Γ^p the solid area and the pore area of Γ , respectively. In Fig. 1 the averaging scheme regarding a pore structure is given following Kubik [25]. All the microscopic quantities are described with respect to the ξ_i coordinates, while the macroscopic quantities are described with respect to the x_i coordinates ($i = 1, 2, 3$).

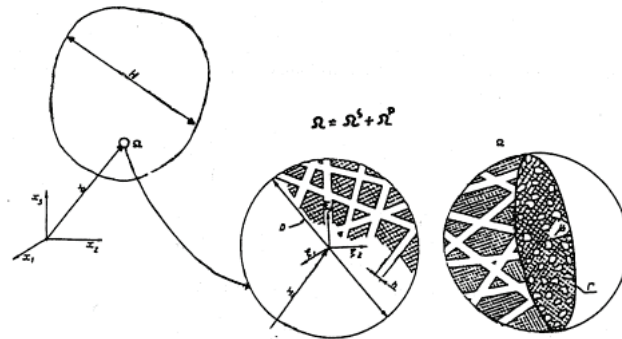


Figure 1: The averaging scheme of a porous structure, following [25].

Then, let $\alpha(\xi)$ be any scalar, spatial vector or second order tensor, describing a microscopic property of the flux of some physical field, flowing through the channel porous space Ω^p , with respect to the ξ coordinates. We assume that such quantity is zero in the solid space Ω^s and on Γ^s . In such a medium we introduce a so called structural permeability tensor à la Kubik, responsible for the structure of a network of porous channels, for any flux of some physical field α_i (in [25] this tensor was introduced for the velocity of the fluid particles) in the following way

$$\bar{\alpha}_i(\mathbf{x}) = r_{ij}(\mathbf{x}, \boldsymbol{\mu}) \overset{*}{\alpha}_j(\mathbf{x}, \boldsymbol{\mu}). \quad (1.1.1)$$

Equation (1.1.1) gives a linear mapping between the bulk-volume average quantity $\bar{\alpha}(\mathbf{x})$ and the channel porous area average $\overset{*}{\alpha}$ of the same quantity passing through the pore area Γ^p of sphere central section. The macroscopic quantities $\bar{\alpha}(\mathbf{x})$ and $\overset{*}{\alpha}$ are defined, respectively, by the following volume and area averaging procedures

$$\bar{\alpha}(\mathbf{x}) = \frac{1}{\Omega} \int_{\tilde{\Omega}} \alpha(\xi) d\tilde{\Omega}, \quad \xi \in \Omega^p, \quad \overset{*}{\alpha}(\mathbf{x}) = \frac{1}{\Gamma^p} \int_{\tilde{\Gamma}} \alpha(\xi) d\tilde{\Gamma}, \quad \xi \in \Gamma^p. \quad (1.1.2)$$

The tensor r_{ij} is symmetric and describes a structure of very thin porous channels inside the medium under consideration [25].

To describe as the defects field evolves (see [36]), we introduce in the thermodynamic state vector the structural permeability field r_{ij} , its gradient $r_{ij,k}$ and its flux \mathcal{V}_{ijk} . We assume that the mass of the fluid filling the porous channels inside the crystal and the same crystal form a two-components mixture. We indicate by ρ_1 the mass of the fluid transported through the elastic porous solid of density ρ_2 . Furthermore, the fluid flow is described by two variables: the concentration of the fluid

$$c = \frac{\rho_1}{\rho}, \quad (1.1.3)$$

and the flux of this fluid j_i^c . Thus, we have the following expression

$$\rho = \rho_1 + \rho_2. \quad (1.1.4)$$

For the mixture of continua as a whole and also for each constituent the following continuity equations are satisfied

$$\dot{\rho} + \rho v_{i,i} = 0, \quad \frac{\partial \rho_1}{\partial t} + (\rho_1 v_{1i})_{,i} = h_1, \quad \frac{\partial \rho_2}{\partial t} + (\rho_2 v_{2i})_{,i} = h_2, \quad (1.1.5)$$

where a superimposed dot denotes the material derivative, h_1 and h_2 are the source terms, that in the following are not taken into consideration, v_{1i} and v_{2i} are the velocities of the fluid particles and the particles of the elastic body, respectively. We introduce the barycentric velocity and the fluid-concentration flux as follows

$$\rho v_i = \rho_1 v_{1i} + \rho_2 v_{2i}, \quad j_i^c = \rho_1 (v_{1i} - v_i). \quad (1.1.6)$$

From equation (1.1.3) we obtain

$$\dot{c} = \frac{\dot{\rho}_1 \rho - \rho_1 \dot{\rho}}{\rho^2},$$

and using equations (1.1.5)₁, (1.1.5)₂ and (1.1.6)₂, we have

$$\begin{aligned} \rho \dot{c} &= \dot{\rho}_1 - \frac{\rho_1 \dot{\rho}}{\rho} = \dot{\rho}_1 + \rho_1 v_{i,i} \\ &= \frac{\partial \rho_1}{\partial t} + v_i \rho_{1,i} + \rho_1 v_{i,i} = -(\rho_1 v_{1i})_{,i} + v_i \rho_{1,i} + \rho_1 v_{i,i} \\ &= -[\rho_{1,i}(v_{1i} - v_i) + \rho_1(v_{1i,i} - v_{i,i})] = -j_{i,i}^c. \end{aligned} \quad (1.1.7)$$

The thermal field is described by the temperature, its gradient and the heat flux q_i . The mechanical field is described by the symmetric total stress tensor τ_{ij} , referred to the whole system considered as a mixture, and by the small strain tensor ε_{ij} , defined by

$$\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}), \quad (1.1.8)$$

being \mathbf{u} the displacement vector. The thermodynamic vector space is chosen as follows

$$\mathcal{E} = \{\varepsilon_{ij}, c, T, r_{ij}, j_i^c, q_i, \mathcal{V}_{ijk}, c_{,i}, T_{,i}, r_{ij,k}\}, \quad (1.1.9)$$

where, we have taken into account the gradients $c_{,i}$, $T_{,i}$ and $r_{ij,k}$, and have ignored the viscous effects, so that $\dot{\varepsilon}_{ij}$ is not in the set \mathcal{E} .

The processes occurring inside the considered nanocrystals are governed by two sets of laws, the first set deals with the classical balance equations:

the balance of mass in the form (obtained by (1.1.7))

$$\rho \dot{c} + j_{i,i}^c = 0; \quad (1.1.10)$$

the momentum balance

$$\rho \dot{v}_i - \tau_{ji,j} - f_i = 0, \quad (1.1.11)$$

where f_i denotes a body force;

the internal energy balance

$$\rho \dot{e} - \tau_{ji} v_{i,j} + q_{i,i} - \rho h = 0, \quad (1.1.12)$$

where e is the internal energy density, h is the energy source density (that in the following will be neglected) and $v_{i,j}$ is the gradient of the velocity of the body given by

$$v_{i,j} = w_{ij} + \frac{d\varepsilon_{ij}}{dt}, \quad \text{with} \quad w_{ij} = \frac{1}{2}(v_{i,j} - v_{j,i}), \quad (1.1.13)$$

being w_{ij} the antisymmetric part of $v_{i,j}$ and $\frac{d\varepsilon_{ij}}{dt}$ the symmetric part of $v_{i,j}$ defined by

$$\frac{d\varepsilon_{ij}}{dt} = \frac{1}{2}(v_{i,j} + v_{j,i}); \quad (1.1.14)$$

the second set of laws concerns the evolution equations of the structural permeability field r_{ij} , its flux \mathcal{V}_{ijk} , the fluid flux j_i^c and the heat flux q_i . These rate equations are constructed obeying the objectivity and frame-indifference principles (see [17], [31] and [32]).

Thus, these rate equations are chosen having the form

$$\dot{r}_{ij}^* + \mathcal{V}_{ijk,k} - \mathcal{R}_{ij}(\mathcal{C}) = 0, \quad (1.1.15)$$

$$\dot{\mathcal{V}}_{ijk}^* - V_{ijk}(\mathcal{C}) = 0, \quad (1.1.16)$$

$$\dot{q}_i^* - Q_i(\mathcal{C}) = 0, \quad (1.1.17)$$

$$\dot{j}_i^c - J_i^c(\mathcal{C}) = 0, \quad (1.1.18)$$

where the symbol (*) denotes the Zaremba-Jaumann derivative defined for a vector, a second rank tensor and a general rank tensor as follows

$$\dot{a}_i^* = \dot{a}_i - w_{ik}a_k, \quad \dot{a}_{ij}^* = \dot{a}_{ij} - w_{ik}a_{kj} - w_{jk}a_{ik}, \quad (1.1.19)$$

$$\dot{a}_{ij\dots m}^* = \dot{a}_{ij\dots m} - w_{ip}a_{pj\dots m} - w_{jp}a_{ip\dots m} - \dots - w_{mp}a_{ij\dots p}, \quad (1.1.20)$$

where $\mathcal{R}_{ij}(\mathcal{C})$ is the source-like term which deals with the creation or annihilation of porous channels, $V_{ijk}(\mathcal{C})$ is the source term for the structural permeability field flux, $Q_i(\mathcal{C})$ is the heat flux source and $J_i^c(\mathcal{C})$ is the fluid-concentration flux source. \mathcal{R}_{ij} , V_{ijk} , Q_i and J_i^c are constitutive functions of the independent variables. In the rate equations (1.1.16)-(1.1.18) the flux terms of \mathcal{V}_{ijk} , q_i and j_i^c are not present, in order to close the system of equations describing the media under consideration. Also, in (1.1.15)-(1.1.18) we use for w_{ij} the expression $w_{ij} = v_{i,j} - \frac{\partial \varepsilon_{ij}}{\partial t}$, to obtain relations in linear approximation.

1.2 ANALYSIS OF ENTROPY PRODUCTION

In order to our considerations concern real physical processes occurring in the considered porous structure filled by a fluid flow, all the admissible solutions of the proposed evolution equations should be restricted by the following entropy inequality

$$\rho \dot{S} + \phi_{i,i} - \frac{\rho h}{T} = \sigma^{(s)} \geq 0, \quad (1.2.1)$$

where S is the entropy density, $\frac{\rho h}{T}$ is the external entropy production source, $\sigma^{(s)}$ is the internal entropy production and ϕ_i is the entropy flux. In the sequel, for the sake of simplicity, the source term h and the body force f_i will be neglected. Furthermore, the total mass density ρ is supposed constant. Let us consider the following set of constitutive functions (dependent functions on the set (1.1.9) of independent variables)

$$\mathcal{Z} = \left\{ \tau_{ij}, e, \mathcal{R}_{ij}, J_i^c, Q_i, V_{ijk}, S, \phi_i, \Pi^c, \Pi_{ij}^r, \Pi_i^j, \Pi_i^q, \Pi_{ijk}^v \right\} \quad (1.2.2)$$

(with Π^c the chemical potential of the fluid concentration field and Π_{ij}^r a potential related to the structural permeability field and $\Pi_i^{j^c}$, Π_i^q , Π_{ijk}^v the generalized affinities conjugated to the respective fluxes j_i^c , q_i and \mathcal{V}_{ijk}) having the general form

$$\mathcal{Z} = \tilde{\mathcal{Z}}(\mathcal{C}), \quad (1.2.3)$$

where both \mathcal{C} and \mathcal{Z} are evaluated at the same point and time. In [36] Liu's theorem [27], that considers all balance and evolution equations as mathematical constraints for the general validity of the inequality (1.2.1), was applied, assuming that the density mass ρ of the considered nanocrystals is constant.

The following results was obtained, introducing the free energy density $F = e - Ts$:

the state laws (defining the constitutive functions via the partial derivatives of the free energy with respect to the respective conjugate variables)

$$\tau_{ij} = \rho \frac{\partial F}{\partial \varepsilon_{ij}}, \quad S = -\frac{\partial F}{\partial T}, \quad (1.2.4)$$

$$\Pi^c = \frac{\partial F}{\partial c}, \quad \Pi_{ij}^r = \rho \frac{\partial F}{\partial r_{ij}}, \quad (1.2.5)$$

$$\frac{\partial F}{\partial c_{,i}} = 0, \quad \frac{\partial F}{\partial T_{,i}} = 0, \quad \frac{\partial F}{\partial r_{ij,k}} = 0; \quad (1.2.6)$$

the affinities

$$\Pi_i^{j^c} = \rho \frac{\partial F}{\partial j_i^c}, \quad \Pi_i^q = \rho \frac{\partial F}{\partial q_i}, \quad \Pi_{ijk}^v = \rho \frac{\partial F}{\partial \mathcal{V}_{ijk}}; \quad (1.2.7)$$

the derivatives of the entropy flux

$$\frac{\partial \phi_k}{\partial \varepsilon_{ij}} = \frac{1}{T} v_k \tau_{ij}, \quad \frac{\partial \phi_k}{\partial j_i^c} = -\frac{1}{T} \Pi^c \delta_{ik}, \quad \frac{\partial \phi_k}{\partial q_i} = \frac{1}{T} \delta_{ik}, \quad \frac{\partial \phi_k}{\partial \mathcal{V}_{ijl}} = -\frac{1}{T} \Pi_{ij}^r \delta_{kl}, \quad (1.2.8)$$

$$\frac{\partial \phi_k}{\partial c_{,i}} = 0, \quad \frac{\partial \phi_k}{\partial T_{,i}} = 0, \quad \frac{\partial \phi_k}{\partial r_{ij,l}} = 0, \quad (1.2.9)$$

from which

the entropy flux

$$\phi_k = \frac{1}{T} (q_k - \Pi^c j_k^c - \Pi_{ij}^r \mathcal{V}_{ijk}), \quad (1.2.10)$$

(where the quantity $k_k = -\frac{1}{T} (\Pi^c j_k^c + \Pi_{ij}^r \mathcal{V}_{ijk})$ represents the extra entropy flux);

the residual inequality

$$T \frac{\partial \phi_i}{\partial c_{,i}} + T \frac{\partial \phi_i}{\partial T} T_{,i} + T \frac{\partial \phi_i}{\partial r_{jk}} r_{jk,i} - \Pi_{ij}^r \mathcal{R}_{ij} - \Pi_i^{j^c} J_i^c - \Pi_i^q Q_i - \Pi_{ijk}^v \mathcal{V}_{ijk} \geq 0. \quad (1.2.11)$$

In order to prove relation (1.2.10), first we observe that from (1.2.9) we have $\phi_k = \phi_k(\varepsilon_{ij}, c, T, r_{ij}, j_i^c, q_i, \mathcal{V}_{ijl})$; secondly, we suppose that the quantities Π^c and Π_{ij}^r do not depend on the fluxes j_i^c , q_i and \mathcal{V}_{ijl} .

Integrating (1.2.8)₁ with respect to ε_{ij} and using the state law (1.2.4)₁, we deduce

$$\phi_k = \frac{1}{T} \rho v_k F + \varphi_k^1(c, T, r_{ij}, j_i^c, q_i, \mathcal{V}_{ijl}), \quad (1.2.12)$$

where φ_k^1 is an arbitrary function of its arguments.

Deriving (1.2.12) with respect to j_i^c and using (1.2.8)₂, we have

$$\frac{\partial \varphi_k^1}{\partial j_i^c} = -\frac{1}{T} \rho v_k \frac{\partial F}{\partial j_i^c} - \frac{1}{T} \Pi^c \delta_{ik}, \quad (1.2.13)$$

from which

$$\varphi_k^1 = -\frac{1}{T} \rho v_k F - \frac{1}{T} \Pi^c j_k^c + \varphi_k^2(c, T, r_{ij}, q_i, \mathcal{V}_{ijl}), \quad (1.2.14)$$

where φ_k^2 is an arbitrary function of its arguments.

Substituting (1.2.14) into (1.2.12), we deduce

$$\phi_k = -\frac{1}{T} \Pi^c j_k^c + \varphi_k^2(c, T, r_{ij}, q_i, \mathcal{V}_{ijl}), \quad (1.2.15)$$

Now we derive (1.2.15) with respect to q_i and we use (1.2.8)₃, so that we obtain

$$\frac{\partial \varphi_k^2}{\partial q_i} = \frac{1}{T} \delta_{ik}, \quad (1.2.16)$$

from which

$$\varphi_k^2 = \frac{1}{T} q_k + \varphi_k^3(c, T, r_{ij}, \mathcal{V}_{ijl}), \quad (1.2.17)$$

where φ_k^3 is an arbitrary function of its arguments.

Substituting (1.2.17) into (1.2.15), we deduce

$$\phi_k = -\frac{1}{T} \Pi^c j_k^c + \frac{1}{T} q_k + \varphi_k^3(c, T, r_{ij}, \mathcal{V}_{ijl}), \quad (1.2.18)$$

Finally, deriving (1.2.18) with respect to \mathcal{V}_{ijl} and using relation (1.2.8)₄, we obtain

$$\frac{\partial \varphi_k^3}{\partial \mathcal{V}_{ijl}} = -\frac{1}{T} \Pi_{ij}^r \delta_{kl}, \quad (1.2.19)$$

that integrated with respect to \mathcal{V}_{ijl} give us

$$\varphi_k^3 = -\frac{1}{T} \Pi_{ij}^r \mathcal{V}_{ijk} + \varphi_k^4(c, T, r_{ij}), \quad (1.2.20)$$

where φ_k^4 is an arbitrary vector function of its arguments and, being an objective function, it must be zero because, following [44], [46], [47], [48], it cannot depend only on scalar functions and second order tensor-value functions. Thus

$$\varphi_k^3 = -\frac{1}{T}\Pi_{ij}^r \mathcal{V}_{ijk}, \quad (1.2.21)$$

that substituted into (1.2.18) give (1.2.10), according to the fact that the entropy flux, from the physical point of view, does not depend on equilibrium variables, as T , c and r_{ij} .

In [36] the expression (1.2.10) was obtained with the help of a new function

$$K_k = \rho F v_k - T \phi_k, \quad (1.2.22)$$

concerning flux-like properties.

From expressions (1.2.4)₁, (1.2.6), (1.2.8), (1.2.9) and (1.2.22) we have

$$\frac{\partial K_k}{\partial \varepsilon_{ij}} = 0, \quad \frac{\partial K_k}{\partial j_i^c} = \Pi^c \delta_{ik} + v_k \Pi_i^{j^c}, \quad \frac{\partial K_k}{\partial q_i} = -\delta_{ik} + v_k \Pi_i^q, \quad (1.2.23)$$

$$\frac{\partial K_k}{\partial \mathcal{V}_{ijl}} = \Pi_{ij}^r \delta_{kl} + v_k \Pi_{ijl}^v, \quad \frac{\partial K_k}{\partial c_i} = 0, \quad \frac{\partial K_k}{\partial T_i} = 0, \quad \frac{\partial K_k}{\partial r_{ij,l}} = 0. \quad (1.2.24)$$

We observe that K_k , unlike ϕ_k , is independent of ε_{ij} so that the procedure of integration is easier than that of ϕ_k . Following the same procedure of integration above, we obtain

$$K_k = -q_k + \Pi^c j_k^c + \Pi_{ij}^r \mathcal{V}_{ijk} + \rho F v_k, \quad (1.2.25)$$

and comparing this last relation with (1.2.22) we deduce the expression (1.2.10).

Furthermore, from equations (1.2.4)-(1.2.7), the free energy is the following function

$$F = F(\varepsilon_{ij}, c, T, r_{ij}, j_i^c, q_i, \mathcal{V}_{ijk}). \quad (1.2.26)$$

1.3 CONSTITUTIVE RELATIONS AND GENERALIZED AFFINITIES

In this Section we derive in the anisotropic case and in the linear approximation the constitutive theory for the system under consideration. We recall that the total mass density ρ has been assumed to be constant. We apply the potential method and expanding the free energy, given by (1.2.26), up to the second-order approximation around

a thermodynamic equilibrium state indicated by “ $_0$ ”, introducing the deviations of the independent variables from this reference state, in particular

$$\begin{aligned} \theta = T - T_0, \quad \text{with } \left| \frac{\theta}{T_0} \right| \ll 1, \quad \tilde{e} = e - e_0, \quad \text{with } \left| \frac{\tilde{e}}{e_0} \right| \ll 1, \quad C = c - c_0, \quad \text{with } \left| \frac{C}{c_0} \right| \ll 1, \\ S = S - S_0, \quad \text{with } \left| \frac{S}{S_0} \right| \ll 1, \quad R_{ij} = r_{ij} - r_{0ij}, \quad \text{with } \left| \frac{R_{ij}}{r_{0ij}} \right| \ll 1, \end{aligned} \quad (1.3.1)$$

assuming

$$(\varepsilon_{ij})_0 = 0, \quad (\tau_{ij})_0 = 0, \quad (r_{ij})_0 = r_{0ij}, \quad (u_i)_0 = u_{0i}, \quad (v_i)_0 = v_{0i}, \quad (1.3.2)$$

and taking into account that

$$\begin{aligned} (\mathcal{V}_{ijk})_0 = 0, \quad (q_i)_0 = 0, \quad (j_i^c)_0 = 0, \quad (\Pi_{ij}^r)_0 = 0, \quad (\Pi^c)_0 = 0, \\ (\Pi_{ijk}^v)_0 = 0, \quad (\Pi_i^{j^c})_0 = 0, \quad (\Pi_i^q)_0 = 0, \end{aligned} \quad (1.3.3)$$

we obtain

$$\begin{aligned} F = F_0 - S_0\theta + \frac{1}{2\rho} c_{ijkl} \varepsilon_{ij} \varepsilon_{lm} - \frac{\lambda_{ij}^{\theta\varepsilon}}{\rho} \theta \varepsilon_{ij} + \frac{\lambda_{ijklm}^{r\varepsilon}}{\rho} \varepsilon_{ij} R_{lm} - \frac{\lambda_{ij}^{c\varepsilon}}{\rho} C \varepsilon_{ij} - \frac{1}{2} \frac{c_v}{T_0} \theta^2 + \frac{\lambda_{ij}^{r\theta}}{\rho} R_{ij} \theta \\ + \frac{\lambda^{\theta c}}{\rho} \theta C + \frac{\lambda_{ijklm}^{rr}}{2\rho} R_{ij} R_{lm} + \frac{\lambda_{ij}^{rc}}{\rho} R_{ij} C + \frac{\lambda^c}{2\rho} C^2 + \frac{\lambda_{ijklmn}^{vv}}{2\rho} \mathcal{V}_{ijk} \mathcal{V}_{lmn} + \frac{\lambda_{ijkl}^{vj^c}}{\rho} \mathcal{V}_{ijk} j_i^c \\ + \frac{\lambda_{ijkl}^{vq}}{\rho} \mathcal{V}_{ijk} q_l + \frac{1}{2\rho} \lambda_{ij}^{qq} q_i q_j + \frac{1}{2\rho} \lambda_{ij}^{j^c j^c} j_i^c j_j^c + \frac{1}{\rho} \lambda_{ij}^{j^c q} j_i^c q_j, \end{aligned} \quad (1.3.4)$$

where

$$\begin{aligned} c_{ijkl} = \rho \left(\frac{\partial^2 F}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} \right)_0, \quad \lambda^c = \rho \left(\frac{\partial^2 F}{\partial c^2} \right)_0, \quad c_v = -T_0 \left(\frac{\partial^2 F}{\partial T^2} \right)_0, \quad \lambda^{j^c j^c} = \rho \left(\frac{\partial^2 F}{\partial j_i^c \partial j_k^c} \right)_0, \\ \lambda_{ijklmn}^{vv} = \rho \left(\frac{\partial^2 F}{\partial \mathcal{V}_{ijk} \partial \mathcal{V}_{lmn}} \right)_0, \quad \lambda_{ijkl}^{vq} = \rho \left(\frac{\partial^2 F}{\partial q_i \partial \mathcal{V}_{jkl}} \right)_0, \quad \lambda_{ijkl}^{rr} = \rho \left(\frac{\partial^2 F}{\partial r_{ij} \partial r_{kl}} \right)_0, \\ \lambda_{ij}^{\theta\varepsilon} = -\rho \left(\frac{\partial^2 F}{\partial \varepsilon_{ij} \partial T} \right)_0, \quad \lambda^{\theta c} = \rho \left(\frac{\partial^2 F}{\partial c \partial T} \right)_0, \quad \lambda_{ij}^{rc} = \rho \left(\frac{\partial^2 F}{\partial c \partial r_{ij}} \right)_0, \quad \lambda_{ij}^{qq} = \rho \left(\frac{\partial^2 F}{\partial q_i \partial q_j} \right)_0, \\ \lambda_{ij}^{c\varepsilon} = -\rho \left(\frac{\partial^2 F}{\partial \varepsilon_{ij} \partial c} \right)_0, \quad \lambda_{ik}^{j^c q} = \rho \left(\frac{\partial^2 F}{\partial j_i^c \partial q_k} \right)_0, \quad \lambda_{ij}^{r\theta} = \rho \left(\frac{\partial^2 F}{\partial T \partial r_{ij}} \right)_0, \\ \lambda_{ijkl}^{r\varepsilon} = \rho \left(\frac{\partial^2 F}{\partial \varepsilon_{ij} \partial r_{kl}} \right)_0, \quad \lambda_{ijkl}^{vj^c} = \rho \left(\frac{\partial^2 F}{\partial j_i^c \partial \mathcal{V}_{jkl}} \right)_0. \end{aligned} \quad (1.3.5)$$

In (1.3.4) we have called the second partial derivatives of free energy with respect to the considered independent variables using the name of the phenomenological coefficients, measurable by experiments, coming from their physical interpretation. In (1.3.4) c_v denotes the specific heat, c_{ijklm} is the elastic tensor, $\lambda_{ij}^{\theta\varepsilon}$ are the thermoelastic constants and the other phenomenological coefficients express simple and coupled effects which can manifest among the fields themselves or the different fields acting during interactions. Also, we have taken into consideration the physical dimensions of the physical quantities and the invariance of F under time reversal, so that the terms containing the fluxes at first order are null. Furthermore, the introduction of the minus sign comes from physical reasons and the constant phenomenological coefficients satisfy the following symmetric relations (because they are defined in terms of second derivatives of F and the tensors ε_{ij} and r_{ij} are symmetric)

$$c_{ijklm} = c_{lmij} = c_{jilm} = c_{ijml} = c_{jiml} = c_{mlji} = c_{mlji} = c_{lmji}, \quad (1.3.6)$$

$$\lambda_{ijklm}^{r\varepsilon} = \lambda_{lmji}^{r\varepsilon} = \lambda_{lmij}^{r\varepsilon} = \lambda_{jilm}^{r\varepsilon} = \lambda_{ijml}^{r\varepsilon} = \lambda_{jiml}^{r\varepsilon} = \lambda_{mlji}^{r\varepsilon} = \lambda_{mlji}^{r\varepsilon}, \quad (1.3.7)$$

$$\lambda_{ijklm}^{rr} = \lambda_{lmij}^{rr} = \lambda_{ijml}^{rr} = \lambda_{jilm}^{rr} = \lambda_{jiml}^{rr} = \lambda_{lmji}^{rr} = \lambda_{mlji}^{rr} = \lambda_{mlji}^{rr}, \quad (1.3.8)$$

$$\lambda_{ij}^{\theta\varepsilon} = \lambda_{ji}^{\theta\varepsilon}, \quad \lambda_{ij}^{qq} = \lambda_{ji}^{qq}, \quad \lambda_{ij}^{rc} = \lambda_{ji}^{rc}, \quad \lambda_{ij}^{c\varepsilon} = \lambda_{ji}^{c\varepsilon}, \quad \lambda_{ij}^{r\theta} = \lambda_{ji}^{r\theta}, \quad \lambda_{ij}^{j^c j^c} = \lambda_{ji}^{j^c j^c}, \quad (1.3.9)$$

$$\lambda_{ijklmn}^{vv} = \lambda_{lmnijk}^{vv}, \quad \lambda_{ij}^{j^c q} = \lambda_{ji}^{j^c q}, \quad \lambda_{ijkl}^{vq} = \lambda_{lijk}^{vq}, \quad \lambda_{ijkl}^{vj^c} = \lambda_{lijk}^{vj^c}. \quad (1.3.10)$$

Using equations (1.2.4), (1.2.5) and (1.2.7), we obtain, in the linear approximation, *the constitutive relations*

$$\tau_{ij} = c_{ijklm}\varepsilon_{lm} - \lambda_{ij}^{\theta\varepsilon}\theta + \lambda_{ijlm}^{r\varepsilon}R_{lm} - \lambda_{ij}^{c\varepsilon}C, \quad (1.3.11)$$

$$S = S_0 + \frac{\lambda_{ij}^{\theta\varepsilon}}{\rho}\varepsilon_{ij} + \frac{c_v}{T_0}\theta - \frac{\lambda_{ij}^{r\theta}}{\rho}R_{ij} - \frac{\lambda^{\theta c}}{\rho}C, \quad (1.3.12)$$

$$\Pi_{ij}^r = \lambda_{ijlm}^{r\varepsilon}\varepsilon_{lm} + \lambda_{ij}^{r\theta}\theta + \lambda_{ijlm}^{rr}R_{lm} + \lambda_{ij}^{rc}C, \quad (1.3.13)$$

$$\Pi^c = -\frac{\lambda_{ij}^{c\varepsilon}}{\rho}\varepsilon_{ij} + \frac{\lambda^{\theta c}}{\rho}\theta + \frac{\lambda_{ij}^{rc}}{\rho}R_{ij} + \frac{\lambda^c}{\rho}C, \quad (1.3.14)$$

and *the generalized affinities*

$$\Pi_{ijk}^v = \lambda_{ijklmn}^{vv}\mathcal{V}_{lmn} + \lambda_{ijkl}^{vq}q_l + \lambda_{ijkl}^{vj^c}j_l^c, \quad (1.3.15)$$

$$\Pi_i^q = \lambda_{ijkl}^{vq}\mathcal{V}_{jkl} + \lambda_{ij}^{qq}q_j + \lambda_{ij}^{qj^c}j_j^c, \quad (1.3.16)$$

$$\Pi_i^{j^c} = \lambda_{ijkl}^{vj^c}\mathcal{V}_{jkl} + \lambda_{ij}^{j^c q}q_j + \lambda_{ij}^{j^c j^c}j_j^c. \quad (1.3.17)$$

1.4 RATE EQUATIONS

The residual inequality (1.2.11) imposes some relations among the source terms \mathcal{R}_{ij} , \mathcal{V}_{ijk} , Q_i , J_i^c and the affinities Π_{ij}^r , $\Pi_i^{j^c}$, Π_i^q and Π_{ijk}^v , respectively. In this Section we

work out the rate equations for the heat and fluid fluxes for the structural permeability tensor and its flux. Here, in particular, expressing the source terms \mathcal{R}_{ij} , V_{ijk} , Q_i and J_i^c as linear polynomials with tensorial constant coefficients, in terms of the independent variables and in the case where we may use the material derivative instead of Zaremba-Jaumann we obtain

$$\begin{aligned} \dot{r}_{ij} + \mathcal{V}_{ijk,k} = & \beta_{ijkl}^1 \varepsilon_{kl} + \beta_{ijkl}^2 r_{kl} + \beta_{ijk}^3 j_k^c + \beta_{ijk}^4 q_k + \beta_{ijklm}^5 \mathcal{V}_{klm} + \beta_{ijk}^6 c_{,k} \\ & + \beta_{ijk}^7 T_{,k} + \beta_{ijklm}^8 r_{kl,m}, \end{aligned} \quad (1.4.1)$$

$$\dot{\mathcal{V}}_{ijk} = \zeta_{ijkl}^1 j_l^c + \zeta_{ijkl}^2 q_l + \zeta_{ijklmn}^3 \mathcal{V}_{lmn} + \zeta_{ijkl}^4 c_{,l} + \zeta_{ijkl}^5 T_{,l} + \zeta_{ijklmn}^6 r_{lm,n}, \quad (1.4.2)$$

$$\dot{q}_i = \alpha_{ij}^1 j_j^c + \alpha_{ij}^2 q_j + \alpha_{ijkl}^3 \mathcal{V}_{jkl} + \alpha_{ij}^4 c_{,j} + \alpha_{ij}^5 T_{,j} + \alpha_{ijkl}^6 r_{jk,l}, \quad (1.4.3)$$

$$\dot{j}_i^c = \eta_{ij}^1 j_j^c + \eta_{ij}^2 q_j + \eta_{ijkl}^3 \mathcal{V}_{jkl} + \eta_{ij}^4 c_{,j} + \eta_{ij}^5 T_{,j} + \eta_{ijkl}^6 r_{jk,l}. \quad (1.4.4)$$

Equations (1.4.1)-(1.4.4) describe propagation of disturbances with finite velocity, following the philosophy of extended thermodynamics, and contain coupled effects among the different fields. In these rate equations the fields q_i , j_i^c , r_{ij} and \mathcal{V}_{ijk} present a relaxation times.

In particular, in equation (1.4.1) the tensor field r_{ij} has the relaxation time tensor $\tau_{ijkl}^r = -(\beta_{ijkl}^2)^{-1}$ and in equation (1.4.2) the tensor field \mathcal{V}_{ijk} has the relaxation time tensor $\tau_{ijklmn}^v = -(\zeta_{ijklmn}^3)^{-1}$.

Furthermore, the rate equation (1.4.3) for the heat flux generalizes Maxwell-Vernotte-Cattaneo relation for the thermal disturbances with finite velocity [3], [12] and denoting by τ_{ij}^q a relaxation time tensor associated to the heat flux, it becomes

$$\tau_{ij}^q \dot{q}_j = \chi_{ij}^1 j_j^c - q_i + \chi_{ijkl}^3 \mathcal{V}_{jkl} + \chi_{ij}^4 c_{,j} - \chi_{ij}^5 T_{,j} + \chi_{ijkl}^6 r_{jk,l}. \quad (1.4.5)$$

In (1.4.5) we have used the following notations

$$\chi_{ik}^1 = \tau_{ij}^q \alpha_{jk}^1, \quad \delta_{ik} = -\tau_{ij}^q \alpha_{jk}^2, \quad \chi_{iklm}^3 = \tau_{ij}^q \alpha_{jklm}^3, \quad (1.4.6)$$

$$\chi_{ik}^4 = \tau_{ij}^q \alpha_{jk}^4, \quad \chi_{ik}^5 = -\tau_{ij}^q \alpha_{jk}^5, \quad \chi_{iklm}^6 = \tau_{ij}^q \alpha_{jklm}^6, \quad (1.4.7)$$

where χ_{ij}^1 is the thermodiffusive kinetic tensor, χ_{ij}^4 is the thermodiffusive tensor and χ_{ij}^5 is the heat conductivity tensor. In the case where the relaxation time tensor τ_{ij}^q has the form $\tau_{ij}^q = \tau^q \delta_{ij}$, equation (1.4.5) becomes

$$\tau^q \dot{q}_i + q_i = \chi_{ij}^1 j_j^c + \chi_{ijkl}^3 \mathcal{V}_{jkl} + \chi_{ij}^4 c_{,j} - \chi_{ij}^5 T_{,j} + \chi_{ijkl}^6 r_{jk,l}. \quad (1.4.8)$$

When the coefficients χ^s ($s = 1, 3, 4, 6$) are negligible, equation (1.4.5) takes the form

$$\tau_{ij}^q \dot{q}_j + q_i = -\chi_{ij}^5 T_{,j}, \quad (1.4.9)$$

that is the anisotropic Maxwell-Cattaneo-Vernotte equation.

In the isotropic case, where $\chi_{ij}^5 = \chi \delta_{ij}$ and $\tau_{ij}^q = \tau^q \delta_{ij}$, from equation (1.4.9) we obtain the well known Maxwell-Cattaneo equation [3], [12]

$$\tau^q \dot{q}_j + q_i = -\chi T_{,i}. \quad (1.4.10)$$

When the thermal propagation has infinite velocity, equation (1.4.9) takes the form of anisotropic Fourier equation

$$q_i = -\chi_{ij}^5 T_{,j}, \quad (1.4.11)$$

having the following well known form in the isotropic case

$$q_i = -\chi T_{,i}, \quad (1.4.12)$$

where χ is the thermal conductivity.

Finally, the rate equation (1.4.4) for the fluid flux generalizes the Fick-Nonnenmacher law. When, we may use the material derivative, denoting by τ_{ij}^{jc} the relaxation time tensor of the fluid-concentration flux, we obtain

$$\tau_{ij}^{jc} \dot{j}_j^c = -j_i^c + \xi_{ij}^2 q_j + \xi_{ijkl}^3 \mathcal{V}_{jkl} - \xi_{ij}^4 c_{,j} + \xi_{ij}^5 T_{,j} + \xi_{ijkl}^6 r_{jk,l}, \quad (1.4.13)$$

where

$$\delta_{ik} = -\tau_{ij}^{jc} \eta_{jk}^1, \quad \xi_{ik}^2 = \tau_{ij}^{jc} \eta_{jk}^2, \quad \xi_{iklm}^3 = \tau_{ij}^{jc} \eta_{ijklm}^3, \quad (1.4.14)$$

$$\xi_{ik}^4 = -\tau_{ij}^{jc} \eta_{jk}^4, \quad \xi_{ik}^5 = \tau_{ij}^{jc} \eta_{jk}^5, \quad \xi_{iklm}^6 = \tau_{ij}^{jc} \eta_{ijklm}^6. \quad (1.4.15)$$

The quantities ξ_{ik}^4 and ξ_{ik}^5 are the diffusion tensor and the thermodiffusive tensor, respectively. In the case where the coefficients ξ_{ij}^2 , ξ_{ijkl}^3 , ξ_{ij}^5 and ξ_{ijkl}^6 are null equation (1.4.13) becomes the anisotropic Fick-Nonnenmacher law.

When the relaxation time tensor τ_{ij}^{jc} takes the isotropic form $\tau_{ij}^{jc} = \tau^{jc} \delta_{ij}$, equation (1.4.13) becomes

$$\tau^{jc} \dot{j}_i^c + j_i^c = \xi_{ij}^2 q_j + \xi_{ijkl}^3 \mathcal{V}_{jkl} - \xi_{ij}^4 c_{,j} + \xi_{ij}^5 T_{,j} + \xi_{ijkl}^6 r_{jk,l}. \quad (1.4.16)$$

In the following we use the rate equations for the fields q_i and j_i^c in the form (1.4.8) and (1.4.16), respectively.

We observe that the phenomenological tensors β^s , $s = 1, \dots, 8$, and the tensor field $\mathcal{V}_{ijk,k}$ in equation (1.4.1) are symmetric in the indexes $\{i, j\}$ because of the symmetry of r_{ij} . Furthermore β^s , $s = 1, 2, 8$, are also symmetric in the indexes $\{k, l\}$ because they are dummy with the indexes of the symmetric tensors ε_{kl} , r_{kl} and $r_{kl,m}$, respectively. Hence, we have the following symmetries

$$\beta_{ijkl}^s = \beta_{jikl}^s = \beta_{ijlk}^s = \beta_{jilk}^s, \quad (s = 1, 2), \quad \beta_{ijklm}^8 = \beta_{jiklm}^8 = \beta_{ijlkm}^8 = \beta_{jilk m}^8, \quad (1.4.17)$$

$$\beta_{ijk}^r = \beta_{jik}^r, \quad (r = 3, 4, 6, 7), \quad \beta_{ijklm}^5 = \beta_{jiklm}^5, \quad \mathcal{V}_{ijk,k} = \mathcal{V}_{jik,k}. \quad (1.4.18)$$

Similarly, from (1.4.2) we deduce

$$\gamma_{ijklmn}^6 = \gamma_{ijkmln}^6, \quad (1.4.19)$$

because of the symmetry $r_{lm,n}$ and from relations (1.4.8) and (1.4.16) we have

$$\chi_{ijkl}^6 = \chi_{ikjl}^6, \quad \xi_{ijkl}^6 = \xi_{ikjl}^6. \quad (1.4.20)$$

1.5 LINEARISED TEMPERATURE EQUATION AND INTERNAL ENERGY EQUATION

In this Section we work out the equation that describes the behaviour of the temperature field T . Moreover we will show the linearised balance internal energy equation. Introducing the free energy given by $F = e - TS$, considering the material derivative of the free energy F

$$\rho T \dot{S} = \rho \dot{e} - \rho S \dot{T} - \rho \dot{F}, \quad (1.5.1)$$

and taking into consideration the balance energy equation

$$\rho \dot{e} = \tau_{ij} \dot{\epsilon}_{ij} - q_{i,i}, \quad (1.5.2)$$

(where the expression for the velocity gradient $v_{i,j} = \dot{\epsilon}_{ij} + \Omega_{ij}$ has been used), we obtain

$$\rho T \dot{S} = \tau_{ij} \dot{\epsilon}_{ij} - q_{i,i} - \rho \dot{T} S - \rho \dot{F}. \quad (1.5.3)$$

From (1.5.3), calculating the material derivative of the free energy we have

$$\begin{aligned} \rho T \dot{S} = & \tau_{ij} \dot{\epsilon}_{ij} - q_{i,i} - \rho \dot{T} S - \rho \frac{\partial F}{\partial \epsilon_{ij}} \dot{\epsilon}_{ij} - \rho \frac{\partial F}{\partial T} \dot{T} - \rho \frac{\partial F}{\partial c} \dot{c} + \\ & - \rho \frac{\partial F}{\partial r_{ij}} \dot{r}_{ij} - \rho \frac{\partial F}{\partial \mathcal{V}_{ijk}} \dot{\mathcal{V}}_{ijk} - \rho \frac{\partial F}{\partial j_i^c} \dot{j}_i^c - \rho \frac{\partial F}{\partial q_i} \dot{q}_i. \end{aligned} \quad (1.5.4)$$

Finally, using the state laws (1.2.4), the definitions of the affinities (1.2.7), we have

$$\rho T \dot{S} = -q_{i,i} - \Pi_{ij}^r \dot{r}_{ij} - \Pi^c \dot{c} - \Pi_{ijk}^v \dot{\mathcal{V}}_{ijk} - \Pi_i^j \dot{j}_i^c - \Pi_i^q \dot{q}_i. \quad (1.5.5)$$

Linearising the equation (1.5.5) around the equilibrium state (1.3.1)-(1.3.3), we obtain

$$\rho(T_0 + \theta)(\dot{S}_0 + \dot{S}) = -q_{i,i} - \Pi_{ij}^r [\dot{r}_{0ij} + \dot{R}_{ij}] - \Pi^c (\dot{c}_0 + \dot{C}) - \Pi_{ijk}^v \dot{\mathcal{V}}_{ijk} - \Pi_i^j \dot{j}_i^c - \Pi_i^q \dot{q}_i \quad (1.5.6)$$

and then,

$$\rho T_0 \dot{S} = -q_{i,i}. \quad (1.5.7)$$

Moreover, from equation (1.5.7), we have also

$$\tau^q \rho T_0 \ddot{S} = -\tau^q \dot{q}_{i,i}. \quad (1.5.8)$$

In (1.5.6)-(1.5.8), the superimposed dot “ $\dot{\cdot}$ ” indicates the linearised time derivative $\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v}_0 \cdot \text{grad}$ and the deviations of the fields from the thermodynamic equilibrium state have been indicated by the same symbols of the fields themselves. From equations (1.3.12), (1.5.7), and (1.4.8), linearised around the considered reference equilibrium state, equation (1.5.8) takes the form

$$\begin{aligned} \tau^q \rho T_0 \left(\frac{\lambda_{ij}^{\theta \epsilon}}{\rho} \ddot{\epsilon}_{ij} + \frac{c_v}{T_0} \ddot{T} - \frac{\lambda_{ij}^{r \theta}}{\rho} \ddot{r}_{ij} - \lambda^{\theta c} \ddot{c} \right) = & -\rho T_0 \left(\frac{\lambda_{ij}^{\theta \epsilon}}{\rho} \dot{\epsilon}_{ij} + \frac{c_v}{T_0} \dot{T} - \frac{\lambda_{ij}^{r \theta}}{\rho} \dot{r}_{ij} - \lambda^{\theta c} \dot{c} \right) \\ & - \chi_{ij}^1 j_{j,i}^c - \chi_{ijkl}^3 \mathcal{V}_{jkl,i} - \chi_{ij}^4 c_{,ji} + \chi_{ij}^5 T_{,ji} - \chi_{ijkl}^6 r_{jk,li}. \end{aligned} \quad (1.5.9)$$

Finally, introducing

$$\gamma_{ij} = \frac{T_0}{\rho c_v} \lambda_{ij}^{\theta \varepsilon}, \quad \varphi = \frac{T_0}{c_v} \lambda^{\theta c}, \quad \eta_{ij} = \frac{T_0}{\rho c_v} \lambda_{ij}^{r\theta}, \quad k_{ij} = \frac{\chi_{ij}^5}{\rho c_v}, \quad (1.5.10)$$

$$v_{ij}^1 = \frac{\chi_{ij}^1}{\rho c_v}, \quad v_{ijkl}^3 = \frac{\chi_{ijkl}^3}{c_v \rho}, \quad v_{ij}^4 = \frac{\chi_{ij}^4}{\rho c_v}, \quad v_{ijkl}^6 = \frac{\chi_{ijkl}^6}{c_v \rho}, \quad (1.5.11)$$

and considering the case where we may replace the material derivative by the partial time derivative, we obtain a generalized telegraph equation heat equation for anisotropic porous nanostructures filled by fluid flow, leading to finite speeds of propagation of thermal disturbances

$$\begin{aligned} \tau^q \ddot{T} + \dot{T} = & -\gamma_{ij}(\tau^q \ddot{\varepsilon}_{ij} + \dot{\varepsilon}_{ij}) + \varphi(\tau^q \ddot{c} + \dot{c}) + \eta_{ij}(\tau^q \ddot{r}_{ij} + \dot{r}_{ij}) + k_{ij} T_{,ji} - v_{ij}^1 j_{j,i}^c \\ & - v_{ijkl}^3 \mathcal{V}_{jkl,i} - v_{ij}^4 c_{,ji} - v_{ijkl}^6 r_{jk,li}. \end{aligned} \quad (1.5.12)$$

Now, we linearise the first law of thermodynamics (1.5.2). From (1.5.7)₁, taking into account (1.3.1)₂, using the relation (1.3.12), and considering the case where we may replace the material derivative by the partial time derivative, we obtain

$$\rho \dot{e} - T_0 \lambda_{ij}^{\theta \varepsilon} \dot{\varepsilon}_{i,j} - \rho c_v \dot{\theta} + T_0 \lambda_{ij}^{r\theta} \dot{R}_{ij} + T_0 \lambda^{\theta c} \dot{c} = 0, \quad (1.5.13)$$

i.e.

$$\rho \dot{e} = T_0 \lambda_{ij}^{\theta \varepsilon} \dot{u}_{i,j} + \rho c_v \dot{T} - T_0 \lambda_{ij}^{r\theta} \dot{r}_{ij} - T_0 \lambda^{\theta c} \dot{c}, \quad (1.5.14)$$

where the second order term $\tau_{ij} v_{i,j}$ has been neglected.

1.6 CLOSURE OF SYSTEM OF GOVERNING EQUATIONS

In this Section, to close the system of equations describing linear anisotropic porous nanocrystals filled by a fluid flow, we linearize the balance equations (1.1.10), (1.1.11) (where the constitutive equations (1.3.11) and (1.3.12) are inserted) and the rate equations (1.4.1), (1.4.2), (1.4.8) and (1.4.16) around the equilibrium state (defined by (1.3.1)-(1.3.3)). Taking into account the linearised temperature equation (1.5.12) and the linearised internal energy balance equation (1.5.14), the definitions $\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i})$ and $v_i = \dot{u}_i$, indicating the deviations of the fields from the thermodynamic equilibrium state by the same symbols of the fields themselves, and considering the case where we may replace the material derivative by the partial time derivative, we obtain the following closed system of 45 equations for 45 unknowns: 1 for c , 3 for u_i , 6 for r_{ij} , 27 for \mathcal{V}_{ijk} , 3 for q_i , 3 for j_i^c , 1 for T , 1 for e

$$\rho \dot{c} + j_{i,i}^c = 0, \quad (1.6.1)$$

$$\rho \ddot{u}_i = c_{ijlm} u_{l,mj} - \lambda_{ij}^{\theta \varepsilon} T_{,j} + \lambda_{ijlm}^{r \varepsilon} r_{lm,j} - \lambda_{ij}^{c \varepsilon} c_{,j}, \quad (1.6.2)$$

$$\begin{aligned} \dot{r}_{ij} + \mathcal{V}_{ijk,k} = & \frac{1}{2} \beta_{ijkl}^1 (u_{k,l} + u_{l,k}) + \beta_{ijkl}^2 r_{kl} + \beta_{ijk}^3 j_k^c + \beta_{ijk}^4 q_k + \beta_{ijklm}^5 \mathcal{V}_{klm} \\ & + \beta_{ijk}^6 c_{,k} + \beta_{ijk}^7 T_{,k} + \beta_{ijklm}^8 r_{kl,m}, \end{aligned} \quad (1.6.3)$$

$$\dot{\mathcal{V}}_{ijk} = \gamma_{ijkl}^1 j_l^c + \gamma_{ijkl}^2 q_l + \gamma_{ijklmn}^3 \mathcal{V}_{lmn} + \gamma_{ijkl}^4 c_{,l} + \gamma_{ijkl}^5 T_{,l} + \gamma_{ijklmn}^6 r_{lm,n}, \quad (1.6.4)$$

$$\tau^q \dot{q}_i + q_i = \chi_{ij}^1 j_j^c + \chi_{ijkl}^3 \mathcal{V}_{jkl} + \chi_{ij}^4 c_{,j} - \chi_{ij}^5 T_{,j} + \chi_{ijkl}^6 r_{jk,l}, \quad (1.6.5)$$

$$\tau^j \dot{j}_i^c + j_i^c = \xi_{ij}^2 q_j + \xi_{ijkl}^3 \mathcal{V}_{jkl} - \xi_{ij}^4 c_{,j} + \xi_{ij}^5 T_{,j} + \xi_{ijkl}^6 r_{jk,l}, \quad (1.6.6)$$

$$\begin{aligned} \tau^q \dot{T} + T = & k_{ij} T_{,ij} - \gamma_{ij} (\tau^q \ddot{u}_{i,j} + \dot{u}_{i,j}) + \varphi (\tau^q \dot{c} + \dot{c}) + \eta_{ij} (\tau^q \dot{r}_{ij} + \dot{r}_{ij}) - \nu_{ij}^1 j_{j,i}^c \\ & - \nu_{ijkl}^3 \mathcal{V}_{jkl,i} - \nu_{ij}^4 c_{,ji} - \nu_{ijkl}^6 r_{jk,li}, \end{aligned} \quad (1.6.7)$$

$$\rho \dot{e} = -T_0 \lambda_{ij}^{\theta \varepsilon} \dot{u}_{i,j} - \rho c_v \dot{T} + T_0 \lambda_{ij}^{r \theta} \dot{r}_{ij} + T_0 \lambda^{\theta c} \dot{c}. \quad (1.6.8)$$

In equations (1.6.2) and (1.6.8) the symmetry of c_{ijlm} and $\lambda_{ij}^{\theta \varepsilon}$ have been used (see (1.3.6) and (1.3.9)). In equation (1.6.7) the symmetry of γ_{ij} have been used (see relation (1.5.10)₁). Also, the disturbances of the structural permeability field and its flux have finite velocity and present a relaxation time. Furthermore, also in the case where we do not take into consideration equation (1.6.8) for the internal energy, the system of equations (1.6.1)-(1.6.7) is still closed.

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2 | NON-EQUILIBRIUM THERMODYNAMICS OF ISOTROPIC POROUS NANOCRYSTALS FILLED BY A FLUID FLOW

In the previous Chapter in the linear and anisotropic case, constitutive relations, rate equations, temperature and energy equations were derived to describe the mechanical, thermal and transport properties of fluid-saturated crystals with porous channels defects, using a model developed by Professor L. Restuccia in the framework of non-equilibrium thermodynamics. A structural permeability tensor à la Kubik, r_{ij} and its flux \mathcal{V}_{ijk} were introduced as internal variables in the thermodynamic state vector. Here, we work out in the isotropic and perfect isotropic linear cases the constitutive functions for the stress tensor, the entropy density, the chemical potentials, and also the rate equations for r_{ij} , \mathcal{V}_{ijk} , the fluid and the heat fluxes, describing disturbances propagating with finite velocity and presenting a relaxation time. The porous defects modify the thermal conductivity and when they have a density higher than a suitable characteristic value the thermal conductivity decreases. Furthermore, the closure of the system of equations, describing the media under consideration and linearized around a thermodynamic equilibrium state is obtained. The derived results may have great relevance in biology, medical sciences and in several technological sectors, like seismic engineering and nanotechnology (where high-frequency waves propagation is present and the properties variation rate of the considered medium is faster than the relaxation times of the fluxes towards their equilibrium values and the volume element size L of the nanostructures along some directions is so small that it becomes comparable (or smaller than) the free mean path l of the heat carriers).

In this Chapter, we use a thermodynamic theory (see [30], [32] and also [36], [37]), developed in the framework of extended irreversible Thermodynamics, [1], [4], [13], [14], [15], [19], [20], [22], [24], [26], [27], [39], with internal variables. More precisely, in [30] and [32] for the media under consideration the basic equations were established, the Liu's theorem [23] was applied and the constitutive theory and the rate equations for the fluxes and the porous field were constructed as objective functions using Smith's theorem [38]. In [36] and [37] constitutive relations, rate equations and other results were derived for the same media in the anisotropic case. In this Chapter we investigate the behaviour of isotropic and perfect isotropic porous structures, having a particular spatial symmetry properties, using a mathematical theory for isotropic cartesian tensors [5], [12]. The influence of porous channels on the other fields, occurring inside the considered medium, is described by a structural permeability tensor à la Kubik [21], giving a macroscopic characterization of the porous matrix. In [7], [9], [10], [11], [16], [17], [25], [28], [29], [33], [34] and [35] models, with some applications, for media with defects having the form of a network of very thin tubes, like porous chan-

nels and dislocations, were formulated, using the same methods of non-equilibrium thermodynamics in the case for instance of piezoelectric, elastic, semiconductor and superlattice structures. Also in [2], [3], [8], [18] and [31] non-equilibrium temperatures and heat equation were studied in media with internal variables and in the same thermodynamic framework of non-equilibrium thermodynamics. A relatively high temperature gradient could produce, for instance, a migration of defects inside the system.

The Chapter is organised as follows. In Sections 2.1 and 2.2 the governing equations of the model, describing the mechanical, thermal and transport properties of solid structure with porous channels, saturated by fluid flow, derived in the framework of extended thermodynamics with internal variables, are worked out when the considered media are isotropic under orthogonal transformations. In fact, the relations obtained in Chapter 1 (the constitutive relations (1.3.11)-(1.3.14), the affinities (1.3.15)-(5.1.20) and the closed system (1.6.1)-(1.6.8)) are quite complicated due to their anisotropic nature. Therefore it may be useful to study a simpler case, i.e. the isotropic one where the existence of spatial symmetry properties in the medium simplifies the form of the constitutive equations, the affinities and the rate equations in such a way the Cartesian components of these equations do not depend on all the Cartesian components of the independent variables of the vector space \mathcal{C} , defined by (1.1.9). This statement is called Curie symmetry principle [4]. There are two types of these symmetries:

- *isotropy, namely symmetry with respect to all rotations of the frame of axes;*
- *perfect isotropy, namely symmetry with respect to all rotations and to inversions of the frame of axes.*

These two types of symmetries are treated in detail and the constitutive, rate, temperature and energy equations are worked out in these two different cases. In particular, the generalized Maxwell-Cattaneo-Vernotte and Fick-Nonnenmacher rate equations for the heat and fluid fluxes and the rate equations for the porous field and its flux are derived, showing the influence of porous defects on the transport properties of the considered media. Finally, the closure of the whole system of equations, describing the behaviour of the isotropic and perfect isotropic porous structures under consideration, is deduced. In Appendix A special forms for third, fourth, fifth and sixth order isotropic tensors, having symmetry properties, coming from the symmetry of the strain tensor ε_{ij} and the structural permeability tensor r_{ij} , and also from the used model, are derived. The expressions are cumbersome but are useful in computer programming for physical phenomena simulations. The obtained results can be applied to simpler real cases, where it is possible to neglect the influence of some fields occurring inside the examined media.

The studies presented in this Chapter are contained in the article [6]:

A. Famà and L. Restuccia. Non-Equilibrium thermodynamics framework for fluid flow and porosity dynamics in porous isotropic media. *Annals of the Academy of Romanian Scientists, Series on Mathematics and its Applications* 12(1-2/2020), pp. 198-225, 2020.

2.1 ISOTROPIC POROUS MEDIA WITH RESPECT TO ALL ROTATIONS OF AXES FRAME

In the following two Subsections we will study the form of the balance equations, the constitutive relations, the rate equations, the temperature equation and the closure of equations system, describing the behaviour of the porous media under consideration having symmetry properties *invariant with respect to all rotations of axes frame*. First, we examine the form of isotropic tensors of ranks up to six.

The tensors of ranks up to three take the form [12]

$$L_i = 0, \quad L_{ij} = L\delta_{ij}, \quad L_{ijk} = L\epsilon_{ijk}, \quad (2.1.1)$$

where ϵ_{ijk} is the Levi-Civita tensor and L is a scalar.

Tensors of order four L_{ijkl} must have the form [12]

$$L_{ijkl} = L_1\delta_{ij}\delta_{kl} + L_2\delta_{ik}\delta_{jl} + L_3\delta_{il}\delta_{jk}, \quad (2.1.2)$$

with L_i ($i = 1, 2, 3$) scalars.

Tensors of order five L_{ijklm} and of order six L_{ijklmn} must have the form, respectively, (see [5])

$$L_{ijklm} = L_1\epsilon_{ijk}\delta_{lm} + L_2\epsilon_{ijl}\delta_{km} + L_3\epsilon_{ijm}\delta_{kl} + L_4\epsilon_{ikl}\delta_{jm} + L_5\epsilon_{ikm}\delta_{lj} + L_6\epsilon_{ilm}\delta_{jk}, \quad (2.1.3)$$

$$\begin{aligned} L_{ijklmn} = & L_1\delta_{ij}\delta_{kl}\delta_{mn} + L_2\delta_{ij}\delta_{km}\delta_{ln} + L_3\delta_{ij}\delta_{kn}\delta_{lm} + L_4\delta_{ik}\delta_{jl}\delta_{mn} + L_5\delta_{ik}\delta_{jm}\delta_{ln} \\ & + L_6\delta_{ik}\delta_{jn}\delta_{lm} + L_7\delta_{il}\delta_{jk}\delta_{mn} + L_8\delta_{il}\delta_{jm}\delta_{kn} + L_9\delta_{il}\delta_{jn}\delta_{km} + L_{10}\delta_{im}\delta_{jk}\delta_{ln} \\ & + L_{11}\delta_{im}\delta_{jl}\delta_{kn} + L_{12}\delta_{im}\delta_{jn}\delta_{kl} + L_{13}\delta_{in}\delta_{jk}\delta_{lm} + L_{14}\delta_{in}\delta_{jl}\delta_{km} + L_{15}\delta_{in}\delta_{jm}\delta_{kl}, \end{aligned} \quad (2.1.4)$$

with L_i ($i = 1, 2, \dots, 15$) scalars.

2.1.1 Constitutive relations, generalized affinities and rate equations in the isotropic case

Taking into account (2.1.1)-(2.1.4), in the case of an isotropic medium with respect to all rotations of axes frame, the *isotropic constitutive relations* for τ_{ij} , Π_{ij}^r , S and Π^c , derived from (1.3.11)-(1.3.14) with $\lambda_{ij}^{\theta\epsilon}$, $\lambda_{ij}^{c\epsilon}$, $\lambda_{ij}^{r\theta}$ and λ_{ij}^{rc} having the form (2.1.1)₂ and c_{ijlm} , $\lambda_{ijlm}^{r\epsilon}$ and λ_{ijlm}^{rr} taking the form (A.3.3) of Appendix A, because of their particular symmetries, are:

for the stress tensor

$$\tau_{ij} = \lambda\delta_{ij}\epsilon_{kk} + 2\mu\epsilon_{ij} - \lambda^{\theta\epsilon}\delta_{ij}\theta + \lambda_1^{r\epsilon}\delta_{ij}R_{kk} + \lambda_2^{r\epsilon}R_{ij} - \lambda^{c\epsilon}\delta_{ij}\mathcal{C}, \quad (2.1.5)$$

where λ and μ are the well known Lamé constants, that represent the two significant independent components of c_{ijklm} , and $\lambda_1^{r\varepsilon}$ and $\lambda_2^{r\varepsilon}$ are the two significant independent components of $\lambda_{ijklm}^{r\varepsilon}$;
for the entropy density

$$S = S_0 + \frac{\lambda^{\theta\varepsilon}}{\rho} \varepsilon_{ii} + \frac{c_v}{T_0} \theta - \frac{\lambda^{r\theta}}{\rho} R_{ii} - \frac{\lambda^{\theta c}}{\rho} \mathcal{C}; \quad (2.1.6)$$

for the potential of porous field

$$\Pi_{ij}^r = \lambda_1^{r\varepsilon} \delta_{ij} \varepsilon_{kk} + \lambda_2^{r\varepsilon} \varepsilon_{ij} + \lambda^{r\theta} \delta_{ij} \theta + \lambda_1^{rr} \delta_{ij} R_{kk} + \lambda_2^{rr} R_{ij} - \lambda^{rc} \delta_{ij} \mathcal{C}, \quad (2.1.7)$$

where λ_1^{rr} and λ_2^{rr} are the two significant independent components of λ_{ijklm}^{rr} ;
for the chemical potential of the mass flux

$$\Pi^c = -\frac{\lambda^{c\varepsilon}}{\rho} \varepsilon_{ii} + \frac{\lambda^{\theta c}}{\rho} \theta + \frac{\lambda^{rc}}{\rho} R_{ii} + \frac{\lambda^c}{\rho} \mathcal{C}. \quad (2.1.8)$$

Also, by virtue of (2.1.1)-(2.1.4), from (1.3.15)-(1.3.17), we deduce the expressions for the isotropic generalized affinities, Π_{ijk}^v , Π_i^q and Π_i^{jc} , where the tensors λ_{ij}^{qq} , $\lambda_{ij}^{qj^c}$ and $\lambda_{ij}^{j^c j^c}$ have the form (2.1.1)₂, λ_{ijkl}^{vq} and $\lambda_{ijkl}^{vj^c}$ keep the form (A.3.9) and the tensor λ_{ijklmn}^{vv} of order six assumes the form (A.4.3) of Appendix A, because of its special symmetry. In particular, we have:

the generalized affinity conjugated to the flux \mathcal{V}_{ijk}

$$\begin{aligned} \Pi_{ijk}^v = & [\lambda_1^{vv} (\delta_{ij} \delta_{kl} \delta_{mn} + \delta_{in} \delta_{jk} \delta_{lm}) + \lambda_2^{vv} (\delta_{ij} \delta_{km} \delta_{ln} + \delta_{ik} \delta_{jn} \delta_{lm}) + \lambda_3^{vv} \delta_{ij} \delta_{kn} \delta_{lm} \\ & + \lambda_4^{vv} (\delta_{ik} \delta_{jl} \delta_{mn} + \delta_{im} \delta_{jk} \delta_{nl}) + \lambda_5^{vv} \delta_{ik} \delta_{jm} \delta_{ln} + \lambda_6^{vv} \delta_{il} \delta_{jk} \delta_{mn} + \lambda_7^{vv} \delta_{il} \delta_{jm} \delta_{kn} \\ & + \lambda_8^{vv} \delta_{il} \delta_{jn} \delta_{km} + \lambda_9^{vv} \delta_{im} \delta_{jl} \delta_{kn} + \lambda_{10}^{vv} (\delta_{im} \delta_{jn} \delta_{kl} + \delta_{in} \delta_{jl} \delta_{km}) + \lambda_{11}^{vv} \delta_{in} \delta_{jm} \delta_{kl}] \mathcal{V}_{lmn} \\ & + [\lambda_1^{vq} \delta_{ik} \delta_{jl} + \lambda_2^{vq} (\delta_{ij} \delta_{kl} + \delta_{il} \delta_{jk})] q_l + [\lambda_1^{vj^c} \delta_{ik} \delta_{jl} + \lambda_2^{vj^c} (\delta_{ij} \delta_{kl} + \delta_{il} \delta_{jk})] j_l^c, \end{aligned} \quad (2.1.9)$$

where λ_s^{vv} ($s = 1, \dots, 11$) are the 11 significant independent components of λ_{ijklmn}^{vv} , λ_1^{vq} , λ_2^{vq} the two significant independent components of λ_{ijklm}^{vq} and $\lambda_1^{vj^c}$, $\lambda_2^{vj^c}$ the two significant independent components of the tensor $\lambda_{ijklm}^{vj^c}$.

Equation (2.1.9) gives

$$\begin{aligned} \Pi_{ijk}^v = & \lambda_1^{vv} (\delta_{ij} \mathcal{V}_{kll} + \delta_{jk} \mathcal{V}_{lli}) + \lambda_2^{vv} (\delta_{ij} \mathcal{V}_{lkl} + \delta_{ik} \mathcal{V}_{llj}) + \lambda_3^{vv} \delta_{ij} \mathcal{V}_{llk} + \lambda_4^{vv} (\delta_{ik} \mathcal{V}_{jll} + \delta_{jk} \mathcal{V}_{lil}) \\ & + \lambda_5^{vv} \delta_{ik} \mathcal{V}_{ljl} + \lambda_6^{vv} \delta_{jk} \mathcal{V}_{ill} + \lambda_7^{vv} \mathcal{V}_{ijk} + \lambda_8^{vv} \mathcal{V}_{ikj} + \lambda_9^{vv} \mathcal{V}_{jik} + \lambda_{10}^{vv} (\mathcal{V}_{kij} + \mathcal{V}_{jki}) \\ & + \lambda_{11}^{vv} \mathcal{V}_{kji} + \lambda_1^{vq} \delta_{ik} q_j + \lambda_2^{vq} (\delta_{ij} q_k + \delta_{jk} q_i) + \lambda_1^{vj^c} \delta_{ik} j_j^c + \lambda_2^{vj^c} (\delta_{ij} j_k^c + \delta_{jk} j_i^c); \end{aligned} \quad (2.1.10)$$

the generalized affinity conjugated to the heat flux q_i

$$\Pi_i^q = \lambda_1^{vq} \mathcal{V}_{kik} + \lambda_2^{vq} (\mathcal{V}_{ikk} + \mathcal{V}_{kki}) + \lambda^{qq} q_i + \lambda^{qj^c} j_i^c; \quad (2.1.11)$$

the generalized affinity conjugated to the mass flux j_i^c

$$\Pi_i^{j^c} = \lambda_1^{vj^c} \mathcal{V}_{kik} + \lambda_2^{vj^c} (\mathcal{V}_{ikk} + \mathcal{V}_{kki}) + \lambda^{j^c q} q_i + \lambda^{j^c j^c} j_i^c. \quad (2.1.12)$$

The isotropic rate equations for the fluxes and the internal variable are derived from (1.4.1), (1.4.2), (1.4.8) and (1.4.16).

In particular, for the structural permeability tensor r_{ij} , because of the tensors β_{ijk}^s ($s = 3, 4, 6, 7$) of order three vanish (see Section A.1 of Appendix A), the fourth order tensor β_{ijkl}^1 and β_{ijkl}^2 have the form (A.3.3) of the Appendix A and the fifth order tensors β_{ijklm}^5 and β_{ijklm}^8 assume the form (A.2.3) and (A.2.6), respectively, of the Appendix A, we work out

$$\begin{aligned} \dot{r}_{ij} + \mathcal{V}_{ijk,k} = & [\beta_1^1 \delta_{ij} \delta_{kl} + \beta_2^1 (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk})] \varepsilon_{kl} + [\beta_1^2 \delta_{ij} \delta_{kl} + \beta_2^2 (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk})] r_{kl} \\ & + [\beta_1^5 (\varepsilon_{ikl} \delta_{jm} + \varepsilon_{jkl} \delta_{im}) + \beta_2^5 (\varepsilon_{ikm} \delta_{lj} + \varepsilon_{jkm} \delta_{li}) + \beta_3^5 (\varepsilon_{ilm} \delta_{jk} + \\ & + \varepsilon_{jlm} \delta_{ik})] \mathcal{V}_{klm} + \beta^8 (\varepsilon_{ikm} \delta_{lj} + \varepsilon_{jkm} \delta_{li} + \varepsilon_{ilm} \delta_{jk} + \varepsilon_{jlm} \delta_{ik}) r_{kl,m}, \end{aligned} \quad (2.1.13)$$

in which β_1^1, β_2^1 and β_1^2, β_2^2 , are the two significant independent components of β_{ijkl}^1 and β_{ijkl}^2 , respectively, β_s^5 ($s = 1, 2, 3$) are the three significant independent components of β_{ijklm}^5 and β^8 is the only one significant independent component of β_{ijklm}^8 , due to its particular symmetry.

Equation (2.1.13) gives

$$\begin{aligned} \dot{r}_{ij} + \mathcal{V}_{ijk,k} = & \beta_1^1 \delta_{ij} \varepsilon_{kk} + \beta_2^1 \varepsilon_{ij} + \beta_1^2 \delta_{ij} r_{kk} + \beta_2^2 r_{ij} + \beta_1^5 (\varepsilon_{ikl} \mathcal{V}_{klj} + \varepsilon_{jkl} \mathcal{V}_{kli}) \\ & + \beta_2^5 (\varepsilon_{ikl} \mathcal{V}_{kjl} + \varepsilon_{jkl} \mathcal{V}_{kil}) + \beta_3^5 (\varepsilon_{ilk} \mathcal{V}_{jlk} + \varepsilon_{jlk} \mathcal{V}_{ilk}) \\ & + \beta^8 (\varepsilon_{ikm} r_{kj,m} + \varepsilon_{jkm} r_{ki,m} + \varepsilon_{jlm} r_{il,m}); \end{aligned} \quad (2.1.14)$$

for the flux \mathcal{V}_{ijk} of the structural permeability tensor r_{ij} , taking into account that the fourth order tensors γ_{ijkl}^r ($r = 1, 2, 4, 5$) and the sixth order tensor γ_{ijklmn}^6 have the form (2.1.2) and (A.4.6), respectively, of the Appendix A, we have:

$$\begin{aligned} \dot{\mathcal{V}}_{ijk} = & (\gamma_1^1 \delta_{ij} \delta_{kl} + \gamma_2^1 \delta_{ik} \delta_{jl} + \gamma_3^1 \delta_{il} \delta_{jk}) j_l^c + (\gamma_1^2 \delta_{ij} \delta_{kl} + \gamma_2^2 \delta_{ik} \delta_{jl} + \gamma_3^2 \delta_{il} \delta_{jk}) q_l \\ & + (\gamma_1^3 \delta_{ij} \delta_{kl} \delta_{mn} + \gamma_2^3 \delta_{ij} \delta_{km} \delta_{ln} + \gamma_3^3 \delta_{ij} \delta_{kn} \delta_{lm} + \gamma_4^3 \delta_{ik} \delta_{jl} \delta_{mn} + \gamma_5^3 \delta_{ik} \delta_{jm} \delta_{ln} \\ & + \gamma_6^3 \delta_{ik} \delta_{jn} \delta_{lm} + \gamma_7^3 \delta_{il} \delta_{jk} \delta_{mn} + \gamma_8^3 \delta_{il} \delta_{jm} \delta_{kn} + \gamma_9^3 \delta_{il} \delta_{jn} \delta_{km} + \gamma_{10}^3 \delta_{im} \delta_{jk} \delta_{ln} \\ & + \gamma_{11}^3 \delta_{im} \delta_{jl} \delta_{kn} + \gamma_{12}^3 \delta_{im} \delta_{jn} \delta_{kl} + \gamma_{13}^3 \delta_{in} \delta_{jk} \delta_{lm} + \gamma_{14}^3 \delta_{in} \delta_{jl} \delta_{km} + \gamma_{15}^3 \delta_{in} \delta_{jm} \delta_{kl}) \mathcal{V}_{lmn} \\ & + (\gamma_1^4 \delta_{ij} \delta_{kl} + \gamma_2^4 \delta_{ik} \delta_{jl} + \gamma_3^4 \delta_{il} \delta_{jk}) c_{,l} + (\gamma_1^5 \delta_{ij} \delta_{kl} + \gamma_2^5 \delta_{ik} \delta_{jl} + \gamma_3^5 \delta_{il} \delta_{jk}) T_{,l} \\ & + [\gamma_1^6 (\delta_{kl} \delta_{mn} + \delta_{km} \delta_{ln}) \delta_{ij} + \gamma_2^6 \delta_{ij} \delta_{kn} \delta_{lm} + \gamma_3^6 (\delta_{jl} \delta_{mn} + \delta_{jm} \delta_{ln}) \delta_{ik} + \gamma_4^6 \delta_{ik} \delta_{jn} \delta_{lm} \\ & + \gamma_5^6 (\delta_{il} \delta_{mn} + \delta_{im} \delta_{ln}) \delta_{jk} + \gamma_6^6 (\delta_{il} \delta_{jm} + \delta_{im} \delta_{jl}) \delta_{kn} + \gamma_7^6 (\delta_{il} \delta_{km} + \delta_{im} \delta_{kl}) \delta_{jn} \\ & + \gamma_8^6 \delta_{in} \delta_{jk} \delta_{lm} + \gamma_9^6 (\delta_{jl} \delta_{km} + \delta_{jm} \delta_{kl}) \delta_{in}] r_{lm,n}, \end{aligned} \quad (2.1.15)$$

in which γ_s^6 ($s = 1, \dots, 9$) are the 9 significant independent components of γ_{ijklmn}^6 .

Equation (2.1.15) can be written as follows

$$\begin{aligned} \dot{\mathcal{V}}_{ijk} = & \gamma_1^1 \delta_{ij} j_k^c + \gamma_2^1 \delta_{ik} j_j^c + \gamma_3^1 \delta_{jk} j_i^c + \gamma_1^2 \delta_{ij} q_k + \gamma_2^2 \delta_{ik} q_j + \gamma_3^2 \delta_{jk} q_i + \gamma_1^3 \delta_{ij} \mathcal{V}_{kl} + \gamma_2^3 \delta_{ij} \mathcal{V}_{lk} \\ & + \gamma_3^3 \delta_{ij} \mathcal{V}_{llk} + \gamma_4^3 \delta_{ik} \mathcal{V}_{jll} + \gamma_5^3 \delta_{ik} \mathcal{V}_{ljl} + \gamma_6^3 \delta_{ik} \mathcal{V}_{llj} + \gamma_7^3 \delta_{jk} \mathcal{V}_{ill} + \gamma_8^3 \mathcal{V}_{ijk} + \gamma_9^3 \mathcal{V}_{ikj} \\ & + \gamma_{10}^3 \delta_{jk} \mathcal{V}_{lil} + \gamma_{11}^3 \mathcal{V}_{jik} + \gamma_{12}^3 \mathcal{V}_{kij} + \gamma_{13}^3 \delta_{jk} \mathcal{V}_{lli} + \gamma_{14}^3 \mathcal{V}_{jki} + \gamma_{15}^3 \mathcal{V}_{kji} + \gamma_1^4 \delta_{ij} c_{,k} \\ & + \gamma_2^4 \delta_{ik} c_{,j} + \gamma_3^4 \delta_{jk} c_{,i} + \gamma_1^5 \delta_{ij} T_{,k} + \gamma_2^5 \delta_{ik} T_{,j} + \gamma_3^5 \delta_{jk} T_{,i} + \gamma_1^6 \delta_{ij} r_{kl,l} + \gamma_2^6 \delta_{ij} r_{ll,k} \\ & + \gamma_3^6 \delta_{ik} r_{jl,l} + \gamma_4^6 \delta_{ik} r_{ll,j} + \gamma_5^6 \delta_{jk} r_{il,l} + \gamma_6^6 r_{ij,k} + \gamma_7^6 r_{ik,j} + \gamma_8^6 \delta_{jk} r_{ll,i} + \gamma_9^6 r_{jk,i}; \end{aligned} \quad (2.1.16)$$

for the heat flux q_i , because the fourth order tensors χ_{ijkl}^3 and χ_{ijkl}^6 have the form (2.1.2) and (A.3.12) of the Appendix A, we obtain the following expression

$$\tau^q \dot{q}_i = \chi^1 j_i^c - q_i + \chi_1^3 \mathcal{V}_{ikk} + \chi_2^3 \mathcal{V}_{kik} + \chi_3^3 \mathcal{V}_{kki} + \chi^4 c_{,i} - \chi^5 T_{,i} + \chi_1^6 r_{ik,k} + \chi_2^6 r_{kk,i}, \quad (2.1.17)$$

with χ_1^6 and χ_2^6 the two significant independent components of χ_{ijkl}^6 .

In the case where the coefficients χ^1 , χ_s^3 ($s = 1, 2, 3$), χ^4 , χ_1^6 , and χ_2^6 are negligible, equation (2.1.17) becomes the well-known Maxwell-Cattaneo-Vernotte equation $\tau^q \dot{q}_i + q_i = -\chi^5 T_{,i}$, allowing finite speeds of thermal propagation and giving Fourier equation $q_i = -\chi^5 T_{,i}$, describing thermal disturbances with infinite velocity of propagation, when the relaxation time τ^q goes to zero;

for the mass flux j_i^c , taking into consideration that the fourth order tensors ξ_{ijkl}^3 and ξ_{ijkl}^6 have the form (2.1.2) and (A.3.12), respectively, of the Appendix A, we obtain

$$\tau^j \dot{j}_i^c = -j_i^c + \xi^2 q_i + \xi_1^3 \mathcal{V}_{ikk} + \xi_2^3 \mathcal{V}_{kik} + \xi_3^3 \mathcal{V}_{kki} + \xi^4 c_{,i} + \xi^5 T_{,i} + \xi_1^6 r_{ik,k} + \xi_2^6 r_{kk,i}, \quad (2.1.18)$$

in which ξ_1^6 and ξ_2^6 are the two significant independent components of ξ_{ijkl}^6 .

The isotropic generalized telegraph temperature equation is deduced from (1.5.12), when the second order tensors k_{ij} , γ_{ij} , η_{ij} , v_{ij}^1 and v_{ij}^2 have the form (2.1.1)₂ and the fourth order tensors v_{ijkl}^3 and v_{ijkl}^6 assume, respectively, the form (2.1.2) and (A.3.12) of Appendix A:

$$\begin{aligned} \tau^q \ddot{T} + \dot{T} = & k T_{,ii} - \gamma (\tau^q \ddot{\epsilon}_{ii} + \dot{\epsilon}_{ii}) + \varphi (\tau^q \ddot{c} + \dot{c}) + \eta (\tau^q \ddot{r}_{ii} + \dot{r}_{ii}) - v^1 j_{i,i}^c - v^4 c_{,ii} \\ & - (v_1^3 \mathcal{V}_{ijj,i} + v_2^3 \mathcal{V}_{jij,i} + v_3^3 \mathcal{V}_{jji,i}) - (v_1^6 r_{ij,ji} + v_2^6 r_{jj,ii}), \end{aligned} \quad (2.1.19)$$

in which v_1^6 and v_2^6 are the two significant independent components of v_{ijkl}^6 .

The evolution equations (2.1.14), (2.1.16), (2.1.17), (2.1.18) and (2.1.19) describe disturbances with finite velocity and fast phenomena having relaxation times comparable or higher than the relaxation times of the materials taken into account. Also, in these equations there are terms taking into consideration non-local effects and relating these rate equations to the inhomogeneities present in the system.

The isotropic linearized internal energy balance is worked out from (1.5.14), when the second order tensors $\lambda_{ij}^{\theta\epsilon}$ and $\lambda_{ij}^{r\theta}$ have the form (2.1.1)₂:

$$\rho \dot{e} = T_0 \lambda^{\theta\epsilon} \dot{u}_{i,i} + \rho c_v \dot{T} - T_0 \lambda^{r\theta} \dot{r}_{ii} - T_0 \lambda^{\theta c} \dot{c}. \quad (2.1.20)$$

2.1.2 Closure of the governing system of equations in the isotropic case

In this Subsection, to close the system of equations describing linear isotropic porous media filled by fluid flow, we linearize the balance equations (1.1.10), (1.1.11) and the rate equations (2.1.14), (2.1.16), (2.1.17) and (2.1.18) around the equilibrium state (1.3.1)-(1.3.3). Taking into account the constitutive relations (2.1.5) and (2.1.6), the linearized temperature equation (2.1.19) and internal energy balance equation (2.1.20), the definitions $\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i})$ and $v_i = \dot{u}_i$, indicating the deviations of the fields from the thermodynamic equilibrium state by the same symbols of the fields themselves, and considering the case where we may replace the material derivative by the partial time derivative, we obtain the following closed system of 45 equations for 45 unknowns: 1 for c , 3 for u_i , 6 for r_{ij} , 27 for \mathcal{V}_{ijk} , 3 for q_i , 3 for j_i^c , 1 for T and 1 for e

$$\rho \frac{\partial c}{\partial t} = -j_{i,i}^c, \quad (2.1.21)$$

$$\rho \frac{\partial^2 u_i}{\partial t^2} = (\lambda + \mu)u_{k,ki} + \mu u_{i,kk} - \lambda^{\theta\varepsilon} T_{,i} + \lambda_1^{r\varepsilon} r_{kk,i} + \lambda_2^{r\varepsilon} r_{ik,k} - \lambda^{c\varepsilon} c_{,i}, \quad (2.1.22)$$

$$\begin{aligned} \frac{\partial r_{ij}}{\partial t} = & -\mathcal{V}_{ijk,k} + \beta_1^1 \delta_{ij} u_{k,k} + \frac{1}{2} \beta_2^1 (u_{i,j} + u_{j,i}) + \beta_1^2 \delta_{ij} r_{kk} + \beta_2^2 r_{ij} \\ & + \beta_1^5 (\varepsilon_{ikl} \mathcal{V}_{klj} + \varepsilon_{jkl} \mathcal{V}_{kli}) + \beta_2^5 (\varepsilon_{ikl} \mathcal{V}_{kjl} + \varepsilon_{jkl} \mathcal{V}_{kil}) \\ & + \beta_3^5 (\varepsilon_{ilk} \mathcal{V}_{jlk} + \varepsilon_{jlk} \mathcal{V}_{ilk}) + \beta^8 (\varepsilon_{ikm} r_{kj,m} + \varepsilon_{jkm} r_{ki,m} + \varepsilon_{jlm} r_{il,m}), \end{aligned} \quad (2.1.23)$$

$$\begin{aligned} \frac{\partial \mathcal{V}_{ijk}}{\partial t} = & \gamma_1^1 \delta_{ij} j_k^c + \gamma_2^1 \delta_{ik} j_j^c + \gamma_3^1 \delta_{jk} j_i^c + \gamma_1^2 \delta_{ij} q_k + \gamma_2^2 \delta_{ik} q_j + \gamma_3^2 \delta_{jk} q_i + \gamma_1^3 \delta_{ij} \mathcal{V}_{kll} \\ & + \gamma_2^3 \delta_{ij} \mathcal{V}_{lkl} + \gamma_3^3 \delta_{ij} \mathcal{V}_{llk} + \gamma_4^3 \delta_{ik} \mathcal{V}_{jll} + \gamma_5^3 \delta_{ik} \mathcal{V}_{ljl} + \gamma_6^3 \delta_{ik} \mathcal{V}_{llj} + \gamma_7^3 \delta_{jk} \mathcal{V}_{ill} \\ & + \gamma_8^3 \mathcal{V}_{ijk} + \gamma_9^3 \mathcal{V}_{ikj} + \gamma_{10}^3 \delta_{jk} \mathcal{V}_{lil} + \gamma_{11}^3 \mathcal{V}_{jik} + \gamma_{12}^3 \mathcal{V}_{kij} + \gamma_{13}^3 \delta_{jk} \mathcal{V}_{lli} \\ & + \gamma_{14}^3 \mathcal{V}_{jki} + \gamma_{15}^3 \mathcal{V}_{kji} + \gamma_1^4 \delta_{ij} c_{,k} + \gamma_2^4 \delta_{ik} c_{,j} + \gamma_3^4 \delta_{jk} c_{,i} + \gamma_1^5 \delta_{ij} T_{,k} \\ & + \gamma_2^5 \delta_{ik} T_{,j} + \gamma_3^5 \delta_{jk} T_{,i} + \gamma_1^6 \delta_{ij} r_{kl,l} + \gamma_2^6 \delta_{ij} r_{ll,k} + \gamma_3^6 \delta_{ik} r_{jl,l} + \gamma_4^6 \delta_{ik} r_{ll,j} \\ & + \gamma_5^6 \delta_{jk} r_{il,l} + \gamma_6^6 r_{ij,k} + \gamma_7^6 r_{ik,j} + \gamma_8^6 \delta_{jk} r_{ll,i} + \gamma_9^6 r_{jk,i}, \end{aligned} \quad (2.1.24)$$

$$\tau^q \frac{\partial q_i}{\partial t} + q_i = \chi^1 j_i^c + \chi_1^3 \mathcal{V}_{ikk} + \chi_2^3 \mathcal{V}_{kik} + \chi_3^3 \mathcal{V}_{kki} + \chi^4 c_{,i} - \chi^5 T_{,i} + \chi_1^6 r_{ik,k} + \chi_2^6 r_{kk,i}, \quad (2.1.25)$$

$$\tau^{j^c} \frac{\partial j_i^c}{\partial t} + j_i^c = \xi^2 q_i + \xi_1^3 \mathcal{V}_{ikk} + \xi_2^3 \mathcal{V}_{kik} + \xi_3^3 \mathcal{V}_{kki} + \xi^4 c_{,i} + \xi^5 T_{,i} + \xi_1^6 r_{ik,k} + \xi_2^6 r_{kk,i}, \quad (2.1.26)$$

$$\begin{aligned} \tau^q \frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} = & k T_{,ii} - \gamma \left(\tau^q \frac{\partial^2 u_{i,i}}{\partial t^2} + \frac{\partial u_{i,i}}{\partial t} \right) + \varphi \left(\tau^q \frac{\partial^2 c}{\partial t^2} + \frac{\partial c}{\partial t} \right) + \eta \left(\tau^q \frac{\partial^2 r_{ii}}{\partial t^2} + \frac{\partial r_{ii}}{\partial t} \right) \\ & - v^1 j_{i,i}^c - v^4 c_{,ii} - (v_1^3 \mathcal{V}_{ijj,i} + v_2^3 \mathcal{V}_{jij,i} + v_3^3 \mathcal{V}_{jji,i}) - (v_1^6 r_{ij,ji} + v_2^6 r_{jj,ii}), \end{aligned} \quad (2.1.27)$$

$$\rho \frac{\partial e}{\partial t} = T_0 \lambda^{\theta\varepsilon} \frac{\partial u_{i,i}}{\partial t} + \rho c_v \frac{\partial T}{\partial t} - T_0 \lambda^{r\theta} \frac{\partial r_{ii}}{\partial t} - T_0 \lambda^{\theta c} \frac{\partial c}{\partial t}. \quad (2.1.28)$$

Notice that also in the case where we do not take into consideration equation (2.1.28) for the internal energy, the system of equations (2.1.21)-(2.1.27) is still closed.

2.2 ISOTROPIC POROUS MEDIA WITH RESPECT TO ALL ROTATIONS AND INVERSIONS OF AXES FRAME (PERFECT ISOTROPIC CASE)

In this Section we consider perfect isotropic porous media having *symmetry properties invariant with respect to all rotations and to inversions of the frame of axes*. In this case *the tensors of odd order vanish* [12], i.e.

$$L_i = 0, \quad L_{ijk} = 0, \quad L_{ijklm} = 0, \quad (2.2.1)$$

the tensors of even order are given by (2.1.1)₂, (2.1.2) and (2.1.4) and *take equal forms to those valid in the isotropic case*, coming from special symmetry properties (see Sections A.3 and A.4 of the Appendix A).

2.2.1 Constitutive relations, generalized affinities, rate, temperature and energy equations in perfect isotropic case

Notice that all the tensors that appear in equations (1.3.11)-(1.3.17), (1.4.2), (1.4.8), (1.4.16), (1.5.12) and (1.5.14) are of even order, so that the constitutive relations, the generalized affinities, the rate equations for the porous field flux, the heat flux and the mass flux, the temperature and energy equations remain unchanged, with respect the isotropic case, and assume the form (2.1.5)-(2.1.8), (2.1.10)-(2.1.12), (2.1.16)-(2.1.18) and (2.1.19), (2.1.20). Taking into account relations (2.2.1), the only different equation in this case is the rate equation (1.4.1) for the internal variable r_{ij} , that takes the form

$$\dot{r}_{ij} = -\mathcal{V}_{ijk,k} + \beta_1^1 \delta_{ij} \varepsilon_{kk} + \beta_2^1 \varepsilon_{ij} + \beta_1^2 \delta_{ij} r_{kk} + \beta_2^2 r_{ij}. \quad (2.2.2)$$

2.2.2 Closure of the governing system of equations in the perfect isotropic case

Linearizing the balance equations (1.1.10), (1.1.11) and the rate equations (2.2.2) and (2.1.16)-(2.1.18) around the equilibrium state (1.3.1)-(1.3.3), taking into account the constitutive relations (2.1.5) and (2.1.6), the linearized temperature and energy equations (2.1.19) and (2.1.20), equations (2.1.21), (2.1.22), (2.1.24)-(2.1.28) remain unchanged and relation (2.2.2) takes the form

$$\frac{\partial r_{ij}}{\partial t} = -\mathcal{V}_{ijk,k} + \beta_1^1 \delta_{ij} \varepsilon_{kk} + \beta_2^1 \varepsilon_{ij} + \beta_1^2 \delta_{ij} r_{kk} + \beta_2^2 r_{ij}, \quad (2.2.3)$$

where we have considered the case in which the material derivative may be replaced by the partial time derivative and the deviations of the fields from the thermodynamic equilibrium state have been indicated by the fields themselves. Thus, in total we have a closed set of 45 equations for the 45 unknowns c , u_i , r_{ij} , \mathcal{V}_{ijk} , q_i , j_i^c , T and e . The obtained results can be applied to real situations. The derived system of equations is very complex but in simpler cases it is possible to find analytical or numerical solutions. In particular, in [7] we have studied coupled harmonic porous defects and fluid flux waves, calculating the dispersion relation and the propagation modes of these complex waves.

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3 | A SIMPLE MODEL OF POROUS MEDIA WITH ELASTIC DEFORMATIONS AND EROSION OR DEPOSITION

This Chapter deals with a model for solids with porous channels filled by an incompressible isotropic fluid. The Darcy-Brinkman-Stokes law is derived, that represents a rate equation for the local mass flux of the fluid, presenting relaxation times in which this flux evolves towards its local-equilibrium value, viscous effects and a permeability tensor referring to a response of the system to an external agent, i.e. the fluid flow produced by a pressure gradient. The erosion/deposition phenomena in an elastic porous matrix are also studied and particular thermal porous metamaterials, that have interesting functionality, like in fluid flow cloaking, are illustrated as application of the obtained results. This derived model is completely in agreement with a theory formulated in the framework of the rational irreversible thermodynamics, where two internal variables are introduced (a symmetric structural porosity tensor and a symmetric second order tensor influencing viscous phenomena, that is interpreted as the symmetric part of the velocity gradient), when the results are considered in a first approximation and some suitable assumptions are done. The constitutive theory is worked out by using Liu's [20] and Wang's theorems [36], [37] and [38]. The obtained theory has applications in several technological sectors, like physics of soil, pharmaceuticals, physiology, etc. and contributes to the study of new porous metamaterials.

In this Chapter, besides considering the effects of elastic coupling of the fluid with the porous solid matrix, we also consider erosive effects of the fluid flow on the solid matrix or, inversely, deposition effects, which lead to ageing effects of the porous medium. To this aim we focus our attention on a particular case sufficiently interesting and simple to explicitly illustrate some practical applications of suitable constitutive equations, that are derived in the present Chapter by the elaboration of an appropriate thermodynamic model. The description of porous media with effects of erosion or deposition are of great interest in the physics of soil, in pharmaceuticals (controlled release of medicals from solid matrices) and in physiology.

The organization of the Chapter is the following. In Section 3.1 an incompressible isotropic fluid through the channels of a porous solid is considered. A porosity tensor r , describing the geometrical anisotropic structure of porous tubes is introduced as internal variable linked to a permeability tensor D , namely $D = D(r)$. The balance equations for a viscous fluid filling the porous skeleton, where the friction between the walls of the porous channels and the fluid is taken into account, are considered. The total fluid flow rate along rectilinear channels and along curved channels is studied and the Darcy-Brinkman-Stokes law [17], [35] is worked out for the local mass flux of the fluid J . In Section 3.2 the description of a fluid flow across a rigid porous ma-

trix is described and a model for erosion of the channels due to the fluid flow along them or solid deposition on their walls is carried out. Some didactic illustrations are presented, like a Poiseuille flow in a cylindrical channel with rigid walls. Section 3.3 regards some practical applications to porous metamaterials, like fluid flow cloaking, barriers for noise isolation and attenuation of seismic waves [39], lenses for ultrasonic inspections [1], analysis of the mechanical response of solid foams [6], [7], [34] and absorbing protections against the noise pollution [19]. Sections 3.4, 3.5 and 3.6 deal with a theoretical model for a fluid through the network of channels of a porous medium, in the framework of rational irreversible thermodynamics with internal variables, where in the thermodynamic state vector, besides the classical thermodynamic variables temperature, T , its gradient, ∇T , and the small strain tensor, ε , two internal variables are introduced: the structural porosity tensor r à la Kubik and the second order symmetric tensor m influencing viscous phenomena, so that the heat flux q and the stress tensor τ are constitutive functions. We apply Liu's theorem [20] where all balance and evolution equations are considered as mathematical constraints for the general validity of the inequality and we derive the Lagrange multipliers, the laws of state and the entropy flux. Using Wang's theorems [36], [37], [38] (see also [33]) we represent the unknown constitutive functions. The obtained theory is completely in accordance with the model for porous media filled by fluid flow with erosion/deposition developed in Sections 3.1 and 3.2, when the internal variable m is interpreted as the symmetric part of the velocity gradient, the results are considered in a first approximation and some suitable assumptions are done. Appendix B is dedicated to the objective representation of scalar, symmetric tensor and vector functions.

The studies presented in this Chapter are contained in the article [5]:

A. Famà, L. Restuccia and D. Jou. A simple model of porous media with elastic deformations and erosion or deposition. *Zeitschrift für angewandte Mathematik und Physik (ZAMP)* 71(124), pp. 1-21, 2020.

3.1 A MODEL FOR POROUS MEDIA

We consider an incompressible isotropic fluid through the network of channels of a porous medium [17], [35]. The equation for the local mass flux of the fluid $J = \rho v$ is

$$\tau^J \cdot \dot{J} + J = -\frac{1}{\eta} D \cdot \nabla p + \tilde{\eta} \Delta J, \quad (3.1.1)$$

or in Cartesian components

$$\tau_{ik}^J \dot{J}_k + J_k = -\frac{1}{\eta} D_{ik} p_{,k} + \tilde{\eta} J_{i,kk}. \quad (3.1.2)$$

In (3.1.1) τ^J is a relaxation-time tensor related to the inertia of the fluid in the pores of the system, i.e. it expresses the typical times in which J will decay to zero after

suddenly setting $\nabla p = \mathbf{0}$, $\mathbf{D} = \mathbf{D}(\mathbf{r})$ is the permeability tensor, linked to the structural porosity tensor $\mathbf{r} \equiv (r_{ij})$, p is the local pressure acting on the fluid, η is the viscosity coefficient of the fluid, Δ is the Laplacian operator and $\bar{\eta}$ has dimensions of length square and proportional to the viscosity of the fluid. The structural porosity tensor \mathbf{r} describes the anisotropic structure of a network of porous channels, of the medium. The permeability tensor \mathbf{D} and the structural porosity tensor \mathbf{r} are deeply related to each other, but they are conceptually different: the concept of permeability refers to a response of the system to an external agent (namely, the fluid flow \mathbf{J} produced by a pressure gradient ∇p); since a pressure gradient in the x direction may produce a fluid flow in the x , the y and z directions, and so on, the coefficient relating the flow and the pressure gradient must be a tensor. On the other side, the concept of structural porosity tensor refers to the geometrical structure of the ensemble of pore channels inside the material (see Fig. 2), independently on whether some fluid is flowing or staying inside them. The trace of \mathbf{r} indicates the relative elementary total volume of the pores, compared to the elementary total volume of the system. It may change from point to point, for small reference volumes, in inhomogeneous systems. Equation

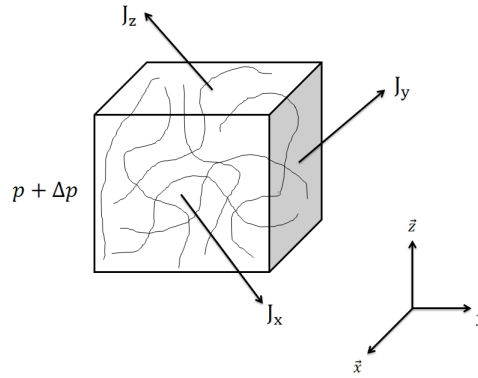


Figure 2: The permeability tensor relates the pressure gradient to the flow of fluid in the material. In the figure a situation sketched, in which pressure gradient is imposed along the y axis. As a result, the fluid flows J_x , J_y and J_z emerge from the porous material through a plane perpendicular to the x axis, the y axis and the z axis, respectively.

(3.1.1) comes from the momentum balance equation for the fluid, having the form

$$\rho \dot{\mathbf{v}} = -\nabla \cdot \mathbf{P} + \rho \mathbf{F}, \quad \rho \dot{v}_i = -P_{ij,j} + \rho F_i, \quad (3.1.3)$$

with \mathbf{v} the local velocity of the fluid, \mathbf{P} the pressure tensor and $\rho \mathbf{F}$ an external force. This equation must be averaged over the channels in the volume being considered. Here we will consider

$$\mathbf{P} = p\mathbf{U} - 2\eta(\nabla \mathbf{v})^s, \quad P_{ij} = p\delta_{ij} - 2\eta v_{(i,j)}, \quad (3.1.4)$$

where $(\nabla \mathbf{v})^s \equiv (v_{(i,j)})$ is the symmetric part of $\nabla \mathbf{v}$, or in particular $v_{(i,j)}$ is given by the time derivative of the small strain tensor ε_{ij} ,

$$v_{(i,j)} = \dot{\varepsilon}_{ij} = \frac{1}{2}(v_{i,j} + v_{j,i}), \quad (3.1.5)$$

p is the local pressure, \mathbf{U} is the unit tensor and η the shear viscosity and

$$\rho \mathbf{F} = -\boldsymbol{\alpha} \cdot \mathbf{v}, \quad \rho F_i = -\alpha_{ik} v_k. \quad (3.1.6)$$

This term describes the friction between the walls of the porous channels and the fluid. The tensor $\boldsymbol{\alpha}$ describes the effect of the walls of the pores when the fluid flows through them. For a Newtonian fluids in rectilinear channels this term is zero and the viscous friction is obtained by integration of the viscous term in the Navier-Stokes equation, namely

$$\rho \dot{\mathbf{v}} = -\nabla p + \eta \Delta \mathbf{v}, \quad \rho \dot{v}_i = -p_{,i} + \eta v_{i,kk}. \quad (3.1.7)$$

From this equation, in a rectilinear cylindrical channel of radius R and length L , and assuming the non-slip boundary condition for the velocity on the walls, one obtains for the total fluid flow rate Q along the channel the Poiseuille law

$$Q = \frac{\pi R^4}{8\eta} \frac{\Delta p}{L}, \quad (3.1.8)$$

where $\frac{\Delta p}{L}$ is the pressure gradient along the channel.

We observe that if we have N parallel and equal channels (see Fig. 3) (same length, same radius R), the total flow rate along them will be

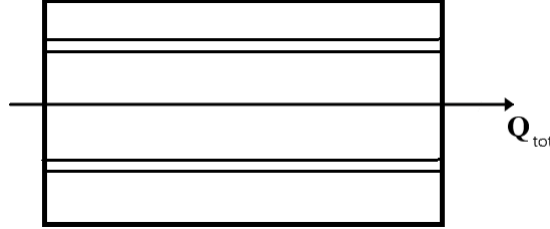


Figure 3: Total flux in parallel and equal channels.

$$Q_{tot} = \sum_i Q_i = \frac{N\pi R^4}{8\eta} \frac{\Delta p}{L}. \quad (3.1.9)$$

The average flow rate per unit of transversal area (let us say A_{yz} , if we consider the flow along the x direction) will be

$$J_{average} = \frac{N\pi R^4}{8\eta A_{yz}} \frac{\Delta p}{L} = -\frac{N\pi R^4}{8\eta A_{yz}} \nabla p, \quad (3.1.10)$$

where we have used $\nabla p = -\frac{\Delta p}{L}$.

Therefore, by comparing with (3.1.1) in steady state, the tensor \mathbf{D} will be in this simple case $D_{xx} \equiv \frac{N\pi R^4}{8A_{yz}}$ (notice that the unit of measurement of permeability is length²). In

the particular geometry of this simple example, the other components of the tensor \mathbf{D} will be zero.

If the channels have different radii R_i , (3.1.9) becomes

$$Q_{tot} = \left(\sum_i \frac{N_i \pi R_i^4}{8\eta} \right) \frac{\Delta p}{L}, \quad (3.1.11)$$

with N_i the number of pores with radius R_i , and therefore

$$J \equiv \underbrace{\left(\frac{1}{\text{Area}} \sum_i \frac{N_i \pi R_i^4}{8} \right)}_{\text{Permeability}} \frac{1}{\eta} \frac{\Delta p}{L}. \quad (3.1.12)$$

Here it is seen that the tensor \mathbf{D} depends on $N_i R_i^4$, i.e. on the fourth moment of the distribution function of the radii of the pores.

If we consider curved channels (see Fig. 4) the total flow rate through them will have components not only in the direction of the pressure gradient, but also in other directions, since for the curved channels $\left(\frac{\Delta p}{L}\right)_x$ drives the flows J_x and J_y .

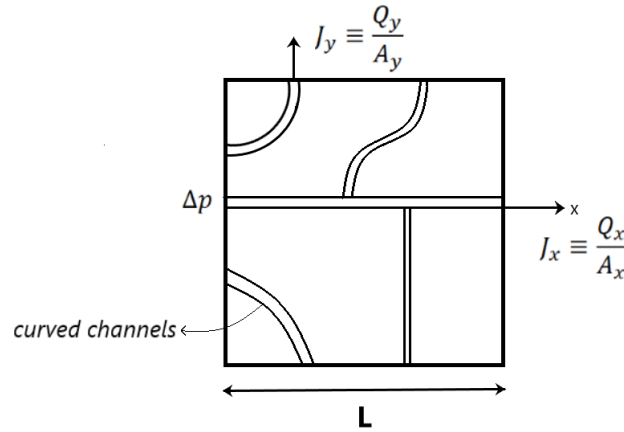


Figure 4: Average flow rate in curved channels.

However, in a porous medium with narrow and curved bifurcating and labyrinthic channels the situation is much more complicated. The velocity \mathbf{v} has a different direction at every point of the medium, depending on the direction of the corresponding channel (the local velocity \mathbf{v} will be parallel to the tangent of the line representing the narrow channel along which the fluid is flowing). In this case, the velocity \mathbf{v} measured will be the average velocity in the channels of the region being studied, and the force on the walls will be phenomenologically described by (3.1.6) whereas the term in $\eta \Delta \mathbf{v}$ will play a secondary role.

Then, making the average of (3.1.3) in a small porous region and writing $\mathbf{J} = \rho \langle \mathbf{v} \rangle$, with $\langle \mathbf{v} \rangle$ the average velocity in the pores of the considered region, we will have

$$\mathbf{J} = -\nabla p - \frac{1}{\rho} \boldsymbol{\alpha} \cdot \mathbf{J} + \frac{\eta}{\rho} \Delta \mathbf{J}, \quad J_i = -p_{,i} - \frac{1}{\rho} \alpha_{ik} J_k + \frac{\eta}{\rho} J_{i,kk}. \quad (3.1.13)$$

In equation (3.1.13) we have taken into account that the fluid is incompressible ($\nabla \cdot \mathbf{J} = 0$).

Now we multiply both sides of equation (3.1.13) times the matrix $\rho \boldsymbol{\alpha}^{-1}$, the inverse of $\boldsymbol{\alpha}$, and have

$$\rho \boldsymbol{\alpha}^{-1} \cdot \dot{\mathbf{J}} + \mathbf{J} = -\frac{1}{\eta} (\rho \eta \boldsymbol{\alpha}^{-1}) \cdot \nabla p + \eta \boldsymbol{\alpha}^{-1} \cdot \Delta \mathbf{J}, \quad \rho \alpha_{ik}^{-1} \dot{J}_k + J_i = -\frac{1}{\eta} (\rho \eta \alpha_{ik}^{-1}) p_{,k} + \eta \alpha_{ik}^{-1} J_{k,ll}. \quad (3.1.14)$$

The tensor $\rho \eta \boldsymbol{\alpha}^{-1}$ may be interpreted as the permeability tensor \mathbf{D} appearing in the well-known Darcy's law, namely

$$\mathbf{J} = -\frac{1}{\eta} \mathbf{D} \cdot \nabla p, \quad J_i = -\frac{1}{\eta} D_{ik} p_{,k}. \quad (3.1.15)$$

We rewrite equation (3.1.14)₁ as

$$\boldsymbol{\tau}^J \cdot \dot{\mathbf{J}} + \mathbf{J} = -\frac{1}{\eta} \mathbf{D} \cdot \nabla p + \widetilde{\boldsymbol{\eta}} \cdot \Delta \mathbf{J},$$

where $\boldsymbol{\tau}^J = \rho \boldsymbol{\alpha}^{-1}$ is the relaxation times tensor expressing the typical times in which \mathbf{J} will decay to $\mathbf{0}$ after suddenly setting $\nabla p = 0$, and $\widetilde{\eta}_{ik} = \eta \alpha_{ik}^{-1} = \frac{1}{\rho} D_{ik}$. This is precisely equation (3.1.1), which is known as Darcy-Brinkman-Stokes law [17], [35], and in it the term in $\widetilde{\boldsymbol{\eta}} \cdot \Delta \mathbf{J}$ is considered a relatively minor correction describing the zones with relatively wide and ordered channels inside the medium. Equations of the form (3.1.1), containing the Laplacian of the flux, are also called Guyer-Krumhansl equation when the variable is the heat flux \mathbf{q} instead of the mass flow \mathbf{J} and ∇T instead of ∇p [8], [9].

3.2 ELASTIC POROUS MATRIX WITH EROSION/DEPOSITION

Equation (3.1.1) is sufficient to describe the fluid flow across a rigid porous matrix. We consider the structural porosity tensor \mathbf{r} as an internal variable of the medium with its own dynamics. In this dynamics we may consider two effects:

- a) the deformability of the material of the matrix, assumed to be elastic, so that the channels may dilate and contract;
- b) a slow erosion of the channels because of the fluid flow along them, indeed we consider that the material of the porous matrix is slightly soluble in the flowing fluid.

Alternatively to erosion, we could consider the slow deposition of some material carried by the fluid on the walls of the porous medium. This would be the case, for instance, of cholesterol carried by the blood and slowly sticking to the walls and accumulating on them. In this case, we could consider some organ of the body as a porous

medium, in the sense that the network of capillaries in the organ may be very complex and tortuous. Thus, incorporating the possibility of erosion or of deposition may be of interest either in geological problems or in physiological problems.

In fact, the combination of erosion/deposition and of elasticity may be of interest as a basis of an analysis of ultrasonic waves through porous media, including expansion-compression of the channels. Indeed, one could consider the consequences of the ultrasound on the erosion or the deposition (by instance, as a means to clean a network of channels of an unwanted deposition of material on their walls) and producing vibrations of the walls.

We assume for the evolution equation of the porosity tensor \mathbf{r} an expression in the form

$$\boldsymbol{\tau}^r : \dot{\mathbf{r}} + \mathbf{r} = (p - p_0)\mathbf{A} + \mathbf{B} \cdot \mathbf{J} + \mathbf{C} : (\mathbf{J} \otimes \mathbf{J}), \quad \tau_{ijkl}^r \dot{r}_{kl} + r_{ij} = (p - p_0)A_{ij} + B_{ijk}J_k + C_{ijkl}J_kJ_l, \quad (3.2.1)$$

where $\boldsymbol{\tau}^r$ is a fourth order tensor, $\mathbf{A} \equiv (A_{ij})$, $\mathbf{B} \equiv (B_{ijk})$ and $\mathbf{C} \equiv (C_{ijkl})$ are second, third and fourth order tensors related to the spatial structure of the porous medium, and p_0 is a reference pressure. The term in $\boldsymbol{\tau}^r \equiv (\tau_{ijkl}^r)$ considers the inertia of the material of the solid matrix. The term in \mathbf{A} assumes that, if the local pressure of the fluid increases, the channels are dilated and the porosity increases. The terms in \mathbf{B} and \mathbf{C} describe how a fluid flow erodes the pores and makes them wider (or narrower, in the case of solid deposition on the walls), increasing (or decreasing) the porosity \mathbf{r} , which is the most suitable form for describing the erosion/deposition phenomenon in the practice. From the mathematical point of view, a positive $\mathbf{B} \cdot \mathbf{J}$ (increase of porosity) would describe erosion, whereas a negative $\mathbf{B} \cdot \mathbf{J}$ would describe deposition of matter on the wall of the channels (decrease of porosity). Something similar could be said about the term $\mathbf{C} : (\mathbf{J} \otimes \mathbf{J})$. In the case where we may represent τ_{ijkl}^r by only one scalar τ^r , equation (3.2.1) reads

$$\tau^r \dot{\mathbf{r}} + \mathbf{r} = (p - p_0)\mathbf{A} + \mathbf{B} \cdot \mathbf{J} + \mathbf{C} : (\mathbf{J} \otimes \mathbf{J}), \quad \tau^r \dot{r}_{ij} + r_{ij} = (p - p_0)A_{ij} + B_{ijk}J_k + C_{ijkl}J_kJ_l. \quad (3.2.2)$$

Equation (3.2.2) can be written in the general form of a rate equation of the following type

$$\tau^r \dot{\mathbf{r}} = \mathcal{R}, \quad (3.2.3)$$

with \mathcal{R} the source term, given by two contributions:

$$\mathcal{R} = \mathcal{R}^{(i)} + \mathcal{R}^{(e)}, \quad (3.2.4)$$

with $\mathcal{R}^{(i)}$ an internal source and $\mathcal{R}^{(e)}$ an external one.

We assume that

$$\mathcal{R}^{(i)} = -\mathbf{r} + (p - p_0)\mathbf{A}, \quad \mathcal{R}_{ij}^{(i)} = -r_{ij} + (p - p_0)A_{ij}, \quad (3.2.5)$$

$$\mathcal{R}^{(e)} = \mathbf{B} \cdot \mathbf{J} + \mathbf{C} : (\mathbf{J} \otimes \mathbf{J}), \quad \mathcal{R}_{ij}^{(e)} = B_{ijk}J_k + C_{ijkl}J_kJ_l. \quad (3.2.6)$$

The expression (3.2.5)₁ has been obtained also taking into account relation (3.6.6) of Section 3.6, where the internal source has been calculated using a theoretical model and the tensor A_{ij} has been interpreted as the small deformation tensor ε_{ij} .

Here we have related $\mathcal{R}^{(i)}$ to a term which modifies the geometry of the porous matrix, but not its composition, whereas $\mathcal{R}^{(e)}$ modifies composition by removing (or accumulating) some material. When there is a fluid flow \mathbf{J} through the system, and it is producing some erosion of the walls, it is expected that the porosity r will increase, i.e. the radius of the channels will slowly increase when the material of the walls is removed by the flow. Since the trace of r yields the fractional volume of the pores, the trace of \dot{r} yields the increase of porosity (in the case of erosion) and is related to the mass (or volume) of the matrix removed per unit time by the fluid flow.

By assuming that erosion (or deposition) are so slow that r is close to the steady state value $(p - p_0)A$ (i.e. $r \approx (p - p_0)A$) in (3.2.2), we will have

$$\tau^r \operatorname{tr}(\dot{r}) = \operatorname{tr}(\mathbf{B} \cdot \mathbf{J}) + \operatorname{tr}(\mathbf{C} : \mathbf{J} \otimes \mathbf{J}), \quad \tau^r \dot{r}_{ii} = B_{iik} J_k + C_{iikl} J_k J_l. \quad (3.2.7)$$

In erosion, $\operatorname{tr}(\dot{r}) > 0$. If \mathbf{B} and \mathbf{C} are assumed independent of \mathbf{J} , it follows that \mathbf{C} must be a positive definite tensor (negative definite in the case of deposition) and that \mathbf{B} must be zero (otherwise, inverting the direction of \mathbf{J} would change erosion into deposition and reciprocally, but in general this is not so). The tensor \mathbf{C} is expected to be related to r . If it is $\mathbf{C} \equiv (-\tilde{\alpha} r_{ij} \delta_{kl})$, relation (3.2.7)₂ reads

$$\tau^r \dot{r}_{ii} = -\tilde{\alpha} r_{ii} J_k J_k. \quad (3.2.8)$$

Thus, the increase of porosity volume will be

$$\tau^{er} \dot{r}_v = -\tilde{\alpha} r_v, \quad (3.2.9)$$

where $r_v = r_{ii}$ is the porous volume density and $\tau^{er} = \tau^r / J^2$ the characteristic time of erosion (in which $J^2 = J_k J_k$). This indicates that the erosion time τ^{er} will decrease as J^{-2} , and it will be infinite (no erosion) for $\mathbf{J} = \mathbf{0}$.

This expression for the erosion time refers to mechanical erosion produced by a relative motion between the fluid and the wall. Another possible diminution of the material of the solid matrix would be present in the case that the material is soluble in the fluid. In this case, the quantity of solid material would be reduced also in the case that the fluid is at rest. However, if the fluid is truly at rest, this reduction would have a limit when the fluid would become saturated; if, instead, the fluid is flowing and the porous system has a finite size, saturation would not be achieved and the solid material would be transported by the fluid away from the limits of the system.

3.2.1 Specific illustration: elastic effects

A simple model illustrating the physical meaning of the first term in $(p - p_0)A$ in equations (3.2.1) and (3.2.2) may be a Poiseuille flow in a cylindrical channel of length

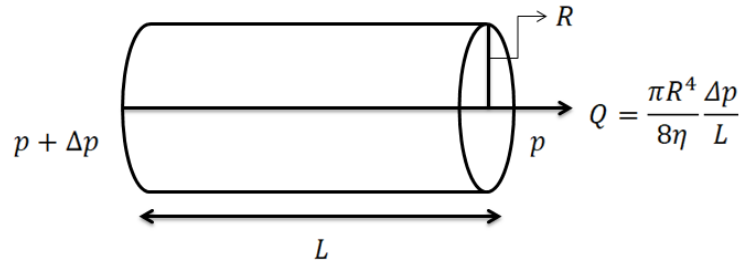


Figure 5: Poiseuille flow in a cylindrical channel with rigid walls.

L and radius R with elastic walls (as in the vascular system in physiology) [17], [35]. In Fig. 5 a Poiseuille flow in a cylindrical channel with rigid walls is illustrated In Fig. 6 a Poiseuille flow in a cylindrical channel with elastic walls is presented In this last

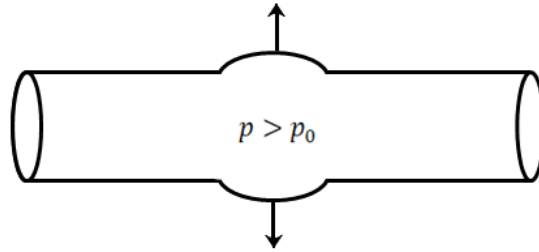


Figure 6: Poiseuille flow in a cylindrical channel with elastic walls.

illustration the dilatation of the wall is counteracted by the elasticity of the wall [17].

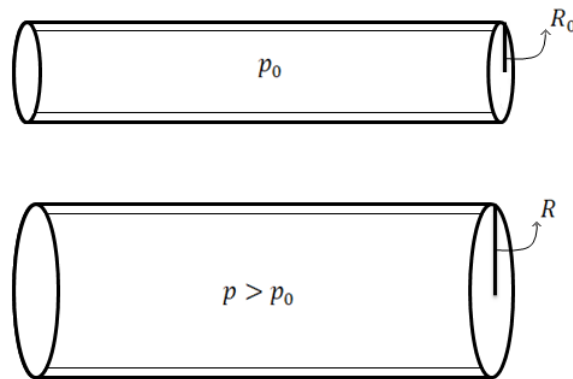


Figure 7: The dilatation of the wall is counteracted by the elasticity of the wall.

The pressure force in the radial direction per unit length of the channel is

$$dF_{\text{pressure}} = (p - p_0)2\pi R dx. \quad (3.2.10)$$

On the other side, if the Young modulus of the wall is E , the elastic extra force opposing the dilatation or the compression of the wall, in a small length dx of the channel will be (see Fig. 8)

$$dF_{\text{elastic}} = -E \frac{R - R_0}{R_0} \delta 2\pi R dx \quad (3.2.11)$$

(remember that $dF/A = \Delta l/l$) and δ is the thickness of the walls (see Fig. 9).

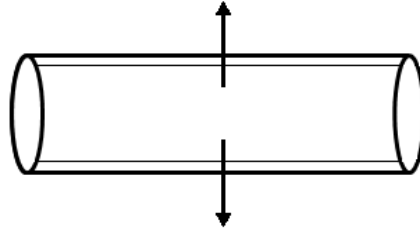


Figure 8: An illustration of elastic force.

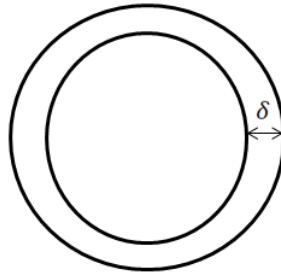


Figure 9: Thickness of the wall.

If ρ' is the mass density of the wall, the transversal equation of motion of the wall as expressed in terms of the changes of R will be

$$\rho' \delta 2\pi R \frac{d^2 R}{dt^2} = -E \frac{R - R_0}{R_0} \delta 2\pi R dx + (p - p_0) 2\pi R dx. \quad (3.2.12)$$

This is the equation for a forced oscillator, with $p - p_0$ the forcing term. The linearised form of (3.2.12) without forcing is

$$\rho' \frac{d^2 R}{dt^2} = -\frac{E}{R_0} (R - R_0). \quad (3.2.13)$$

From here one may identify a frequency ω_0 , given by $\omega_0^2 \equiv \frac{E}{R_0 \rho'}$, which is the characteristic vibration frequency of the elastic walls. Including the forcing term, (3.2.12) may be written as

$$\rho' \delta \frac{d^2 R}{dt^2} = -E \frac{R - R_0}{R_0} \delta + (p - p_0). \quad (3.2.14)$$

Thus, an oscillating fluid flow in the channel (produced for instance by an oscillating pressure difference between the two ends of the channels) having the frequency ω_0 will exhibit a resonance with the elastic oscillations of the channels. The dependence of the frequency ω_0 with the unperturbed value R_0 of the radius indicates that if the channels have different values of the radius R_0 not all the channels will enter in resonance with an oscillating flow of a given frequency, but only those having the suitable value of R_0 .

3.3 POROUS METAMATERIALS

Notice that Darcy's law (3.1.15) in the steady state and neglecting the Laplacian term, is $\mathbf{J} = -(\mathbf{D}/\eta)\nabla p$. Thus is analogous to Fourier's law $\mathbf{q} = -\boldsymbol{\lambda} \cdot \nabla T$, with $\boldsymbol{\lambda}$ the thermal conductivity tensor. This analogy makes that several of the recent progress in thermal metamaterials [4], [25], [26], [32] may also be applied to porous metamaterials. Indeed, two particularly interesting functionalities of the thermal metamaterials are thermal cloaking and thermal concentration. In thermal cloak, it is intended to deviate the heat flux along a suitable annular region in order that heat does not penetrate a given region inside the annulus. This is done in such a way that the flow is not arriving at the plane at T_2 red is the same as it would arrive if the system between walls 1 and 2 were homogeneous instead of having annular region inside it.

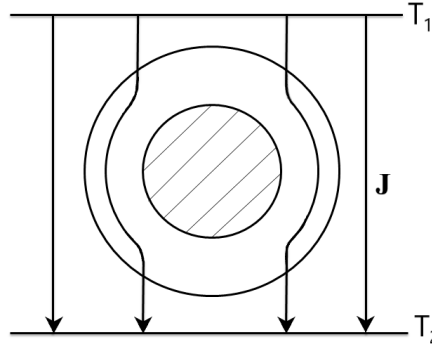


Figure 10: An illustration of thermal cloaking and of fluid flow cloaking: in thermal cloaking, the heat flow is deviated around the central region; in fluid cloaking, the fluid flow is deviated around the central region.

In porous systems, such a technique could be useful to improve the protection of, for instance, a cylindrical column, against the flow of water in the surrounding soil from a plane at pressure p_1 to a parallel plane at pressure p_2 . To achieve this, the permeability tensor in the annular region should be given a particular form analogous to that of the thermal conductivity tensor of cloaking metamaterials, namely [32]

$$D_{rr} = D_0 \left(\frac{R_2}{R_2 - R_1} \right)^2 \left(\frac{r - R_1}{R_2 - R_1} \right)^2 < D_0 \quad (3.3.1)$$

$$D_{\theta\theta} = D_0 \frac{R_2^2}{R_2^2 - R_1^2} > D_0, \quad (3.3.2)$$

with D_0 the isotropic permeability of the medium surrounding the annular region and D_{rr} and $D_{\theta\theta}$ are the rr and $\theta\theta$ components of \mathbf{D} , with R_2 and R_1 the external and internal radii of the annulus in Fig. 10.

The second functionality, namely, flow concentration (see Fig. 11), could be useful instead to concentrate the flow of water in a porous region on a particular zone, for

instance in a well to be filled with water flowing from pressure p_1 to pressure p_2 . In this case, the anisotropic permeability of the annular region should satisfy $D_{rr}D_{\theta\theta} = D_0^2$.

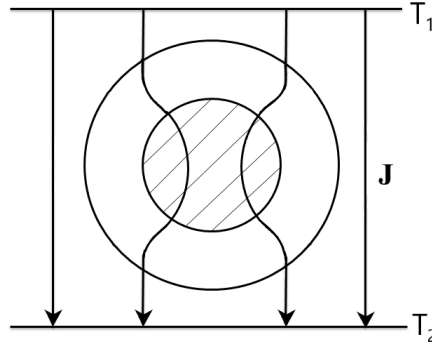


Figure 11: An illustration of flow concentration.

In this way, progress in metamaterials could be used in porous media. In order that the annular region has the required values of the permeability, one needs organizing the pores in some particular arrangements, usually not found in natural materials.

There are many practical applications regarding studies of porous metamaterials in different technological sectors.

In [39], a study on the wave propagation in one-dimensional fluid-saturated porous metamaterials described by Biot's model and, supporting two longitudinal waves, is developed. The material parameters of the pore fluid (among which the viscosity and the porosity) have a strong influence on both complex band structures and frequency response function curves. With an increase (decrease) in viscosity (porosity), the attenuation in the passing bands is first improved and then reduced. The results are relevant in controlling acoustic wave propagation, creating noise isolation and to reduce the vibrations due, for instance, to seismic waves. Then, practical applications can be obtained in earthquake engineering, geophysics, hydrology, etc.

Recently, there is great interest in increasing the capabilities of ultrasonic imaging (sonography) and a rapid emergence of a new class of lenses based on metamaterials (with periodic or aperiodic structure, as illustrated in [1]), offering extraordinary possibilities to control electromagnetic or acoustic waves [1], and improving medical diagnostic procedures, using high frequency mechanical acoustic waves and having poor resolution.

In [34] numerical studies deal with the conductivity and Young's modulus of porous metamaterials, based on a Gibson-Ashby's cells model, having the behaviour of cellular materials with high-porosity properties (porosity higher than 70%), i.e. the so-called solid foams. Gibson and Ashby (see [6], [7]) proposed that the mechanical properties of solid foams can be described considering the porous material as a periodic assembly of open cubic cells and studied the behaviour of polyurethane, polyethylene, and aluminium foams (closed or open cells), establishing constitutive equations based on the analysis of the mechanical response of an ideal structure of a foam.

In [19] the fact that the protection against acoustic pollution can be obtained in terms of sound absorption by means of porous materials, namely acoustic metafoam, mineral wool, fiber glass and others, efficient by virtue of their air-solid microstructure, is discussed. In particular, a new approach consisting in a combination of traditional poroelastic materials with locally resonant units embedded inside the pores is proposed, because even after optimisation of foams microstructural design, the low frequency performance of these metamaterials is still arduous.

3.4 THEORETICAL MODEL, INCLUDING TEMPERATURE VARIATIONS

In this Section, in the framework of extended irreversible thermodynamics with internal variables [2], [3], [11], [12], [13], [14], [15], [18], [21], [27], we develop a model for a fluid through the network of channels of a porous medium, taking into account a previous formulation for porous media saturated by a fluid flow [28], [29] (see also [30], [31] and Chapters 1 and 2). The thermal field is described by the temperature T , its gradient $T_{,i}$ and the heat flux q_i . The mechanical field is described by the symmetric stress tensor τ_{ij} and by the small strain tensor $\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i})$, being \mathbf{u} the displacement vector. The viscous effects are illustrated by an internal variable \mathbf{m} , influencing the viscous phenomena. A further internal variable, the symmetric structural porosity tensor r_{ij} à la Kubik [16], describes the geometrical structure of the porous channels saturated by fluid flow.

We assume that the mass of the fluid filling the porous channels, and the elastic porous skeleton form a two-components mixture of density $\tilde{\rho}$ [28], [29]. We indicate by ρ the mass of the fluid in the porous matrix of density $\hat{\rho}$. Thus, we have the following expression: $\tilde{\rho} = \rho + \hat{\rho}$. For the mixture of continua as a whole and also for each constituent the following continuity equations are satisfied: $\dot{\tilde{\rho}} + \tilde{\rho}v_{i,i} = 0$, $\frac{\partial \rho}{\partial t} + (\rho v_{1i})_{,i} = 0$, $\frac{\partial \hat{\rho}}{\partial t} + (\hat{\rho} v_{2i})_{,i} = 0$, where a superimposed dot denotes the material derivative, v_{1i} and v_{2i} are the velocities of the fluid particles and of the particles of the elastic porous matrix, respectively, and v_i is the barycentric velocity of the whole body defined by $\tilde{\rho}v_i = \rho v_{1i} + \hat{\rho}v_{2i}$.

In order to formulate a model for a porous medium with elastic deformations and erosion or deposition, filled by fluid flow, we suppose that all two mass densities $\tilde{\rho}$ and $\hat{\rho}$ are constant and that the solid velocity is much smaller than the fluid one

$$v_{2i} \ll v_{1i}, \quad (3.4.1)$$

so that by virtue of (3.4.1) we can do the two following approximations

$$\tilde{\rho}v_i \simeq \rho v_{1i}, \quad \text{and then} \quad \rho v_{1i} \simeq \rho v_i, \quad (3.4.2)$$

and, in the following, we take into account the solid matrix only considering its geometric structure with elastic porous channels influencing the viscous fluid filling them.

Also, we may assume the porous skeleton at rest but with the pores expanding or contracting, depending on the local pressure of the fluid.

Then, in our treatment we focus our attention on the behaviour of the fluid and we choose the following thermodynamic state vector

$$\mathcal{C} = \{T, \nabla T, \boldsymbol{\varepsilon}, \mathbf{m}, \mathbf{r}\}, \quad (3.4.3)$$

where $\nabla T \equiv (T_{,i})$ is the temperature gradient, so that the heat flux \mathbf{q} and the stress tensor τ_{ij} are constitutive functions, dependent on the variables of this set.

The processes occurring inside the considered media are governed by two sets of laws. The first set deals with the classical *balance equations*:

The balance of mass, that in the considered case of fluid with mass density, represents *The incompressibility condition*:

$$\nabla \cdot \mathbf{J} = 0, \quad J_{i,i} = 0, \quad (3.4.4)$$

where $\mathbf{J} = \rho \mathbf{v}$,

The momentum balance:

$$\rho \dot{\mathbf{v}} = -\nabla \cdot \mathbf{P} - \boldsymbol{\alpha} \cdot \mathbf{v}, \quad \rho \dot{v}_i = -P_{ij,j} - \alpha_{ik} v_k, \quad (3.4.5)$$

where $\mathbf{P} \equiv (P_{ij})$ is the stress tensor of the fluid and $\boldsymbol{\alpha} \cdot \mathbf{v}$ denotes a body force.

The internal energy balance:

$$\rho \dot{e} = \mathbf{P} : \nabla \mathbf{v} - \nabla \cdot \mathbf{q}, \quad \rho \dot{e} = P_{ji} v_{i,j} - q_{i,i}, \quad (3.4.6)$$

where e and \mathbf{q} are the internal energy per unit mass and the heat flux in the fluid. The second set of laws concerns the evolution equations of the internal variables: the structural porosity symmetric second-order tensor r_{ij} and the internal field \mathbf{m} responsible for the viscous effects, also represented by a symmetric second-order tensor. These rate equations are constructed obeying the objectivity and frame-indifference principles (see [10], [23] and [24]) and are chosen having the form

$$\overset{*}{\mathbf{m}} = \mathcal{M}(\mathcal{C}), \quad \overset{*}{m}_{ij} = \mathcal{M}_{ij}(\mathcal{C}), \quad (3.4.7)$$

$$\overset{*}{\mathbf{r}} = \mathcal{R}, \quad \overset{*}{r}_{ij} = \mathcal{R}_{ij}, \quad (3.4.8)$$

where the symbol (*) denotes the *Zaremba-Jaumann* derivative, defined for a second rank tensor a_{ij} : $\overset{*}{a}_{ij} = \dot{a}_{ij} - w_{ik} a_{kj} - w_{jk} a_{ik}$, with w_{ij} the antisymmetric part of the velocity gradient of the body, $\mathcal{M}(\mathcal{C})$ is a source term for the variable \mathbf{m} and \mathcal{R} is a source-like term, dealing with the porous channels, and precisely $\mathcal{R} = \mathcal{R}^{(i)}(\mathcal{C}) + \mathcal{R}^{(e)}$, with $\mathcal{R}^{(i)}(\mathcal{C})$ an internal source and $\mathcal{R}^{(e)}$ the external one as stated in (3.2.4). In the rate equations (3.4.7) and (3.4.8) the flux terms of m_{ij} and r_{ij} are not considered in order to close the system of equations describing the media under consideration and \mathcal{M} and $\mathcal{R}^{(i)}$ are constitutive functions, dependent on the variables of the set \mathcal{C} .

3.5 SECOND-LAW RESTRICTIONS

In order to the physical processes occurring in the considered medium are admissible from the thermodynamic point of view, they have not contradict the second law of thermodynamics. Thus, all the admissible solutions of the proposed balance and evolution equations have to satisfy the following *entropy inequality*

$$\rho \dot{S} + \phi_{k,k} \geq 0, \quad (3.5.1)$$

where S is the specific entropy per unit mass and $\boldsymbol{\phi}$ is the flux of the entropy associated with the fields of the set \mathcal{C} (3.4.3).

Thus, the following set of constitutive functions, dependent variables, has to be derived

$$W = \{P_{ij}, e, \mathcal{M}_{ij}, q_i, \mathcal{R}^{(i)} S, \Pi_{ij}^r, \Pi_{ij}^m\}, \quad \text{with} \quad W = \widetilde{W}(\mathcal{C}), \quad (3.5.2)$$

where Π_{ij}^r and Π_{ij}^m are the potentials related to the porosity field and the other internal variable \mathbf{m} , influencing the viscous effects inside the medium. Both \mathcal{C} and W are evaluated at the same point and time. Among the various methods to analyse the entropy inequality (3.5.1) we choose that one based on Liu's theorem [20], where all balance and evolution equations are considered as mathematical constraints for the general validity of the inequality (3.5.1).

Then, the system of equations (3.4.5)-(3.5.1) and the entropy inequality (3.5.1) can be written, respectively, in the following matrix form

$$\mathbf{A}\mathbf{X} + \mathbf{B} = \mathbf{0}, \quad A_{\Delta\zeta} X_\zeta + B_\Delta = 0, \quad (3.5.3)$$

$$\boldsymbol{\gamma} \cdot \mathbf{X} + \beta \geq 0, \quad \gamma_\zeta X_\zeta + \beta \geq 0, \quad (3.5.4)$$

where \mathbf{A} is a suitable matrix and \mathbf{X} , \mathbf{B} , $\boldsymbol{\gamma}$ and β are suitable quantities (see below (3.5.11)-(3.5.14)). Then, analysing the entropy inequality by Liu's theorem, we have

$$\boldsymbol{\gamma} \cdot \mathbf{X} + \beta - \boldsymbol{\Lambda} \cdot (\mathbf{A}\mathbf{X} + \mathbf{B}) \geq 0, \quad \gamma_\zeta X_\zeta + \beta - \Lambda_\Delta (A_{\Delta\zeta} X_\zeta + B_\Delta) \geq 0, \quad (3.5.5)$$

and this inequality is equivalent to

$$\boldsymbol{\gamma} - \boldsymbol{\Lambda}\mathbf{A} = \mathbf{0}, \quad \gamma_\zeta - \Lambda_\Delta A_{\Delta\zeta} = 0 \quad (3.5.6)$$

$$\beta - \boldsymbol{\Lambda} \cdot \mathbf{B} \geq 0, \quad \beta - \Lambda_\Delta B_\Delta \geq 0, \quad (3.5.7)$$

where the so called Lagrange-Liu multipliers Λ_Δ , accounting for equations (3.4.5)-(3.5.1) are defined by

$$\boldsymbol{\Lambda} = (\Lambda_i^v, \Lambda^e, \Lambda_{pq}^m, \Lambda_{pq}^r). \quad (3.5.8)$$

Thus, the first requirement of Liu's theorem, gives (3.5.5) in the form

$$\begin{aligned} & \rho \frac{\partial S}{\partial t} + \rho v_k S_{,k} + \phi_{k,k} - \Lambda_i^v \left(\rho \frac{\partial v_i}{\partial t} + \rho v_k v_{i,k} + P_{ij,j} + \alpha_{ik} v_k \right) \\ & - \Lambda^e \left(\rho \frac{\partial e}{\partial t} + \rho v_k e_{,k} - P_{ji} v_{i,j} + q_{i,i} \right) - \Lambda_{pq}^m \left(\frac{\partial m_{pq}}{\partial t} + v_k m_{pq,k} - w_{pk} m_{kq} - w_{qk} m_{pk} - \mathcal{M}_{pq} \right) \\ & - \Lambda_{pq}^r \left(\frac{\partial r_{pq}}{\partial t} + v_k r_{pq,k} - w_{pk} r_{kq} - w_{qk} r_{pk} - \mathcal{R}_{pq} \right) \geq 0. \quad (3.5.9) \end{aligned}$$

The entropy inequality is an objective law, then in (3.5.5) Λ^e is an objective scalar function, Λ_i^v is an objective polar vectorial function, Λ_{ij}^m and Λ_{ij}^r are objective tensorial functions of second order. Taking into account that the entropy function S , the stress tensor P_{ij} , the heat flux q_i , the entropy flux ϕ_i , the internal energy e are constitutive functions of the independent variables ε_{ij} , T , $T_{,i}$, m_{ij} , r_{ij} , from (3.5.5)-(3.5.7) and (3.5.9) we obtain the following quantities:

the matrix A having the form

$$A = \begin{pmatrix} \rho & 0 & 0 & 0 & 0 & 0 & \rho \delta_{ik} v_l & \vdots \\ 0 & \rho \frac{\partial e}{\partial T} & \rho \frac{\partial e}{\partial T_{,i}} & \rho \frac{\partial e}{\partial \varepsilon_{kl}} & \rho \frac{\partial e}{\partial m_{kl}} & \rho \frac{\partial e}{\partial r_{kl}} & -P_{kl} & \vdots \\ 0 & 0 & 0 & \delta_{pk} m_{lq} + \delta_{kq} m_{pl} & 0 & \delta_{pk} \delta_{ql} & -\delta_{pk} m_{lq} - \delta_{kq} m_{pl} & \vdots \\ 0 & 0 & 0 & \delta_{pk} r_{lq} + \delta_{kq} r_{pl} & 0 & \delta_{pk} \delta_{ql} & -\delta_{pk} r_{lq} - \delta_{kq} r_{pl} & \vdots \\ \vdots & -\frac{\partial P_{ij}}{\partial T_{,k}} & -\frac{\partial P_{ij}}{\partial \varepsilon_{kl}} & -\frac{\partial P_{ij}}{\partial m_{kl}} & -\frac{\partial P_{ij}}{\partial r_{kl}} & & & \vdots \\ \rho v_j \frac{\partial e}{\partial T_{,k}} + \frac{\partial q_j}{\partial T_{,k}} & \rho v_j \frac{\partial e}{\partial \varepsilon_{kl}} + \frac{\partial q_j}{\partial \varepsilon_{kl}} & \rho v_j \frac{\partial e}{\partial m_{kl}} + \frac{\partial q_j}{\partial m_{kl}} & \rho v_j \frac{\partial e}{\partial r_{kl}} + \frac{\partial q_j}{\partial r_{kl}} & & & & \vdots \\ \vdots & 0 & v_j (\delta_{pk} m_{lq} + \delta_{kq} m_{pl}) & 0 & v_j \delta_{pk} \delta_{ql} & & & \vdots \\ \vdots & 0 & v_j (\delta_{pk} r_{lq} + \delta_{kq} r_{pl}) & 0 & v_j \delta_{pk} \delta_{ql} & & & \vdots \end{pmatrix} \quad (3.5.10)$$

and the other quantities \mathbf{X} , \mathbf{B} , γ , β

$$\mathbf{X} \equiv \{X_\zeta\} = \left(\frac{\partial v_i}{\partial t}, \frac{\partial T}{\partial t}, \frac{\partial T_{,i}}{\partial t}, \frac{\partial \varepsilon_{kl}}{\partial t}, \frac{\partial m_{kl}}{\partial t}, \frac{\partial r_{kl}}{\partial t}, v_{k,l}, T_{,jk}, \varepsilon_{kl,j}, m_{kl,j}, r_{kl,j} \right), \quad (3.5.11)$$

$$\mathbf{B} \equiv \{B_\Delta\} = \left(-\frac{\partial P_{ij}}{\partial T_{,k}} T_{,kj} + \alpha_{ij} v_j, \rho v_j \left(\frac{\partial F}{\partial T} + S + T \frac{\partial S}{\partial T} \right) T_{,j} + \frac{\partial q_j}{\partial T}, -\mathcal{M}_{pq}, -\mathcal{R}_{pq} \right), \quad (3.5.12)$$

$$\gamma \equiv \{\gamma_\zeta\} = \left(0, \rho \frac{\partial S}{\partial T}, \rho \frac{\partial S}{\partial T_i}, \rho \frac{\partial S}{\partial \varepsilon_{kl}}, \rho \frac{\partial S}{\partial m_{kl}}, \rho \frac{\partial S}{\partial r_{kl}}, 0, \rho v_j \frac{\partial S}{\partial T_{,k}} + \frac{\partial \phi_j}{\partial T_{,k}}, \rho v_j \frac{\partial S}{\partial \varepsilon_{kl}} + \frac{\partial \phi_j}{\partial \varepsilon_{kl}}, \right. \\ \left. \rho v_j \frac{\partial S}{\partial m_{kl}} + \frac{\partial \phi_j}{\partial m_{kl}}, \rho v_j \frac{\partial S}{\partial r_{kl}} + \frac{\partial \phi_j}{\partial r_{kl}} \right), \quad (3.5.13)$$

$$\beta = \left(\rho v_j \frac{\partial S}{\partial T} + \frac{\partial \phi_j}{\partial T} \right) T_{,j}, \quad (3.5.14)$$

where we have used the relation $e = F + TS$, being F the Helmholtz free energy per unit mass.

From (3.5.6) and (3.5.7), after some calculations, we obtain the following results

$$\Lambda_i^v = 0 \quad (3.5.15)$$

$$\rho \frac{\partial S}{\partial T} - \Lambda^e \left(\rho \frac{\partial F}{\partial T} + \rho S + \rho T \frac{\partial S}{\partial T} \right) = 0 \quad (3.5.16)$$

$$\rho \frac{\partial S}{\partial T_{,i}} - \Lambda^e \left(\rho \frac{\partial F}{\partial T_{,i}} + \rho S + \rho T \frac{\partial S}{\partial T_{,i}} \right) = 0 \quad (3.5.17)$$

$$\rho \frac{\partial S}{\partial \varepsilon_{kl}} - \Lambda^e \left(\rho \frac{\partial F}{\partial \varepsilon_{kl}} + \rho T \frac{\partial S}{\partial \varepsilon_{kl}} \right) - \Lambda_{pq}^m (\delta_{pk} m_{lq} + \delta_{kq} m_{pl}) - \Lambda_{pq}^r (\delta_{pk} r_{lq} + \delta_{kq} r_{pl}) = 0 \quad (3.5.18)$$

$$\frac{\partial S}{\partial m_{kl}} - \Lambda^e \left(\rho \frac{\partial F}{\partial m_{kl}} + \rho T \frac{\partial S}{\partial m_{kl}} \right) - \Lambda_{kl}^m = 0 \quad (3.5.19)$$

$$\frac{\partial S}{\partial r_{kl}} - \Lambda^e \left(\rho \frac{\partial F}{\partial r_{kl}} + \rho T \frac{\partial S}{\partial r_{kl}} \right) - \Lambda_{kl}^r = 0 \quad (3.5.20)$$

$$\Lambda^e P_{kl} + \Lambda_{pq}^m (\delta_{pk} m_{lq} + \delta_{kq} m_{pl}) + \Lambda_{pq}^r (\delta_{pk} r_{lq} + \delta_{kq} r_{pl}) = 0 \quad (3.5.21)$$

$$\rho v_j \frac{\partial S}{\partial T_{,k}} + \frac{\partial \phi_j}{\partial T_{,k}} - \rho v_j \Lambda^e \left(\frac{\partial F}{\partial T_{,k}} + T \frac{\partial S}{\partial T_{,k}} \right) - \Lambda^e \frac{\partial q_j}{\partial T_{,k}} = 0 \quad (3.5.22)$$

$$\rho v_j \frac{\partial S}{\partial \varepsilon_{kl}} + \frac{\partial \phi_j}{\partial \varepsilon_{kl}} - \rho v_j \Lambda^e \left(\frac{\partial F}{\partial \varepsilon_{kl}} + T \frac{\partial S}{\partial \varepsilon_{kl}} \right) - \Lambda^e \frac{\partial q_j}{\partial \varepsilon_{kl}} \quad (3.5.23)$$

$$- v_j \left[\Lambda_{pq}^m (\delta_{pk} m_{lq} + \delta_{kq} m_{pl}) + \Lambda_{pq}^r (\delta_{pk} r_{lq} + \delta_{kq} r_{pl}) \right] = 0$$

$$\rho v_j \frac{\partial S}{\partial m_{kl}} + \frac{\partial \phi_j}{\partial m_{kl}} - \rho v_j \Lambda^e \left(\frac{\partial F}{\partial m_{kl}} + T \frac{\partial S}{\partial m_{kl}} \right) - \Lambda^e \frac{\partial q_j}{\partial m_{kl}} - v_j \Lambda_{kl}^m = 0 \quad (3.5.24)$$

$$\rho v_j \frac{\partial S}{\partial r_{kl}} + \frac{\partial \phi_j}{\partial r_{kl}} - \rho v_j \Lambda^e \left(\frac{\partial F}{\partial r_{kl}} + T \frac{\partial S}{\partial r_{kl}} \right) - \Lambda^e \frac{\partial q_j}{\partial r_{kl}} - v_j \Lambda_{kl}^r = 0, \quad (3.5.25)$$

and the residual inequality in the form

$$\left(\frac{\partial \phi_j}{\partial T} - \frac{1}{T} \frac{\partial q_j}{\partial T} \right) T_{,j} - \frac{1}{T} \Pi_{pq}^m \mathcal{M}_{pq} - \frac{1}{T} \Pi_{pq}^r \mathcal{R}_{pq} \geq 0. \quad (3.5.26)$$

From the above equations we obtain the *Lagrange multipliers* $\Lambda_i^v, \Lambda^e, \Lambda_{pq}^m, \Lambda_{pq}^r$, the *laws of state* (defining the variables in terms of the partial derivatives of the free energy respect to own conjugate variables) and the *entropy flux* ϕ_i , respectively, in the form

$$\Lambda_i^v = 0, \quad \Lambda^e = \frac{1}{T}, \quad \Lambda_{pq}^m = -\frac{1}{T}\Pi_{pq}^m, \quad \Lambda_{pq}^r = -\frac{1}{T}\Pi_{pq}^r, \quad (3.5.27)$$

$$\frac{\partial F}{\partial T_i} = 0, \quad S = -\frac{\partial F}{\partial T}, \quad P_{kl} = \rho \frac{\partial F}{\partial \varepsilon_{kl}}, \quad \Pi_{kl}^m = \rho \frac{\partial F}{\partial m_{kl}}, \quad \Pi_{kl}^r = \rho \frac{\partial F}{\partial r_{kl}} \quad (3.5.28)$$

$$\phi_i = \frac{1}{T}q_i. \quad (3.5.29)$$

Regarding (3.5.27)₂ see [22]. Furthermore, relations (3.5.28) establish that the free energy F is a function only of the fields $T, \boldsymbol{\varepsilon}, \boldsymbol{m}, \boldsymbol{r}$, i.e. $F = F(T, \boldsymbol{\varepsilon}, \boldsymbol{m}, \boldsymbol{r})$ and, then, also the specific entropy S and the constitutive functions $P_{kl}, \Pi_{kl}^m, \Pi_{kl}^r$ depend on the same set of variables, i.e. $S = S(T, \boldsymbol{\varepsilon}, \boldsymbol{m}, \boldsymbol{r})$, $P_{kl} = P_{kl}(T, \boldsymbol{\varepsilon}, \boldsymbol{m}, \boldsymbol{r})$, $\Pi_{kl}^m = \Pi_{kl}^m(T, \boldsymbol{\varepsilon}, \boldsymbol{m}, \boldsymbol{r})$, $\Pi_{kl}^r = \Pi_{kl}^r(T, \boldsymbol{\varepsilon}, \boldsymbol{m}, \boldsymbol{r})$. From the above results, also, we obtain that the tensors Π_{kl}^m and Π_{kl}^r are symmetric, because of their definition in terms of the partial derivative of F respect to own conjugate symmetric variable.

3.6 CONSTITUTIVE RELATIONS AND RATE EQUATIONS

In this Section, in order to obtain a closed system of equations having the same number of equations and unknown variables (independent and dependent), by the help Wang's [36], [37], [38] and Smith's [33] theorems, that use isotropic polynomial representations of proper functions obeying the objectivity and material indifference principles, the constitutive theory and the source terms for the porosity field $\mathcal{R}^{(i)}(\mathcal{C})$ and the internal variable $\mathcal{M}^{(i)}(\mathcal{C})$ are derived.

3.6.1 Objective representations of $S, P_{ij}, \mathcal{M}_{ij}, \mathcal{R}_{ij}^{(i)}$ and q_i

In this Subsection we represent in a first approximation the objective functions $S, P, \mathcal{M}, \mathcal{R}^{(i)}$ and q , following [33], [36], [37], [38]. Then, being the entropy S a *scalar* objective function, $S = S(T, \boldsymbol{\varepsilon}, \boldsymbol{m}, \boldsymbol{r})$, Wang's theorems establish that S can be expressed as function built on appropriate invariants of the set $\{T, \boldsymbol{\varepsilon}, \boldsymbol{m}, \boldsymbol{r}\}$ (see (B.1.5) of Appendix B). If we assume that the internal variable \boldsymbol{m} is the symmetric part of the velocity gradient, i.e. $\boldsymbol{m} \equiv (\nabla \boldsymbol{v})^s = \dot{\boldsymbol{\varepsilon}}$, S may be written in a first approximation in the following polynomial form

$$S = S^1 T + S^2 \text{tr } \boldsymbol{\varepsilon} + S^3 \text{tr } \dot{\boldsymbol{\varepsilon}} + S^4 \text{tr } \boldsymbol{r}, \quad S = S^1 T + S^2 \varepsilon_{kk} + S^3 \dot{\varepsilon}_{kk} + S^4 r_{kk}, \quad (3.6.1)$$

with $S^\alpha = S^\alpha(T, \boldsymbol{\varepsilon}, \dot{\boldsymbol{\varepsilon}}, \boldsymbol{r})$, $\alpha = 1, \dots, 4$, objective scalar functions, and then depending on suitable invariants, see (B.1.3) in Appendix B, where we identify \boldsymbol{m} with $\dot{\boldsymbol{\varepsilon}}$.

Being $\mathbf{P} = \mathbf{P}(T, \boldsymbol{\varepsilon}, \mathbf{m}, \mathbf{r})$ an objective *second order symmetric tensor*, following [33], [36], [37] and [38] \mathbf{P} can be expressed as function built on appropriate invariants of the set $\{T, \boldsymbol{\varepsilon}, \mathbf{m}, \mathbf{r}\}$ (see (B.2.4) of Appendix B). If we assume that the internal variable \mathbf{m} is the symmetric part of the velocity gradient, i.e. $\mathbf{m} \equiv (\nabla \mathbf{v})^s = \dot{\boldsymbol{\varepsilon}}$ (see equation (3.1.5)), \mathbf{P} can be written in a first approximation in the following polynomial form

$$\mathbf{P} = P^1 \mathbf{U} + P^2 \boldsymbol{\varepsilon} + P^3 \mathbf{m} + P^4 \mathbf{r}, \quad P_{ij} = P^1 \delta_{ij} + P^2 \varepsilon_{ij} + P^3 m_{ij} + P^4 r_{ij}, \quad (3.6.2)$$

where $P^\alpha = P^\alpha(T, \boldsymbol{\varepsilon}, \mathbf{m}, \mathbf{r})$, $\alpha = 1, \dots, 4$, are objective scalar functions, and then depending on suitable invariants (see (B.1.3) in Appendix B).

In the case where we may neglect in (3.6.2) the influence of the fields $\boldsymbol{\varepsilon}$ and \mathbf{r} , and we assume $\mathbf{m} \equiv \dot{\boldsymbol{\varepsilon}} = (\nabla \mathbf{v})^s$, $P^1 = p$, $P^3 = -2\eta$, we obtain relation (3.1.4)₁ of Section 3.1

$$\mathbf{P} = P^1 \mathbf{U} + P^3 \dot{\boldsymbol{\varepsilon}} = p \mathbf{U} - 2\eta (\nabla \mathbf{v})^s, \quad P_{ij} = P^1 \delta_{ij} + P^3 \dot{\varepsilon}_{ij} = p \delta_{ij} - 2\eta v_{(i,j)}. \quad (3.6.3)$$

Thus, we have obtained a thermodynamic model for the media under consideration, illustrating from the theoretical point view the form (3.1.4)₁ of the pressure tensor \mathbf{P} . We can derive expressions analogous to (3.6.2) for the symmetric tensors Π_{kl}^m and Π_{kl}^m .

Being $\mathcal{M}(T, \nabla T, \boldsymbol{\varepsilon}, \mathbf{m}, \mathbf{r})$ and $\mathcal{R}^{(i)}(T, \nabla T, \boldsymbol{\varepsilon}, \mathbf{m}, \mathbf{r})$ objective *second order symmetric tensors* (that depend also on the vector ∇T), following [36], [37], [38] they can be expressed as functions built on appropriate invariants of the set $\{T, \boldsymbol{\varepsilon}, \mathbf{m}, \mathbf{r}\}$ (see Appendix B). Then, if we assume that the internal variable \mathbf{m} is the symmetric part of the velocity gradient, i.e. $\mathbf{m} \equiv (\nabla \mathbf{v})^s = \dot{\boldsymbol{\varepsilon}}$, \mathcal{M} and $\mathcal{R}^{(i)}$ may be written in a first approximation in the following polynomial form (see (B.2.8) and (B.2.9) in Appendix B)

$$\mathcal{M} = M^1 \mathbf{U} + M^2 \boldsymbol{\varepsilon} + M^3 \dot{\boldsymbol{\varepsilon}} + M^4 \mathbf{r}, \quad \mathcal{M}_{ij} = M^1 \delta_{ij} + M^2 \varepsilon_{ij} + M^3 \dot{\varepsilon}_{ij} + M^4 r_{ij}, \quad (3.6.4)$$

and

$$\mathcal{R}^{(i)} = R^1 \mathbf{U} + R^2 \boldsymbol{\varepsilon} + R^3 \dot{\boldsymbol{\varepsilon}} + R^4 \mathbf{r}, \quad \mathcal{R}_{ij}^{(i)} = R^1 \delta_{ij} + R^2 \varepsilon_{ij} + R^3 \dot{\varepsilon}_{ij} + R^4 r_{ij}, \quad (3.6.5)$$

where $M^\alpha(T, \nabla T, \boldsymbol{\varepsilon}, \dot{\boldsymbol{\varepsilon}}, \mathbf{r})$ and $R^\alpha(T, \nabla T, \boldsymbol{\varepsilon}, \dot{\boldsymbol{\varepsilon}}, \mathbf{r})$, $\alpha = 1, \dots, 4$, are scalar objective functions, and then depending on suitable invariants (see (B.2.10) in Appendix B, where we have assumed $\mathbf{m} = \dot{\boldsymbol{\varepsilon}}$). In the expression (3.6.5)₁, supposing that we may disregard the influence of the first field and the symmetric part of the velocity gradient and

$$R^4 = -(\tau^r)^{-1}, \quad R^2 = (p - p_0), \quad (3.6.6)$$

in the case where we may use the material derivative instead of Zaremba-Jaumann derivative, $\mathcal{R}^{(i)}$ assumes the form

$$\mathcal{R}^{(i)} = -(\tau^r)^{-1} \mathbf{r} + (p - p_0) \boldsymbol{\varepsilon}. \quad (3.6.7)$$

Then, from relation (3.4.8), having the external source $\mathcal{R}^{(e)}$ the form (3.2.6) and $\mathcal{R}^{(i)}$ the form (3.6.7), we derive

$$\dot{\mathbf{r}} = -(\tau^r)^{-1} \mathbf{r} + (p - p_0) \boldsymbol{\varepsilon} + \mathbf{B} \cdot \mathbf{J} + \mathbf{C} : (\mathbf{J} \otimes \mathbf{J}), \quad \dot{r}_{ij} = -(\tau^r)^{-1} r_{ij} + (p - p_0) \varepsilon_{ij} + B_{ijk} J_k + C_{ijkl} J_k J_l, \quad (3.6.8)$$

and then we obtain relation (3.2.2), when we indicate by the same symbols ε , \mathbf{B} , \mathbf{C} the tensors $\bar{\varepsilon}$, $\bar{\mathbf{B}}$, $\bar{\mathbf{C}}$, defined by

$$\bar{\varepsilon} = \tau^r \varepsilon, \quad \bar{\mathbf{B}} = \tau^r \mathbf{B}, \quad \bar{\mathbf{C}} = \tau^r \mathbf{C}. \quad (3.6.9)$$

Thus, using the obtained thermodynamic model for the media under consideration, we can illustrate from the theoretical point view the form the rate equation (3.2.2).

Finally, being $\mathbf{q}(T, \nabla T, \varepsilon, \mathbf{m}, \mathbf{r})$ an objective *vector-value function*, following [33], [36], [37] and [38] and it can be expressed as function built on appropriate invariants of the set $\{T, \nabla T, \varepsilon, \mathbf{m}, \mathbf{r}\}$ (see Appendix B). If we assume that the internal variable \mathbf{m} is the symmetric part of the velocity gradient, i.e. $\mathbf{m} \equiv (\nabla v)^s = \dot{\varepsilon}$, \mathbf{q} can be written in a first approximation in the following polynomial form (see (B.3.4) in Appendix B)

$$\mathbf{q} = q^1 \nabla T, \quad q_i = q^1 T_{,i}, \quad (3.6.10)$$

where $q^1 = q^1(T, \nabla T, \varepsilon, \dot{\varepsilon}, \mathbf{r})$, is an objective scalar function, and then depending on suitable invariants (see (B.2.10) in Appendix B, where we have assumed $\mathbf{m} = \dot{\varepsilon}$).

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4 | PROPAGATION OF COUPLED POROSITY AND FLUID-CONCENTRATION WAVES IN ISOTROPIC POROUS MEDIA

This Chapter deals with an application of a theory, previously formulated in 1 and 2 in the framework of rational extended irreversible thermodynamics, that describes the thermal, mechanical and transport properties of a porous medium filled by a fluid. Here, starting from the anisotropic rate equations for the porosity field, its flux, and for the heat and fluid-concentration fluxes, the isotropic case is studied when the body has symmetry properties invariant for all rotations and inversions of the frame axes and, furthermore, the phenomenological tensors have special symmetry properties coming from the used theoretic model. Then, the propagation in one direction of coupled porosity and fluid-concentration waves is investigated. The dispersion relation is carried out and the wave propagation velocities as functions of the wavenumber are calculated and represented in a diagram for a given numerical set of the several coefficients characterizing the considered porous media. The achievements of this Chapter can be applied in several science fields, like seismology, medical sciences, geology and nanotechnology, where there are situations of propagation of high-frequency waves. In particular, in this Chapter we apply a thermodynamic theory (see [18], [19], [21], [22]), formulated in the framework of rational extended thermodynamics [1], [2], [8], [9], [10], [11], [12], [13], [15], [16], [17], [24], with internal variables for the description of the behaviour of porous media, to the study of a problem of propagation of coupled porosity and fluid-concentration waves in isotropic media.

The studies of phenomena regarding porous structures saturated by a fluid have great importance (see also [3], [6], [23]) and the obtained results can be used in several technological fields, like seismic waves, medical sciences, biology, geology and nanotechnology where the Knudsen number $Kn = l/L \geq 1$ and there are high-frequency waves propagation and the transport properties of these systems have a rate variation faster than the time scale of the relaxation times of the fluxes to their equilibrium values.

The organization of this Chapter is the following. Section 4.1 is addressed to an application of the presented theory to a problem of wave propagation in a porous medium, supposed at rest, when only the porosity field, its flux, the fluid-concentration field and its flux are taken into account. In particular, starting from the anisotropic case (see [21], [22]) we derive in a special case a system of equations describing the propagation of coupled porosity and fluid-concentration waves in a porous isotropic medium, having symmetry properties invariant with respect to all rotations and inversions of frame axes (see [4], [7]).

Precisely, using the system of equations (2.1.21), (2.1.22), (2.1.23)-(2.1.28) and (2.2.2), valid for the perfect isotropic medium under consideration, we focus our attention on

the fields related to the fluid-concentration c and its flux j_i^c and on the porosity field r_{ij} and its flux \mathcal{V}_{ijk} , neglecting the contributions of the other fields and we assume that the porosity tensor r_{ij} has only a scalar component r and its flux \mathcal{V}_{ijk} has only a vectorial component \mathcal{V}_k .

Then, in Section 4.1 we construct, in the one-dimensional case, a simpler system of equations, having a structure such that we can study the propagation of plane waves of the exponential form $Ae^{ik(x-vt)}$, that travel along the x -axis direction with amplitude A and speed v . The dispersion relation is obtained and the values of the wave propagation velocities are worked out as functions of the wavenumber k . The dispersion curves are represented in a diagram for a given numerical set of the several coefficients characterizing the considered porous media.

In Appendix A particular forms for fourth, and sixth order isotropic tensors having special symmetry properties and the detailed derivation of the transport equations for the porosity field and fluid-concentration flux are derived.

A similar propagation problem of coupled waves was studied by L. Restuccia in isotropic n-type semiconductors (see [20]). The difference between both situations is that in [20] the considered media were semiconductors with dislocation lines, described as thin channels by an internal variable, the dislocation core tensor [14] (defined on the basis of the structural permeability tensor à la Kubik), and the fluid-concentration flux field was the flux of the concentration of electronic charge carriers.

The studies presented in this Chapter are contained in the article [5]:

A. Famà and L. Restuccia. Propagation of coupled porosity and fluid-concentration waves in isotropic porous media. *Electronic Journal of Differential Equations*, pp. 1-16, 2020.

4.1 EVOLUTION EQUATIONS FOR POROSITY AND FLUID-CONCENTRATION FIELDS AND THEIR FLUXES

In this Section we apply the theory presented in the Chapters 1 and 2 to a problem of wave propagation for the porous defects and fluid mass fields and their fluxes in a porous medium, supposed at rest, and we study, starting from the anisotropic case, an isotropy situation, when the medium has symmetry properties *invariant with respect to all rotations and inversions of frame axes, i.e. is perfect isotropic*. Let us consider the system of equations (1.1.10), (1.4.1), (1.4.2) and (1.4.16). We neglect in (1.4.1), (1.4.2) and (1.4.16) the influences of the thermal phenomena, i.e. the presence of the fields q_i and $T_{,j}$. Furthermore, in equation (1.4.1) we disregard the influence of the small deformations ε_{ij} and of the porous defects r_{ij} field, in the rate equation (1.4.2) the contribution of the fluid mass field j_i^c and in the rate equation (1.4.16) the influence of the porous defects field flux \mathcal{V}_{ijk} . Thus, we obtain

$$\rho \frac{\partial c}{\partial t} = -j_{k,k}^c, \quad (4.1.1)$$

$$\frac{\partial r_{ij}}{\partial t} + \mathcal{V}_{ijk,k} = \beta_{ijk}^3 j_k^c + \beta_{ijklm}^5 \mathcal{V}_{klm} + \beta_{ijk}^6 c_{,k} + \beta_{ijklm}^8 r_{kl,m}, \quad (4.1.2)$$

$$\frac{\partial \mathcal{V}_{ijk}}{\partial t} = \gamma_{ijklmn}^3 \mathcal{V}_{lmn} + \gamma_{ijkl}^4 c_{,l} + \gamma_{ijklmn}^6 r_{lm,n}, \quad (4.1.3)$$

$$\tau^{jc} \frac{\partial j_i^c}{\partial t} = -j_i^c - \xi_{ij}^4 c_{,j} + \xi_{ijkl}^6 r_{jk,l}. \quad (4.1.4)$$

We remind that, because of the symmetry of r_{ij} , i.e. $r_{ij} = r_{ji}$, the phenomenological coefficients β_{ijk}^3 , β_{ijklm}^5 , β_{ijk}^6 and β_{ijklm}^8 , present in the rate equation (4.1.2), have the symmetries (1.4.17)₂ and (1.4.18)_{1,2}. Furthermore, the tensors γ_{ijklmn}^6 and ξ_{ijkl}^6 have the symmetries (1.4.19) and (1.4.20)₂, respectively.

These symmetries relations reduce the number of the significant components of the considered phenomenological tensors in these equations. The number of these significant components has a further reduction if we establish some other assumption.

Being r_{ij} a second order tensor, we can introduce its deviator, \tilde{r}_{ij} , and its scalar (or spherical) part, r , in the following way

$$\tilde{r}_{ij} = r_{ij} - \frac{1}{3} r \delta_{ij}, \quad r = \frac{1}{3} r_{kk}, \quad (i, j, k = 1, 2, 3), \quad (4.1.5)$$

where Einstein convention for the dummy indices is used, and r_{ij} can be written in the form

$$r_{ij} = \tilde{r}_{ij} + r \delta_{ij}, \quad \text{with } \tilde{r}_{kk} = 0, \quad (4.1.6)$$

where, being r_{ij} symmetric, also \tilde{r}_{ij} is symmetric.

Furthermore, we consider the case in which \mathcal{V}_{ijk} can be written as the sum of three symmetric contributions

$$\mathcal{V}_{ijk} = \mathcal{V}_k \delta_{ij} + \mathcal{V}_i \delta_{jk} + \mathcal{V}_j \delta_{ik}. \quad (4.1.7)$$

For the sake of simplicity in the following we will consider only the spherical part $r_{ij} = r \delta_{ij}$ of the porosity field and the contribution $\mathcal{V}_k \delta_{ij}$ of its flux, i. e.

$$r_{ij} = r \delta_{ij}, \quad \mathcal{V}_{ijk} = \mathcal{V}_k \delta_{ij}, \quad (4.1.8)$$

where $\mathcal{V}_k \delta_{ij}$ is symmetric in the indexes $\{i, j\}$.

Thus, by virtue of the assumptions (4.1.8), the rate equations (3.4.8)-(4.1.4) keep the form

$$\frac{\partial r}{\partial t} \delta_{ij} + \mathcal{V}_{k,k} \delta_{ij} = \beta_{ijk}^3 j_k^c + \beta_{ijklm}^5 \mathcal{V}_m \delta_{kl} + \beta_{ijk}^6 c_{,k} + \beta_{ijklm}^8 r_{,m} \delta_{kl}, \quad (4.1.9)$$

$$\frac{\partial \mathcal{V}_k}{\partial t} \delta_{ij} = \gamma_{ijklmn}^3 \mathcal{V}_n \delta_{lm} + \gamma_{ijkl}^4 c_{,l} + \gamma_{ijklmn}^6 r_{,n} \delta_{lm}, \quad (4.1.10)$$

$$\tau^{jc} \frac{\partial j_i^c}{\partial t} = -j_i^c - \xi_{ij}^4 c_{,j} + \xi_{ijkl}^6 r_{,l} \delta_{jk}. \quad (4.1.11)$$

In (4.1.10) the following symmetries are valid

$$\begin{aligned} \gamma_{ijkl}^4 = \gamma_{jikl}^4, \quad \gamma_{ijklmn}^3 = \gamma_{jiklmn}^3 = \gamma_{ijkmln}^3 = \gamma_{jikmln}^3, \\ \gamma_{ijklmn}^6 = \gamma_{jiklmn}^6 = \gamma_{ijkmln}^6 = \gamma_{jikmln}^6. \end{aligned} \quad (4.1.12)$$

The properties (4.1.12)₁ and (4.1.12)₂ come from the symmetry of $\mathcal{V}_k \delta_{ij}$ and from the fact that in γ_{ijklmn}^3 and in γ_{ijklmn}^6 the indexes $\{l, m\}$ are dummy indexes with the indexes of the tensors $\mathcal{V}_n \delta_{lm}$ and $r_{,n} \delta_{lm}$, symmetric in $\{l, m\}$. In the last part of relation (4.1.12)₃ the symmetry property (1.4.20)₂ has been included.

Also, in (4.1.11) we have

$$\xi_{ijkl}^6 = \xi_{ikjl}^6, \quad (4.1.13)$$

because in ξ_{ijkl}^6 the indexes $\{j, k\}$ are dummy indexes with the indexes of the tensor $r_{,l} \delta_{jk}$, symmetric in $\{j, k\}$.

4.1.1 System of equations describing the propagation of coupled porosity and fluid-concentration waves in an isotropic medium

As seen in Chapter 2, the existence of spatial symmetry properties in a material system may simplify the form of the rate equations in such a way that the number of the significant Cartesian components of the phenomenological tensors present in them have a further reduction. Thus, in this Subsection we consider perfect isotropic systems for which we remind that the symmetry properties are invariant with respect to all rotations and the inversion of the frame of axes (under orthogonal transformations) and we will study a problem of propagation of the coupled waves of porous defects and fluid concentration fields. In this case, *the tensors of odd order vanish* (see relation (2.2.1)₂), so that in equation (4.1.9) we have

$$\beta_{ijk}^3 = \beta_{ijklm}^5 = \beta_{ijk}^6 = \beta_{ijklm}^8 = 0; \quad (4.1.14)$$

the tensors of order two keep the form (2.1.1)₂, so that the phenomenological tensor ξ_{ij}^4 in equation (4.1.10) takes the form

$$\xi_{ij}^4 = \xi^4 \delta_{ij}; \quad (4.1.15)$$

the tensors of order four must have the form (2.1.2), therefore γ_{ijkl}^4 and ξ_{ijkl}^6 in equations (4.1.10) and (4.1.11) have only three independent components; the tensors of order six (see γ_{ijklmn}^3 and γ_{ijklmn}^6 present in (4.1.10)) assume the form (2.1.4).

Taking into account the isotropic forms (2.1.2), (2.1.4), (4.1.14) and (4.1.15) of the phenomenological tensors and their symmetry properties (1.4.20)₂ and (4.1.12) we derive from (1.1.10), (4.1.9), (4.1.10) and (4.1.11) the following simplified system of equations governing the evolution of porosity and fluid-concentration fields and their fluxes

$$\rho \frac{\partial c}{\partial t} + j_{k,k}^c = 0, \quad (4.1.16)$$

$$\frac{\partial r}{\partial t} + \mathcal{V}_{k,k} = 0, \quad (4.1.17)$$

$$\tau^v \frac{\partial \mathcal{V}_k}{\partial t} = -\mathcal{V}_k - D_v r_{,k} + \alpha_v c_{,k}, \quad (4.1.18)$$

$$\tau^{j^c} \frac{\partial j_i^c}{\partial t} = -j_i^c + \alpha_c r_{,i} - \rho D_c c_{,i}, \quad (4.1.19)$$

where τ^v is the relaxation time of the field $\mathcal{V}_{ijk} = \mathcal{V}_k \delta_{ij}$, given by relation (4.1.24)₁, D_v and D_c are the diffusion coefficients of porosity field and fluid-concentration flux, respectively, given by the relations (4.1.25) and (4.1.28)₂, α_v and α_c are coupling coefficients given by relations (4.1.24)₂ and (4.1.28)₁, respectively, being

$$\tau^v \geq 0, \quad \tau^{j^c} \geq 0, \quad D_v \geq 0, \quad D_c \geq 0. \quad (4.1.20)$$

To obtain equation (4.1.18), we use (4.1.8) and the special forms (A.3.3) and (A.4.15), established in Appendix A, assumed by the fourth order tensor γ_{ijkl}^4 and the sixth order tensors γ_{ijklmn}^r ($r = 3, 6$), so that equation (4.1.3) takes the form

$$\begin{aligned} \delta_{ij} \frac{\partial \mathcal{V}_k}{\partial t} = & \left\{ \gamma_1^3 (\delta_{kl} \delta_{mn} + \delta_{km} \delta_{ln}) \delta_{ij} + \gamma_2^3 \delta_{ij} \delta_{kn} \delta_{lm} + \gamma_3^3 [(\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \delta_{mn} \right. \\ & + (\delta_{ik} \delta_{jm} + \delta_{im} \delta_{jk}) \delta_{ln}] + \gamma_4^3 (\delta_{ik} \delta_{jn} + \delta_{in} \delta_{jk}) \delta_{lm} + \gamma_5^3 (\delta_{il} \delta_{jm} + \delta_{im} \delta_{jl}) \delta_{kn} \\ & \left. + \gamma_6^3 [(\delta_{il} \delta_{jn} + \delta_{in} \delta_{jl}) \delta_{km} + (\delta_{im} \delta_{jn} + \delta_{in} \delta_{jm}) \delta_{kl}] \right\} \mathcal{V}_n \delta_{lm} \\ & + [\gamma_1^4 \delta_{ij} \delta_{kl} + \gamma_2^4 (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk})] c_{,l} + \left\{ \gamma_1^6 (\delta_{kl} \delta_{mn} + \delta_{km} \delta_{ln}) \delta_{ij} + \gamma_2^6 \delta_{ij} \delta_{kn} \delta_{lm} \right. \\ & + \gamma_3^6 [(\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \delta_{mn} + (\delta_{ik} \delta_{jm} + \delta_{im} \delta_{jk}) \delta_{ln}] + \gamma_4^6 (\delta_{ik} \delta_{jn} + \delta_{in} \delta_{jk}) \delta_{lm} \\ & + \gamma_5^6 (\delta_{il} \delta_{jm} + \delta_{im} \delta_{jl}) \delta_{kn} + \gamma_6^6 [(\delta_{il} \delta_{jn} + \delta_{in} \delta_{jl}) \delta_{km} \\ & \left. + (\delta_{im} \delta_{jn} + \delta_{in} \delta_{jm}) \delta_{kl}] \right\} r_{,n} \delta_{lm}, \end{aligned} \quad (4.1.21)$$

where γ_s^3 and γ_s^6 ($s = 1, \dots, 6$) are the 6 independent significant components of the sixth order tensors γ_{ijklmn}^3 and γ_{ijklmn}^6 , respectively, and γ_1^4, γ_2^4 are the 2 independent significant components of the fourth order tensor γ_{ijkl}^4 .

Then, from (4.1.21) we get

$$\begin{aligned} \delta_{ij} \frac{\partial \mathcal{V}_k}{\partial t} = & \left[(2\gamma_1^3 + 3\gamma_3^3 + 2\gamma_5^3) \mathcal{V}_k + (2\gamma_1^6 + 3\gamma_3^6 + 2\gamma_5^6) r_{,k} + \gamma_1^4 c_{,k} \right] \delta_{ij} \\ & + \left[(3\gamma_2^3 + 2\gamma_4^3 + 2\gamma_6^3) \mathcal{V}_j + (3\gamma_2^6 + 2\gamma_4^6 + 2\gamma_6^6) r_{,j} + \gamma_2^4 c_{,j} \right] \delta_{ik} \\ & + \left[(3\gamma_2^3 + 2\gamma_4^3 + 2\gamma_6^3) \mathcal{V}_i + (3\gamma_2^6 + 2\gamma_4^6 + 2\gamma_6^6) r_{,i} + \gamma_2^4 c_{,i} \right] \delta_{jk}. \end{aligned} \quad (4.1.22)$$

Thus, when $i = j$ we have

$$\begin{aligned} \frac{\partial \mathcal{V}_k}{\partial t} = & (2\gamma_1^3 + 6\gamma_2^3 + 3\gamma_3^3 + 4\gamma_4^3 + 2\gamma_5^3 + 4\gamma_6^3) \mathcal{V}_k + (\gamma_1^4 + 2\gamma_2^4) c_{,k} \\ & + (2\gamma_1^6 + 6\gamma_2^6 + 3\gamma_3^6 + 4\gamma_4^6 + 2\gamma_5^6 + 4\gamma_6^6) r_{,k}, \end{aligned} \quad (4.1.23)$$

i.e. equation (4.1.18), $\tau^v \frac{\partial \mathcal{V}_k}{\partial t} = -\mathcal{V}_k - D_v r_{,k} + \alpha_v c_{,k}$, when we introduce the following definitions, coming from physical reasons

$$2\gamma_1^3 + 6\gamma_2^3 + 3\gamma_3^3 + 4\gamma_4^3 + 2\gamma_5^3 + 4\gamma_6^3 = -(\tau^v)^{-1}, \quad \alpha_v = \tau^v (\gamma_1^4 + 2\gamma_2^4), \quad (4.1.24)$$

$$D_v = -\tau^v (2\gamma_1^6 + 6\gamma_2^6 + 3\gamma_3^6 + 4\gamma_4^6 + 2\gamma_5^6 + 4\gamma_6^6). \quad (4.1.25)$$

To derive (4.1.19), we use equation (4.1.4), the assumption (4.1.8)₁ and the special form (4.1.15) and (A.3.12) of the tensors ξ_{ij}^4 and ξ_{ijkl}^6 (see Appendix A), so that we obtain

$$\tau^{jc} \frac{\partial j_i^c}{\partial t} = -j_i^c - \xi^4 \delta_{ij} c_{,j} + [\xi_1^6 \delta_{il} \delta_{jk} + \xi_2^6 (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl})] r_{,l} \delta_{jk}, \quad (4.1.26)$$

where ξ_1^6, ξ_2^6 are the 2 significant independent components of the fourth tensor ξ_{ijkl}^6 and ξ^4 is the only one significant component of the second order tensor ξ_{ij}^4 . Then, equation (4.1.26) keeps the form

$$\tau^{jc} \frac{\partial j_i^c}{\partial t} = -j_i^c - \xi^4 c_{,i} + (3\xi_1^6 + 2\xi_2^6) r_{,i}, \quad (4.1.27)$$

i.e. equation (4.1.19), $\tau^{jc} \frac{\partial j_i^c}{\partial t} = -j_i^c + \alpha_c r_{,i} - \rho D_c c_{,i}$, when we introduce the following definitions

$$\alpha_c = 3\xi_1^6 + 2\xi_2^6, \quad D_c = \frac{\xi^4}{\rho}. \quad (4.1.28)$$

From equation (4.1.16), its derivative with respect to time and (4.1.19) we obtain

$$\tau^{jc} \frac{\partial^2 c}{\partial t^2} + \frac{\partial c}{\partial t} + \bar{\alpha}_c r_{,ii} - D_c c_{,ii} = 0, \quad (4.1.29)$$

where $\bar{\alpha}_c = \frac{\alpha_c}{\rho}$. In analogous way, from equation (4.1.17), its derivative with respect to time and (4.1.18) we have

$$\tau^v \frac{\partial^2 r}{\partial t^2} + \frac{\partial r}{\partial t} - D_v r_{,ii} + \alpha_v c_{,ii} = 0. \quad (4.1.30)$$

The system of equations (4.1.29), (4.1.30) describes the coupled porosity and fluid-concentration waves in a perfect isotropic medium. The aim of this Chapter is to find, from the dispersion relation, the wave propagation velocities as functions of the wave-number and to obtain some particular propagation mathematical conditions.

We confine our considerations to one-dimensional plane waves. We suppose that the porous medium occupies the whole space and we consider the propagation of the coupled waves along x direction. Thus, assuming that the solutions of the set of equations (4.1.29) and (4.1.30) have the form

$$r(x, t) = \widehat{r}e^{ik(x-vt)}, \quad (4.1.31)$$

$$c(x, t) = \widehat{c}e^{ik(x-vt)}, \quad (4.1.32)$$

with \widehat{r} and \widehat{c} the amplitudes of the waves $r(x, t)$ and $c(x, t)$, k the wavenumber, v the wave velocity, defined by $v = \omega/k$ [ms^{-1}], with ω the angular frequency, $\omega = 2\pi f$ [s^{-1}], being f the wave frequency and $k = 2\pi/\lambda$ [m^{-1}], with λ the wavelength.

Thus, using the relations (4.1.31), (4.1.32) and their derivatives in (4.1.29)-(4.1.30) we obtain the following system of equations

$$(D_c k - \tau^{jc} k v^2 - i v) \widehat{c} - \bar{\alpha}_c k \widehat{r} = 0, \quad (4.1.33)$$

$$\alpha_v k^2 \widehat{c} + (\tau^v k^2 v^2 - D_v k^2 + i k v) \widehat{r} = 0, \quad (4.1.34)$$

that has non-trivial solutions only if its determinant vanishes, i.e.

$$\mathcal{D} = \begin{vmatrix} D_c k - \tau^{jc} k v^2 - i v & -\bar{\alpha}_c k \\ \alpha_v k^2 & \tau^v k^2 v^2 - D_v k^2 + i k v \end{vmatrix} = 0. \quad (4.1.35)$$

Developing \mathcal{D} we derive the following *dispersion relation* for the wave propagation velocity v , concerning four possible modes:

$$\begin{aligned} & \tau^{jc} \tau^v k^2 v^4 + i k (\tau^{jc} + \tau^v) v^3 - [(D_c \tau^v + D_v \tau^{jc}) k^2 + 1] v^2 \\ & - i k (D_c + D_v) v + k^2 (D_c D_v - \bar{\alpha}_c \alpha_v) = 0. \end{aligned} \quad (4.1.36)$$

From the real part of the dispersion relation (4.1.36), we obtain

$$\tau^{jc} \tau^v k^2 v^4 - [(D_c \tau^v + D_v \tau^{jc}) k^2 + 1] v^2 + k^2 (D_c D_v - \bar{\alpha}_c \alpha_v) = 0, \quad (4.1.37)$$

from which we have two possible modes

$$v_{(1)} = \sqrt{\mathcal{G}_1 + \sqrt{\mathcal{G}_1^2 - \mathcal{G}_2}}, \quad v_{(2)} = \sqrt{\mathcal{G}_1 - \sqrt{\mathcal{G}_1^2 - \mathcal{G}_2}}, \quad (4.1.38)$$

where

$$\mathcal{G}_1 = \frac{D_c \tau^v + D_v \tau^{jc}}{2 \tau^{jc} \tau^v} + \frac{1}{2 \tau^{jc} \tau^v k^2}, \quad \text{being } \mathcal{G}_1 > 0, \quad (4.1.39)$$

$$\mathcal{G}_2 = \frac{D_c D_v - \bar{\alpha}_c \alpha_v}{\tau^{jc} \tau^v}. \quad (4.1.40)$$

From the imaginary part of the dispersion relation (4.1.36), we derive

$$k(\tau^{j^c} + \tau^\nu)v^3 - k(D_c + D_\nu)v = 0, \quad (4.1.41)$$

from which we obtain the other two values for v

$$v_{(3)} = 0, \quad v_{(4)} = \sqrt{\frac{D_c + D_\nu}{\tau^{j^c} + \tau^\nu}}, \quad \text{being} \quad \frac{D_c + D_\nu}{\tau^{j^c} + \tau^\nu} > 0. \quad (4.1.42)$$

From (4.1.42)₃ and (4.1.20) the velocity $v_{(4)}$ is always real, whereas the velocity $v_{(1)}$ is real when

$$\mathcal{G}_1^2 - \mathcal{G}_2 \geq 0, \quad (4.1.43)$$

namely when

$$\left[(D_c\tau^\nu - D_\nu\tau^{j^c})^2 + 4\tau^{j^c}\tau^\nu\bar{\alpha}_c\alpha_\nu \right] k^4 + 2(D_c\tau^\nu + D_\nu\tau^{j^c})k^2 + 1 \geq 0, \quad (4.1.44)$$

that is always true because sum of positive quantities, and then also the velocity $v_{(1)}$ is always real.

From (4.1.42)₃ the velocity $v_{(2)}$ is real when

$$\mathcal{G}_1 - \sqrt{\mathcal{G}_1^2 - \mathcal{G}_2} \geq 0, \quad (4.1.45)$$

from which we obtain

$$\mathcal{G}_2 \geq 0, \quad (4.1.46)$$

and thus

$$D_c D_\nu \geq \bar{\alpha}_c \alpha_\nu, \quad (4.1.47)$$

Thus, in the assumption that (4.1.46) (or (4.1.47)) holds $v_{(2)}$ is real.

Notice that the velocities $v_{(1)}$ and $v_{(2)}$ are stable:

$$\lim_{k \rightarrow +\infty} v_{(1)} = \sqrt{\frac{D_c\tau^\nu + D_\nu\tau^{j^c}}{2\tau^{j^c}\tau^\nu} + \sqrt{\left(\frac{D_c\tau^\nu + D_\nu\tau^{j^c}}{2\tau^{j^c}\tau^\nu}\right)^2 - \mathcal{G}_2}}, \quad (4.1.48)$$

$$\lim_{k \rightarrow +\infty} v_{(2)} = \sqrt{\frac{D_c\tau^\nu + D_\nu\tau^{j^c}}{2\tau^{j^c}\tau^\nu} - \sqrt{\left(\frac{D_c\tau^\nu + D_\nu\tau^{j^c}}{2\tau^{j^c}\tau^\nu}\right)^2 - \mathcal{G}_2}}; \quad (4.1.49)$$

furthermore $v_{(1)}$ is a monotonically decreasing function of k because

$$\frac{dv_{(1)}}{dk} = \frac{1}{2\sqrt{\mathcal{G}_1 + \sqrt{\mathcal{G}_1^2 - \mathcal{G}_2}}} \left[1 + \frac{\mathcal{G}_1}{\sqrt{\mathcal{G}_1^2 - \mathcal{G}_2}} \right] \frac{d\mathcal{G}_1}{dk} < 0, \quad (4.1.50)$$

being

$$\frac{d\mathcal{G}_1}{dk} = -\frac{k}{\tau^{j^c}\tau^\nu k^4} < 0, \quad (4.1.51)$$

and $v_{(2)}$ is a monotonically increasing function of k because

$$\frac{dv_{(2)}}{dk} = \frac{1}{2\sqrt{\mathcal{G}_1 + \sqrt{\mathcal{G}_1^2 - \mathcal{G}_2}} \left[1 - \frac{\mathcal{G}_1}{\sqrt{\mathcal{G}_1^2 - \mathcal{G}_2}} \right]} \frac{d\mathcal{G}_1}{dk} > 0, \quad (4.1.52)$$

being condition $\frac{\mathcal{G}_1}{\sqrt{\mathcal{G}_1^2 - \mathcal{G}_2}} > 1$ true only if $\mathcal{G}_2 > 0$, that is (4.1.46). Thus, the velocities $v_{(1)}$ and $v_{(2)}$ are continuous functions of k , monotonically decreasing and increasing functions, respectively, and they have an horizontal asymptote definite by the right-hand members of equations (4.1.48) and (4.1.49).

In Fig. 12 the wave propagation speeds $v_{(1)}$, $v_{(2)}$ and $v_{(4)}$ as functions of k are represented for a given numerical set of the several coefficients present in the examined problem: $D_c = 10^{-1} \text{ m}^2 \text{ s}^{-1}$, $D_v = 10^{-1} \text{ m}^2 \text{ s}^{-1}$, $\tau^{jc} = 10^{-2} \text{ s}$, $\tau^v = 10^{-3} \text{ s}$, $\alpha_v = 10^{-2} \text{ s}^{-1}$ and $\bar{\alpha}_c = 10^{-1} \text{ m}^4 \text{ s}^{-1}$, being $\alpha_c = \bar{\alpha}_c \rho$, with $\rho = 10^3 \text{ kg m}^{-3}$ and $\alpha_c = 10^{-2} \text{ kg m s}^{-1}$. In this assumption the condition (4.1.47) is satisfied and thus the velocity $v_{(4)}$ is real.

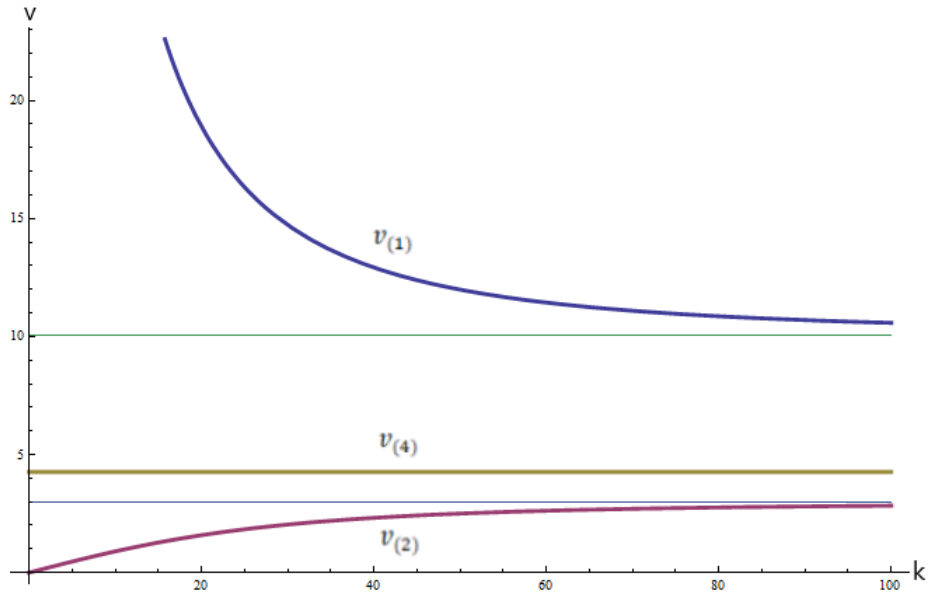


Figure 12: Representation of the three wave propagation speeds $v_{(1)}$, $v_{(2)}$ and $v_{(4)}$ as functions of k , for a given numerical set of several coefficients present in the studied problem. The two horizontal lines are the horizontal asymptotes of the wave propagation velocities $v_{(1)}$ and $v_{(2)}$, respectively.

The results presented in Fig. 12 show that for bigger values of k (for shorter wave lengths λ) the propagation velocity $v_{(1)}$ decreases, while the propagation velocity $v_{(2)}$ increases and the velocity $v_{(4)}$ remains constant.

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5

WEAK DISCONTINUITY WAVES IN
ISOTROPIC POROUS MEDIA FILLED BY A
FLUID FLOW

In this Chapter the propagation of weak discontinuity waves is investigated in an isotropic, homogeneous and elastic porous body. To this aim we introduce a new variable related to the surface across which the solutions or/and some of their derivatives undergo a jump. Following a Boillat's methodology for quasi-linear and hyperbolic systems of the first order, we obtain Bernoulli's equation governing the propagation of weak discontinuities and the critical time is obtained and discussed.

The theoretical interest in non-linear waves was manifest as early as the years '50 and '60 of the last century and a lot of applications to various branches of physics were worked out [1], [2], [3], [4], [8], [9], [14], [15], [16], [17], [18], [19], [20], [21]. The physical behaviour of a large number of media is described by nonlinear hyperbolic PDEs. Following A. Jeffrey in [15], the solution hypersurfaces of systems of PDEs are referred to as waves because they may be interpreted as representing propagating wavefronts. When physical problems are associated with such interpretation the solution on the side of the wavefront towards which propagation takes place may then be regarded as being the undisturbed solution ahead of the wavefront, whilst the solution on the other side may be regarded as a propagating disturbance wave which is entering a region occupied by the undisturbed solution.

Some of the solutions present various types of discontinuities, some others not. In the first case, as some surface is crossed, the solution or/and its derivatives undergo a jump. In this case it is said that the solution presents a *shock*, or it is a *shock wave* or that we are in presence of a *discontinuity waves* (jumps of the first order derivatives) [1], [3], [15], [18]. In the second case, instead of the jump we have smooth solutions of the non linear hyperbolic PDEs that present a steep variation in the normal direction to the associated wavefront and called *asymptotic waves* (see [5], [6], [7], [11], [12], [13], [22]). Both these types of solutions are called *nonlinear waves* because they satisfy nonlinear hyperbolic PDEs and they are investigated because the closed-form solutions of nonlinear PDEs are rare. Thus, the solutions are looked for in approximated forms where a new variable is present related to the surface across which the solutions or/and some of their derivatives undergo a jump.

In this Chapter the propagation of weak discontinuities in a homogeneous, elastic and isotropic porous medium filled by a fluid flow is studied. In particular, in Section 5.1, a system of non-linear PDEs describing the porosity and the fluid-concentration fields and their fluxes are considered and we introduce a new variable related to the surface across which the solutions or/and some of their derivatives undergo a jump. Assuming one-dimensional propagation, following the methodology established by

Boillat in [1] for quasi-linear and hyperbolic systems of the first order, we write the evolution law of the discontinuities in a constant state and we obtain Bernoulli's equation governing the propagation of weak discontinuities.

The studies presented in this Chapter are contained in the article [10]:

A. Famà and L. Restuccia. Weak discontinuity waves in isotropic nanostructures with porous defects filled by a fluid flow. *Submitted to Electronic Journal of Differential Equations*, 2020.

5.1 WEAK DISCONTINUITY WAVES IN A MODEL FOR FLUID CONCENTRATION AND POROSITY FIELDS AND THEIR FLUXES

In this Section we investigate the weak discontinuity waves of the following PDEs system

$$\rho \frac{\partial c}{\partial t} + j_{k,k}^c = 0, \quad (5.1.1)$$

$$\frac{\partial r}{\partial t} + \mathcal{V}_{k,k} = 0, \quad (5.1.2)$$

$$\tau^v \frac{\partial \mathcal{V}_k}{\partial t} = -\mathcal{V}_k - D_v r_{,k} + \alpha_v(c) c_{,k}, \quad (5.1.3)$$

$$\tau^{j^c} \frac{\partial j_i^c}{\partial t} = -j_i^c + \alpha_c(v) r_{,i} - \rho D_c c_{,i}, \quad (5.1.4)$$

(see (4.1.16)-(4.1.18)) where we have supposed that $\alpha_c = \alpha_c(r)$, $\alpha_v = \alpha_v(c)$ are coupling functions reflecting some new cross-kinetic effects during concentration-porous interactions. We also remind that τ^v and τ^{j^c} are the relaxation time of the fields \mathcal{V}_{ijk} and j_i^c , respectively and D_c , D_v are the diffusion coefficients on concentration and porous field, respectively.

First of all, we observe that the above mentioned system of equations can be written in the following matrix form:

$$A^\alpha(\mathbf{U}) \mathbf{U}_\alpha = \mathbf{B}(\mathbf{U}) \quad (\alpha = 0, 1, 2, 3). \quad (5.1.5)$$

where $x^0 = t$ (time), x^1, x^2, x^3 are the space coordinates, $\mathbf{U}_\alpha = \frac{\partial \mathbf{U}}{\partial x^\alpha}$, \mathbf{U} is the vector of the unknown function (which depends on x^α):

$$\mathbf{U} = (c, j_1^c, j_2^c, j_3^c, r, \mathcal{V}_1, \mathcal{V}_2, \mathcal{V}_3)^T, \quad (5.1.6)$$

the vector \mathbf{B} is defined by

$$\mathbf{B} = (0, -j_1^c, -j_2^c, -j_3^c, 0, -\mathcal{V}_1, -\mathcal{V}_2, -\mathcal{V}_3)^T, \quad (5.1.7)$$

and finally A^α ($\alpha = 0, \dots, 3$) are the following 8×8 square matrices

$$A^0 = \begin{pmatrix} \rho & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \tau^{jc} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \tau^{jc} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \tau^{jc} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \tau^\nu & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \tau^\nu & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \tau^\nu \end{pmatrix}, \quad A^1 = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ \rho D_c & 0 & 0 & 0 & -\alpha_c & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ -\alpha_\nu & 0 & 0 & 0 & D_\nu & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \quad (5.1.8)$$

$$A^2 = \begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \rho D_c & 0 & 0 & 0 & -\alpha_c & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -\alpha_\nu & 0 & 0 & 0 & D_\nu & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}, \quad A^3 = \begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \rho D_c & 0 & 0 & 0 & -\alpha_c & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -\alpha_\nu & 0 & 0 & 0 & D_\nu & 0 & 0 & 0 \end{pmatrix}. \quad (5.1.9)$$

In (5.1.6) and (5.1.7) the symbol $(\dots)^T$ means that \mathbf{U} and \mathbf{B} are column vectors. Since $A^\alpha = A^\alpha(\mathbf{U})$, the PDEs system (5.1.5) is a quasi-linear system.

We suppose that the system admits a known solution in the *uniform unperturbed state* \mathbf{U}^0 that satisfy the following condition

$$A^\alpha(\mathbf{U}^0)\mathbf{U}_\alpha^0 = \mathbf{B}(\mathbf{U}^0), \quad (\alpha = 0, 1, 2, 3). \quad (5.1.10)$$

Moreover, we admit that the system (5.1.5) describes a perturbation propagating into a state characterized by the vector \mathbf{U}^0 and $\varphi(x^\alpha) = 0$ is the surface, called *wavefront*, that separates the region perturbed, $\varphi(x^\alpha) = 0^+$, by the unperturbed, $\varphi(x^\alpha) = 0^-$ and moves in the Euclidean space E^{3+1} (when the time flows).

We remind that the wavefront

$$\varphi(x^\alpha) = 0 \quad (5.1.11)$$

is still an unknown function. In order to determine it, we recall that along the wavefront we have $\frac{d\varphi}{dt} = 0$, implying

$$\frac{\partial \varphi}{\partial t} + \mathbf{v} \cdot \text{grad } \varphi = 0, \quad (5.1.12)$$

or, equivalently,

$$\frac{\partial \varphi / \partial t}{|\text{grad } \varphi|} + \mathbf{v} \cdot \frac{\text{grad } \varphi}{|\text{grad } \varphi|} = 0, \quad (5.1.13)$$

with $(\text{grad})_i = \frac{\partial}{\partial x^i}$.

Obviously,

$$\frac{\text{grad } \varphi}{|\text{grad } \varphi|} = \mathbf{n}, \quad (5.1.14)$$

that is the *normal unit vector* to the surface φ , such that the previous equality reads

$$\frac{\partial \varphi / \partial t}{|\text{grad } \varphi|} + \mathbf{v} \cdot \mathbf{n} = 0. \quad (5.1.15)$$

Introduce the notation

$$\lambda = -\frac{\partial \varphi / \partial t}{|\text{grad } \varphi|}, \quad (5.1.16)$$

so that

$$\lambda(\mathbf{U}, \mathbf{n}) = \mathbf{v} \cdot \mathbf{n}, \quad (5.1.17)$$

where λ is called the *velocity normal to the progressive wave*.

We suppose that the function $\mathbf{U}(x^\alpha)$ is piecewise continuous and presents a discontinuity across the surface $\varphi(x^\alpha) = 0$, i.e. the first derivatives of \mathbf{U} present a jump across the front wave $\varphi(x^\alpha) = 0$ (the first derivations are continue in the one and the other part of the wave front but they tend to two different limits).

Introducing the function $\varphi = \varphi(x^\alpha)$ as new variable, continuous together with its first and second derivatives, the derivative with respect to x^α is written

$$\mathbf{U}_\alpha = \mathbf{U}_\varphi \varphi_\alpha, \quad (5.1.18)$$

where $\mathbf{U}_\varphi = \frac{\partial \mathbf{U}}{\partial \varphi}$ and $\varphi_\alpha = \frac{\partial \varphi}{\partial x^\alpha}$.

Moreover, we introduce the symbol denoting the *jump*

$$[\] = \lim_{\varphi \rightarrow 0^+} (\) - \lim_{\varphi \rightarrow 0^-} (\), \quad (5.1.19)$$

given by the difference between the value of a quantity in the unperturbed state and the perturbed state calculated on the surface $\varphi(x^\alpha) = 0$ and, consequently, denoting with $\mathbf{\Pi}$ the jump of the normal derivative \mathbf{U}_φ , we have:

$$[\mathbf{U}] = \mathbf{0}, \quad \mathbf{\Pi} = [\mathbf{U}_\varphi] = \lim_{\varphi \rightarrow 0^+} (\mathbf{U}_\varphi) - \lim_{\varphi \rightarrow 0^-} (\mathbf{U}_\varphi). \quad (5.1.20)$$

From equations (5.1.5), (5.1.10) and (5.1.18) we have the following relations:

$$A^\alpha(\mathbf{U})\mathbf{U}_\varphi\varphi_\alpha = \mathbf{B}(\mathbf{U}) \quad \text{and} \quad A^\alpha(\mathbf{U}^0)\mathbf{U}_\varphi^0\varphi_\alpha = \mathbf{B}(\mathbf{U}^0). \quad (5.1.21)$$

Subtracting equation (5.1.21)₂ from equation (5.1.21)₁ and by computing on the surface $\varphi(x^\alpha) = 0$, where $\mathbf{U} = \mathbf{U}^0$ and $A^\alpha(\mathbf{U}^0) = A^\alpha(\mathbf{U})$, we get

$$(A^\alpha)_0\varphi_\alpha[\mathbf{U}_\varphi] = \mathbf{0}, \quad \text{i.e.} \quad (A^\alpha)_0\varphi_\alpha\mathbf{\Pi} = \mathbf{0}, \quad (5.1.22)$$

where $(A^\alpha)_0 \varphi_\alpha$ represents a 8×8 matrix and equation (5.1.22)₂ is a homogeneous system in the 8 components of $\mathbf{\Pi}$.

Introducing the quantities λ and \mathbf{n} , defined in equations (5.1.14) and (5.1.16), the system (5.1.22)₂ takes the form

$$(A^i n_i - \lambda A^0) \mathbf{\Pi} = \mathbf{0}. \quad (5.1.23)$$

In order to have a solution different from the zero solution it must be

$$\det \|A_n - \lambda A^0\| = 0. \quad (5.1.24)$$

with $A_n = A^i n_i$. Equation (5.1.23) shows that $\mathbf{\Pi}$ can be taken proportional to the right-eigenvector \mathbf{r} of A_n , corresponding to some eigenvalue λ . In the case where the eigenvalue λ has multiplicity 1, $\mathbf{\Pi}$ has the form

$$\mathbf{\Pi} = \pi(x, t) \mathbf{r}. \quad (5.1.25)$$

Consequently, in order to determine $\mathbf{\Pi}$ we must determine the function $\pi = \pi(x^\alpha)$.

Since A^0 is a non-singular matrix, the system (5.1.5) can be written in the form

$$\mathbf{U}_t + (A^0)^{-1} A^i \mathbf{U}_i = (A^0)^{-1} \mathbf{B}(\mathbf{U}), \quad (i = 1, 2, 3), \quad (5.1.26)$$

where

$$(A^0)^{-1} = \begin{pmatrix} \frac{1}{\rho} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{\tau^{j^c}} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{\tau^{j^c}} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{\tau^{j^c}} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{\tau^v} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{\tau^v} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{1}{\tau^v} \end{pmatrix}, \quad (5.1.27)$$

is the inverse matrix of A^0 .

In the follows we continue to call A^i the matrices $(A^0)^{-1} A^i$, and \mathbf{B} the vector $(A^0)^{-1} \mathbf{B}$, so the system assumes the following form

$$\mathbf{U}_t + A^i \mathbf{U}_i = \mathbf{B}(\mathbf{U}), \quad (i = 1, 2, 3), \quad (5.1.28)$$

From equation (5.1.24) we have the following eigenvalues problem

$$\det \|A_n - \lambda I\| = 0, \quad (5.1.29)$$

with $A_n = A^i n_i$ ($i = 1, 2, 3$).

5.1.1 Wave front and first approximation of \mathbf{U}

Following the general theory [1] we introduce the quantity

$$\Psi(x^\alpha, \varphi_\alpha) = \varphi_t + |\text{grad } \varphi| \lambda(\mathbf{U}(x^\alpha), \mathbf{n}), \quad (5.1.30)$$

that, by virtue of the relations (5.1.14) and (5.1.16), becomes zero on the wavefront having velocity $\lambda = \lambda^0$, i.e.

$$\Psi(x^\alpha, \varphi_\alpha) = \varphi_t + |\text{grad } \varphi| \lambda^0 = \Psi^0 = 0. \quad (5.1.31)$$

To solve the above partial differential equation are introduced the *characteristic rays*, called characteristic curves of the system (5.1.5), given by the following differential equations

$$\frac{dx^\alpha}{d\sigma} = \frac{\partial \Psi^0}{\partial \varphi_\alpha}, \quad (5.1.32)$$

$$\frac{d\varphi_\alpha}{d\sigma} = -\frac{\partial \Psi^0}{\partial x^\alpha}, \quad (5.1.33)$$

where σ is the time along the characteristic rays. From equation (5.1.33), considering the propagation in a uniform state \mathbf{U}^0 , we have $\frac{\partial \Psi^0}{\partial x^\alpha} = 0$ and, consequently, φ_α are constants along the characteristic rays.

Furthermore, equation (5.1.32) gives the components of a speed, called *radial velocity* Λ and defined by

$$\Lambda_i(\mathbf{U}, \mathbf{n}) = \frac{\partial \Psi}{\partial \varphi_i} = \lambda n_i + \frac{\partial \lambda}{\partial n_i} - \left(\mathbf{n} \cdot \frac{\partial \lambda}{\partial \mathbf{n}} \right) n_i, \quad (i = 1, 2, 3). \quad (5.1.34)$$

From equation (5.1.34) we have

$$\Lambda_i n_i = \lambda, \quad (5.1.35)$$

i.e. the velocity of propagation of the wavefront λ is the component of radial velocity Λ along the normal to the wavefront. By integration of equation (5.1.32) one obtains

$$x^0 = t = \sigma, \quad (5.1.36)$$

$$x^i(t) = x_0^i + \Lambda_i^0 t, \quad (i = 1, 2, 3), \quad (5.1.37)$$

with

$$x_0^i = x^i|_{t=0} \quad \text{and} \quad \Lambda_i^0 = \Lambda_i(\mathbf{U}^0, \mathbf{n}^0), \quad (i = 1, 2, 3). \quad (5.1.38)$$

If we denote by φ^0 the given initial surface, we have $\varphi|_{t=0} = \varphi^0(x_0^i)$ and \mathbf{n}^0 represents the unit normal vector to the wavefront at the point x_0^i defined by

$$\mathbf{n}^0 = \left(\frac{\text{grad } \varphi}{|\text{grad } \varphi|} \right)_{t=0} = \frac{\text{grad}^0 \varphi^0}{|\text{grad}^0 \varphi^0|}, \quad (5.1.39)$$

where

$$(\text{grad}^0)_i \equiv \frac{\partial}{\partial x_0^i}, \quad (i = 1, 2, 3). \quad (5.1.40)$$

Thus, $\mathbf{x} = \mathbf{x}|_{t=0} + \mathbf{\Lambda}^0 t$ and since the Jacobian J of the transformation $\mathbf{x} \rightarrow \mathbf{x}|_{t=0}$ is non-vanishing, i.e.

$$J = \det \left| \frac{\partial \Lambda_k^0}{\partial x_0^i} t + \delta_{ik} \right| \neq 0, \quad (i, k = 1, 2, 3), \quad (5.1.41)$$

x_0^i can be deduced from (5.1.36) and (5.1.37), and φ takes the following form

$$\varphi(t, x^i) = \varphi^0(x^i - \Lambda_i^0 t). \quad (5.1.42)$$

Taking into account the initial conditions, we can deduce the phase $\varphi(x, t)$ of the considered wave.

Then, developing by the Taylor's formula the vector \mathbf{U} in a neighbourhood of the wavefront $\varphi(x^\alpha) = 0$ we have

$$\mathbf{U} = (\mathbf{U})_{\varphi=0^+} + \left(\frac{\partial \mathbf{U}}{\partial \varphi} \right)_{\varphi=0^+} + \mathcal{O}(\varphi^2), \quad (5.1.43)$$

$$\mathbf{U}^0 = (\mathbf{U}^0)_{\varphi=0^-} + \left(\frac{\partial \mathbf{U}^0}{\partial \varphi} \right)_{\varphi=0^-} + \mathcal{O}(\varphi^2). \quad (5.1.44)$$

Operating the difference between (5.1.43) and (5.1.44) we obtain

$$\mathbf{U} = \mathbf{U}^0 + \varphi \mathbf{\Pi} + \mathcal{O}(\varphi^2), \quad (5.1.45)$$

where $\mathcal{O}(\varphi^2)$ is the Landau's notation and represents infinitesimals of higher order respect to φ . In (5.1.45), following [1], the amplitude of discontinuity π satisfies Bernoulli's equation having the form

$$(\mathbf{l}^0 \cdot \mathbf{r}^0) \left[\frac{d\pi}{dt} + (\nabla \Psi \cdot \mathbf{r})^0 \pi^2 + \frac{d}{dt} \ln \sqrt{J} \pi \right] + F^0 \pi = 0, \quad (5.1.46)$$

in which we have to take into account equation (5.1.37) (so that $\pi = \pi(t, x_0^i)$) and where

$$(\nabla \Psi \cdot \mathbf{r})^0 = |\text{grad} \varphi| (\nabla \lambda \cdot \mathbf{r})^0, \quad F^0 = -(\nabla(\mathbf{l} \cdot \mathbf{B}) \cdot \mathbf{r})^0, \quad (5.1.47)$$

$$\nabla \equiv \left(\frac{\partial}{\partial c}, \frac{\partial}{\partial j_1^c}, \frac{\partial}{\partial j_2^c}, \frac{\partial}{\partial j_3^c}, \frac{\partial}{\partial r}, \frac{\partial}{\partial \nu_1}, \frac{\partial}{\partial \nu_2}, \frac{\partial}{\partial \nu_3} \right), \quad (5.1.48)$$

and \mathbf{r}^0 is the right eigenvector corresponding to the eigenvalue λ^0 . Equations (5.1.25), (5.1.32), (5.1.33) and (5.1.46) determine the discontinuity. We remind that the quantity $\mathbf{l}^0 \cdot \mathbf{r}^0$ is always different from zero by virtue of the hyperbolicity of the system [9].

In [1] it was seen that is possible to solve the equation (5.1.46) with the position

$$\pi = \frac{h(t)}{\sqrt{J} \Phi(t)}, \quad (5.1.49)$$

where

$$h(t) = \exp\left[-\int_0^t \frac{F^0}{(\mathbf{l} \cdot \mathbf{r})_0} dt\right], \quad \Phi(t) = 1 + \int_0^t \frac{(\nabla \Psi \cdot \mathbf{r})_0}{\sqrt{J(\tau)}} h(\tau) d\tau, \quad (5.1.50)$$

with

$$h(0) = \pi(0). \quad (5.1.51)$$

From (5.1.49) follows that if there exists a time t_c where $J(t_c) = 0$ or $\Phi(t_c) = 0$, then $\pi \rightarrow \infty$, and this correspond to a shock wave [1].

5.1.2 One-dimensional case

Now, we consider the one-dimensional case. Assuming that the propagation of weak discontinuity waves, regarding the fields of fluid-concentration and its flux and the porosity and its flux, is along the x axis, the involved quantities depend on x_1 , denoted by x , $x_2 = x_3 = 0$, the system (4.1.16)-(4.1.18) takes the following form:

$$\frac{\partial c}{\partial t} + \frac{1}{\rho} \frac{\partial j_1^c}{\partial x} = 0, \quad (5.1.52)$$

$$\frac{\partial j_1^c}{\partial t} - \frac{\alpha_c}{\tau^{j^c}} \frac{\partial r}{\partial x} + \frac{\rho D_c}{\tau^{j^c}} \frac{\partial c}{\partial x} = -\frac{j_1^c}{\tau^{j^c}}, \quad (5.1.53)$$

$$\frac{\partial j_2^c}{\partial t} = -\frac{j_2^c}{\tau^{j^c}}, \quad (5.1.54)$$

$$\frac{\partial j_3^c}{\partial t} = -\frac{j_3^c}{\tau^{j^c}}, \quad (5.1.55)$$

$$\frac{\partial r}{\partial t} + \frac{\partial \mathcal{V}_1}{\partial x} = 0, \quad (5.1.56)$$

$$\frac{\partial \mathcal{V}_1}{\partial t} + \frac{D_v}{\tau^v} \frac{\partial r}{\partial x} - \frac{\alpha_v}{\tau^v} \frac{\partial c}{\partial x} = -\frac{\mathcal{V}_1}{\tau^v}, \quad (5.1.57)$$

$$\frac{\partial \mathcal{V}_2}{\partial t} = -\frac{\mathcal{V}_2}{\tau^v}, \quad (5.1.58)$$

$$\frac{\partial \mathcal{V}_3}{\partial t} = -\frac{\mathcal{V}_3}{\tau^v}. \quad (5.1.59)$$

where we remind that we supposed $\alpha_c = \alpha_c(r)$ and $\alpha_v = \alpha_v(c)$. From the above system we have

$$j_2^c(x, t) = f_2(x) e^{-\frac{t}{\tau^{j^c}}}, \quad j_3^c(x, t) = f_3(x) e^{-\frac{t}{\tau^{j^c}}}, \quad (5.1.60)$$

$$\mathcal{V}_2(x, t) = g_2(x) e^{-\frac{t}{\tau^v}}, \quad \mathcal{V}_3(x, t) = g_3(x) e^{-\frac{t}{\tau^v}}. \quad (5.1.61)$$

with $f_1(x)$, $f_2(x)$, $g_1(x)$ and $g_2(x)$ arbitrary functions of the real argument x . Then, we consider the following reduced system

$$\mathbf{U}_t + \mathbf{A}(\mathbf{U}) \mathbf{U}_x = \mathbf{B}(\mathbf{U}), \quad (5.1.62)$$

where

$$\mathbf{U} = (c, j_1^c, r, \mathcal{V}_1)^T, \quad (5.1.63)$$

$$\mathbf{B} = \left(0, -\frac{j_1^c}{\tau^{j^c}}, 0, -\frac{\mathcal{V}_1}{\tau^\nu} \right)^T, \quad (5.1.64)$$

and

$$\mathbf{A} = \begin{pmatrix} 0 & \frac{1}{\rho} & 0 & 0 \\ \frac{\rho D_c}{\tau^{j^c}} & 0 & -\frac{\alpha_c}{\tau^{j^c}} & 0 \\ 0 & 0 & 0 & 1 \\ -\frac{\alpha_\nu}{\tau^\nu} & 0 & \frac{D_\nu}{\tau^\nu} & 0 \end{pmatrix}. \quad (5.1.65)$$

In our one dimensional case, in equation (5.1.23), being $\mathbf{n} = (n_1, 0, 0) = (1, 0, 0)$, we have $\mathbf{A}_n(\mathbf{U}) = \mathbf{A}$. We remark that in this particular case, since \mathbf{n}^0 is constant, Λ_k^0 do not depends on x_0^i , so from (5.1.41) we deduce $J = 1$.

5.1.3 Eigenvalues and eigenvectors of the matrix A

The matrix \mathbf{A} admits the following simple eigenvalues:

$$\lambda_1^{(\pm)} = \pm \sqrt{\frac{\rho D_\nu \tau^{j^c} + \rho D_c \tau^\nu - G}{2\rho \tau^{j^c} \tau^\nu}}, \quad (5.1.66)$$

$$\lambda_2^{(\pm)} = \pm \sqrt{\frac{\rho D_\nu \tau^{j^c} + \rho D_c \tau^\nu + G}{2\rho \tau^{j^c} \tau^\nu}}, \quad (5.1.67)$$

where

$$G = \sqrt{(\rho D_\nu \tau^{j^c} - \rho D_c \tau^\nu)^2 + 4\rho \alpha_c \alpha_\nu \tau^{j^c} \tau^\nu}. \quad (5.1.68)$$

The radicand of the quantity G is positive, so G is real; moreover the eigenvalues $\lambda_1^{(\pm)}$ are real when the condition $\rho D_\nu \tau^{j^c} + \rho D_c \tau^\nu - G \geq 0$ is valid (i.e. $\alpha_c \alpha_\nu \leq \rho D_c D_\nu$). The eigenvalues $\lambda_2^{(\pm)}$ are always real.

The left eigenvectors $\mathbf{l}_1^{(\pm)}, \mathbf{l}_2^{(\pm)}$, and the right eigenvectors $\mathbf{r}_1^{(\pm)}, \mathbf{r}_2^{(\pm)}$ corresponding, to eigenvalues $\lambda_1^{(\pm)}, \lambda_2^{(\pm)}$, have the form

$$\mathbf{l}_1^{(\pm)} = \left(\frac{\lambda_1^{(\pm)} \mathcal{R}}{2\alpha_c \tau^\nu}, \frac{\mathcal{R}}{2\rho \alpha_c \tau^\nu}, \lambda_1^{(\pm)}, 1 \right), \quad \mathbf{l}_2^{(\pm)} = \left(\frac{\lambda_2^{(\pm)} \mathcal{S}}{2\alpha_c \tau^\nu}, \frac{\mathcal{S}}{2\rho \alpha_c \tau^\nu}, \lambda_2^{(\pm)}, 1 \right), \quad (5.1.69)$$

$$\mathbf{r}_1^{(\pm)} = \left(\frac{2\alpha_c (\tau^{j^c})^2 \lambda_1^{(\pm)}}{\mathcal{C}}, -\frac{\alpha_c \tau^\nu \mathcal{P}}{\tau^{j^c} \mathcal{C}}, \frac{\lambda_1^{(\pm)} \tau^\nu \mathcal{S}}{\mathcal{C}}, 1 \right)^T, \quad (5.1.70)$$

$$\mathbf{r}_2^{(\pm)} = \left(\frac{2\alpha_c (\tau^{j^c})^2 \lambda_2^{(\pm)}}{\mathcal{L}}, -\frac{\alpha_c \tau^\nu \mathcal{Q}}{\tau^{j^c} \mathcal{L}}, \frac{\lambda_2^{(\pm)} \tau^\nu \mathcal{R}}{\mathcal{L}}, 1 \right)^T, \quad (5.1.71)$$

with

$$\mathcal{R} = \rho D_v \tau^{j^c} - \rho D_c \tau^v + G, \quad \mathcal{S} = \rho D_v \tau^{j^c} - \rho D_c \tau^v - G, \quad (5.1.72)$$

$$\mathcal{P} = \rho D_v \tau^{j^c} + \rho D_c \tau^v - G, \quad \mathcal{Q} = \rho D_v \tau^{j^c} + \rho D_c \tau^v + G, \quad (5.1.73)$$

$$\mathcal{C} = D_v (\rho D_c \tau^v + G) - \rho D_v^2 \tau^{j^c} - 2\alpha_c \alpha_v \tau^v, \quad \mathcal{L} = D_v (\rho D_c \tau^v - G) - \rho D_v^2 \tau^{j^c} - 2\alpha_c \alpha_v \tau^v. \quad (5.1.74)$$

We have $\mathbf{l}_1^{(+)} \cdot \mathbf{r}_1^{(-)} = 0$, $\mathbf{l}_1^{(+)} \cdot \mathbf{r}_2^{(\pm)} = 0$, $\mathbf{l}_1^{(-)} \cdot \mathbf{r}_1^{(+)} = 0$, $\mathbf{l}_1^{(-)} \cdot \mathbf{r}_2^{(\pm)} = 0$, $\mathbf{l}_2^{(+)} \cdot \mathbf{r}_1^{(\pm)} = 0$, $\mathbf{l}_2^{(+)} \cdot \mathbf{r}_2^{(-)} = 0$, $\mathbf{l}_2^{(-)} \cdot \mathbf{r}_1^{(\pm)} = 0$ and $\mathbf{l}_2^{(-)} \cdot \mathbf{r}_2^{(+)} = 0$, in accordance with the general theory. The quantities \mathcal{C} , \mathcal{L} are supposed different than zero and this lead to the condition $\alpha_c \alpha_v \neq \rho D_c D_v$. We observe also that $G \neq 0$ (so $\lambda_1^{(\pm)} \neq \lambda_2^{(\pm)}$) because the relation $(\rho D_v \tau^{j^c} - \rho D_c \tau^v)^2 \neq -4\rho \alpha_c \alpha_v \tau^{j^c} \tau^v$ is always verified. In fact the left-hand member is positive whereas the right-hand member is negative. The members are equal only if they are both null but the right-hand member is different from zero by hypothesis. In the hypothesis above the eigenvalues of the matrix \mathbf{A} are real and the left and right eigenvectors are linearly independent, so that the system of PDEs (5.1.62) is hyperbolic. The discontinuity waves which are propagating with the velocity given by $\lambda_1^{(\pm)}$ and $\lambda_2^{(\pm)}$ are not exceptional waves in the sense of Lax-Boillat [1], when

$$\nabla \lambda_1^{(\pm)} \cdot \mathbf{r}_1^{(\pm)} = \mp \frac{\tau^v}{2G\mathcal{C}} \left[2\rho \alpha_c^2 \tau^v \frac{\partial \alpha_v}{\partial c} + \alpha_v \mathcal{S} \frac{\partial \alpha_c}{\partial r} \right] \neq 0, \quad (5.1.75)$$

$$\nabla \lambda_2^{(\pm)} \cdot \mathbf{r}_2^{(\pm)} = \pm \frac{\tau^v}{2G\mathcal{L}} \left[2\rho \alpha_c^2 \tau^v \frac{\partial \alpha_v}{\partial c} + \alpha_v \mathcal{R} \frac{\partial \alpha_c}{\partial r} \right] \neq 0, \quad (5.1.76)$$

with

$$\nabla \equiv \left(\frac{\partial}{\partial c}, \frac{\partial}{\partial j_1^c}, \frac{\partial}{\partial r}, \frac{\partial}{\partial v_1} \right), \quad (5.1.77)$$

$$\nabla \lambda_1^{(\pm)} = \left(\mp \frac{\alpha_c}{2G\lambda_1^{(\pm)}} \frac{\partial \alpha_v}{\partial c}, 0, \mp \frac{\alpha_v}{2G\lambda_1^{(\pm)}} \frac{\partial \alpha_c}{\partial r}, 0 \right), \quad (5.1.78)$$

$$\nabla \lambda_2^{(\pm)} = \left(\pm \frac{\alpha_c}{2G\lambda_2^{(\pm)}} \frac{\partial \alpha_v}{\partial c}, 0, \pm \frac{\alpha_v}{2G\lambda_2^{(\pm)}} \frac{\partial \alpha_c}{\partial r}, 0 \right). \quad (5.1.79)$$

The scalar product between eigenvectors left and right referred to the same eigenvalue satisfy the following relations (whose value is different than zero for the supposed hyperbolicity of the system)

$$\mathbf{l}_1^{(\pm)} \cdot \mathbf{r}_1^{(\pm)} = 1 + \frac{\mathcal{P}(\mathcal{R} + 2G)}{2\rho \tau^{j^c} \mathcal{C}}, \quad (5.1.80)$$

$$\mathbf{l}_2^{(\pm)} \cdot \mathbf{r}_2^{(\pm)} = 1 + \frac{\mathcal{Q}(3\rho D_v \tau^{j^c} - 3\rho D_c \tau^v - G)}{2\rho \tau^{j^c} \mathcal{L}}. \quad (5.1.81)$$

In the follows we fix our attention on $\lambda = \lambda_2^{(+)}$, which corresponds to a progressive fast wave travelling to the right. Analogous results are valid for the waves propagating with the other velocities.

5.1.4 Determination of the approximated solution of the PDEs system

Now, we consider an uniform unperturbed state in which \mathbf{U}^0 , solution of the system (5.1.62), has the form

$$\mathbf{U}^0 = (c^0, 0, r^0, 0), \quad (5.1.82)$$

with c^0 and r^0 constants. In \mathbf{U}^0 we have

$$\left(\lambda_2^{(+)}\right)^0 = \sqrt{\frac{\rho D_v \tau^{jc} + \rho D_c \tau^v + G^0}{2\rho \tau^{jc} \tau^v}}, \quad (5.1.83)$$

$$\left(\mathbf{l}_2^{(+)}\right)^0 = \left(\frac{\left(\lambda_2^{(+)}\right)^0 \mathcal{S}^0}{2\alpha_c^0 \tau^v}, \frac{\mathcal{S}^0}{2\rho \alpha_c^0 \tau^v}, \left(\lambda_2^{(+)}\right)^0, 1 \right), \quad (5.1.84)$$

$$\left(\mathbf{r}_2^{(+)}\right)^0 = \left(\frac{2\alpha_c^0 (\tau^{jc})^2 \left(\lambda_2^{(+)}\right)^0}{\mathcal{L}^0}, -\frac{\alpha_c^0 \tau^v \mathcal{Q}^0}{\tau^{jc} \mathcal{L}^0}, \frac{\left(\lambda_2^{(+)}\right)^0 \tau^v \mathcal{R}^0}{\mathcal{L}^0}, 1 \right), \quad (5.1.85)$$

$$\left(\mathbf{l}_2^{(+)} \cdot \mathbf{r}_2^{(+)}\right)^0 = 1 + \frac{\mathcal{Q}^0 (3\rho D_v \tau^{jc} - 3\rho D_c \tau^v - G^0)}{2\rho \tau^{jc} \mathcal{L}^0}, \quad (5.1.86)$$

and

$$\left(\nabla \lambda_2^{(+)} \cdot \mathbf{r}_2^{(+)}\right)^0 = \frac{\tau^v}{2G^0 \mathcal{L}^0} \left[2\rho (\alpha_c^0)^2 \tau^v \left(\frac{\partial \alpha_v}{\partial c}\right)^0 + \alpha_v^0 \mathcal{R}^0 \left(\frac{\partial \alpha_c}{\partial r}\right)^0 \right], \quad (5.1.87)$$

where the symbols “ 0 ” indicate that the quantities are calculated in \mathbf{U}^0 . The radial velocity along the characteristic rays is

$$\mathbf{\Lambda}^0(\mathbf{U}^0, \mathbf{n}^0) = \left(\lambda_2^{(+)}\right)^0 \mathbf{n}^0 = \left(\left(\lambda_2^{(+)}\right)^0, 0, 0 \right). \quad (5.1.88)$$

and the characteristic rays are

$$\frac{dt}{d\sigma} = 1, \quad \frac{dx_i}{d\sigma} = \frac{\partial \Psi^0}{\partial \varphi_\alpha} = \left(\lambda_2^{(+)}\right)^0, \quad \frac{d\varphi_\alpha}{d\sigma} = 0. \quad (5.1.89)$$

By integration of (5.1.89) one obtain

$$x^0 = \sigma = t, \quad x(t) = (x)_0 + \left(\lambda_2^{(+)}\right)^0 t, \quad (5.1.90)$$

and the wave front in explicit form is

$$\varphi(x, t) = \varphi^0 \left(x - \left(\lambda_2^{(+)} \right)^0 t \right). \quad (5.1.91)$$

The amplitude π satisfies the following equation (see equation (5.1.46) with $J = 1$):

$$\left(\mathbf{l}_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0 \left[\frac{d\pi}{dt} + |\varphi_x^0| \left(\nabla \lambda_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0 \pi^2 \right] + F^0 \pi = 0, \quad (5.1.92)$$

where

$$F^0 = - \left[\nabla \left(\mathbf{l}_2^{(+)} \cdot \mathbf{B} \right) \cdot \mathbf{r}_2^{(+)} \right]^0. \quad (5.1.93)$$

Thanks to the hyperbolicity of the system, we have $\left(\mathbf{l}_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0 \neq 0$, i.e. $\alpha_c \alpha_v \neq \rho D_c D_v$.

Taking into account that

$$\mathbf{l}_2^{(+)} \cdot \mathbf{B} = - \frac{j_1^c \mathcal{S}}{2\rho \alpha_c \tau^{j^c} \tau^v} - \frac{\nu_1}{\tau^v}, \quad (5.1.94)$$

$$\nabla \left(\mathbf{l}_2^{(+)} \cdot \mathbf{B} \right) = \left(\frac{j_1^c}{G} \frac{\partial \alpha_v}{\partial c}, - \frac{\mathcal{S}}{2\rho \alpha_c \tau^{j^c} \tau^v}, \frac{j_1^c}{2\rho \alpha_c^2 \tau^{j^c} \tau^v} \left(\frac{2\rho \alpha_c \alpha_v \tau^{j^c} \tau^v}{G} + \mathcal{S} \right) \frac{\partial \alpha_c}{\partial r}, - \frac{1}{\tau^v} \right), \quad (5.1.95)$$

in \mathbf{U}^0 , we obtain

$$\begin{aligned} & \left[\nabla \left(\mathbf{l}_2^{(+)} \cdot \mathbf{B} \right) \right]^0 = \\ & \left(\frac{j_1^c}{G^0} \left(\frac{\partial \alpha_v}{\partial c} \right)^0, - \frac{\mathcal{S}^0}{2\rho \alpha_c^0 \tau^{j^c} \tau^v}, \frac{j_1^c}{2\rho (\alpha_c^0)^2 \tau^{j^c} \tau^v} \left(\frac{2\rho \alpha_c^0 \alpha_v^0 \tau^{j^c} \tau^v}{G^0} + \mathcal{S}^0 \right) \left(\frac{\partial \alpha_c}{\partial r} \right)^0, - \frac{1}{\tau^v} \right), \end{aligned} \quad (5.1.96)$$

and

$$\begin{aligned} F^0 = & - \frac{2\alpha_c^0 (\tau^{j^c})^2 j_1^c \left(\lambda_2^{(+)} \right)^0}{G^0 \mathcal{L}^0} \left(\frac{\partial \alpha_v}{\partial c} \right)^0 - \frac{j_1^c \mathcal{R}^0 \left(\lambda_2^{(+)} \right)^0}{2\rho \mathcal{L}^0 (\alpha_c^0)^2 \tau^{j^c}} \left(\frac{2\rho \alpha_c^0 \alpha_v^0 \tau^{j^c} \tau^v}{G^0} + \mathcal{S}^0 \right) \left(\frac{\partial \alpha_c}{\partial r} \right)^0 \\ & - \frac{\mathcal{Q}^0 \mathcal{S}^0}{2\rho (\tau^{j^c})^2 \mathcal{L}^0} + \frac{1}{\tau^v}. \end{aligned} \quad (5.1.97)$$

We solve equation (5.1.92) with the position $\pi = \frac{h(t)}{\Phi(t)}$ (see equation (5.1.49) with $J = 1$). By (5.1.50)₁, with the initial condition (5.1.51), we obtain

$$h(t) = \pi^0 \exp \left[- \frac{F^0}{\left(\mathbf{l}_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0 t} \right], \quad (5.1.98)$$

where $\pi^0 = \pi(0)$.

Substituting equation (5.1.98) into (5.1.50)₂ (with $J = 1$) we have

$$\Phi(t) = 1 - \frac{\pi^0}{H^0} |\varphi_x^0| \left(\nabla \lambda_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0 (e^{-H^0 t} - 1), \quad (5.1.99)$$

where $H^0 = \frac{F^0}{\left(\mathbf{l}_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0}$, that is supposed different than zero.

From equations (5.1.98) and (5.1.99) we can write the amplitude π :

$$\pi(t) = \frac{\pi^0 H^0 e^{-H^0 t}}{H^0 - \pi^0 |\varphi_x^0| \left(\nabla \lambda_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0 (e^{-H^0 t} - 1)}. \quad (5.1.100)$$

We observe that the amplitude $\pi(t)$ is a limited function:

$$\lim_{t \rightarrow \infty} \pi(t) = \begin{cases} -\frac{H^0}{|\varphi_x^0| \left(\nabla \lambda_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0}, & \text{if } H^0 < 0, \\ 0, & \text{if } H^0 > 0. \end{cases} \quad (5.1.101)$$

In the case where there exists a critical time t_c in which $\Phi(t_c) = 0$, i.e.

$$t_c = \frac{1}{H^0} \ln \left(\frac{\pi^0 |\varphi_x^0| \left(\nabla \lambda_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0}{H^0 + \pi^0 |\varphi_x^0| \left(\nabla \lambda_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0} \right), \quad (5.1.102)$$

this correspond to a shock wave [1]. Of course in equation (5.1.102) the function t_c exists if

$$\frac{1}{H^0} \ln \left(\frac{\pi^0 |\varphi_x^0| \left(\nabla \lambda_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0}{H^0 + \pi^0 |\varphi_x^0| \left(\nabla \lambda_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0} \right) > 0 \quad \text{and} \quad \frac{\pi^0 |\varphi_x^0| \left(\nabla \lambda_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0}{H^0 + \pi^0 |\varphi_x^0| \left(\nabla \lambda_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0} > 0. \quad (5.1.103)$$

If (5.1.103) is not verified, there is not a shock wave.

Finally, by virtue of relations (5.1.25), (5.1.45), (5.1.82), (5.1.85), (5.1.91) and (5.1.100) we can write the explicit form of the first approximation of the solution \mathbf{U} of the system (5.1.62):

$$(c, j_1^c, r, \nu_1)^T = (c^0, 0, r^0, 0)^T + \Gamma^0 \left(\frac{2\alpha_c^0 (\tau^n)^2 \left(\lambda_2^{(+)} \right)^0}{\mathcal{L}^0}, -\frac{\alpha_c^0 \tau^\nu \mathcal{Q}^0}{\tau^{jc} \mathcal{L}^0}, \frac{\left(\lambda_2^{(+)} \right)^0 \tau^\nu \mathcal{R}^0}{\mathcal{L}^0}, 1 \right)^T, \quad (5.1.104)$$

with

$$\Gamma^0 = \frac{\varphi^0 \left(x - \left(\lambda_2^{(+)} \right)^0 t \right) \pi^0 H^0 e^{-H^0 t}}{H^0 - \pi^0 |\varphi_x^0| \left(\nabla \lambda_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0 (e^{-H^0 t} - 1)}. \quad (5.1.105)$$

From (5.1.104) we obtain the first approximation of the fields responsible of the mono-dimensional concentration-porous propagation discontinuity waves

$$c(x, t) = c^0 + \frac{2\varphi^0 \left(x - \left(\lambda_2^{(+)} \right)^0 t \right) \pi^0 H^0 \alpha_c^0 (\tau^n)^2 \left(\lambda_2^{(+)} \right)^0 e^{-H^0 t}}{\mathcal{L}^0 \left[H^0 - \pi^0 |\varphi_x^0| \left(\nabla \lambda_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0 (e^{-H^0 t} - 1) \right]}, \quad (5.1.106)$$

$$j_1^c(x, t) = - \frac{\varphi^0 \left(x - \left(\lambda_2^{(+)} \right)^0 t \right) \pi^0 H^0 \alpha_c^0 \tau^\nu \mathcal{Q}^0 e^{-H^0 t}}{\tau^{j^c} \mathcal{L}^0 \left[H^0 - \pi^0 |\varphi_x^0| \left(\nabla \lambda_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0 (e^{-H^0 t} - 1) \right]}, \quad (5.1.107)$$

$$r(x, t) = r^0 + \frac{\left(\lambda_2^{(+)} \right)^0 \varphi^0 \left(x - \left(\lambda_2^{(+)} \right)^0 t \right) \pi^0 H^0 \tau^\nu \mathcal{R}^0 e^{-H^0 t}}{\mathcal{L}^0 \left[H^0 - \pi^0 |\varphi_x^0| \left(\nabla \lambda_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0 (e^{-H^0 t} - 1) \right]}, \quad (5.1.108)$$

$$\mathcal{V}_1(x, t) = \frac{\varphi^0 \left(x - \left(\lambda_2^{(+)} \right)^0 t \right) \pi^0 H^0 e^{-H^0 t}}{H^0 - \pi^0 |\varphi_x^0| \left(\nabla \lambda_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0 (e^{-H^0 t} - 1)}. \quad (5.1.109)$$

To these obtained relations, we have to add also the results (5.1.60) and (5.1.61).

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6

ASYMPTOTIC WAVES IN POROUS ISOTROPIC MEDIA FILLED BY A FLUID FLOW

This Chapter is dedicated to the application of a general method devised to construct approximate smooth solutions to the nonlinear hyperbolic partial differential equations describing the interaction among the fluid-concentration and the porosity fields and their fluxes in homogeneous, isotropic porous nanostructures with porous defects filled by a fluid flow.

These approximated solutions are called *asymptotic waves* (see [12], [13], [14], [17]). In this case, instead of the jump there is a steep variation and to obtain these solutions we use a perturbative method derived by Boillat [1], [2], and generalized by Fusco in [10], following also [3], [15] and [18].

In particular, in Section 6.1, in the one dimensional case, one of these approximated solutions is analysed and its propagation into a uniform unperturbed state is studied, the expression of the velocity along the characteristic rays and the equation of the wave front are determined. Finally, it is seen that the transport equation for the first perturbation term of the asymptotic solution, using a suitable transformation, can be reduced to an equation valid along the characteristic rays.

Applications of the mathematical theory of asymptotic waves were carried out in the context of rheological media by L. Restuccia (see for instance [4], [6], [8]).

The studies presented in this Chapter are contained in the article [9]:

A. Famà and L. Restuccia. Asymptotic waves in isotropic nanostructures with porous defects filled by a fluid flow. *Submitted to Annals of the Academy of Romanian Scientists, Series on Mathematics and its Applications*, 2020.

6.1 ASYMPTOTIC WAVES IN A MODEL FOR FLUID CONCENTRATION AND POROSITY FIELDS AND THEIR FLUXES

In this Section we find one solution of PDEs system, consisting of equations (5.1.52), (5.1.53), (5.1.56) and (5.1.57), having the matrix form (5.1.62)

$$\mathbf{U}_t + \mathbf{A}(\mathbf{U})\mathbf{U}_x = \mathbf{B}(\mathbf{U}),$$

with \mathbf{U} , \mathbf{B} and \mathbf{A} given by (5.1.63)-(5.1.65), written in terms of a formal power series (at second order). Also we deduce the conditions for the propagation of the asymptotic wave, corresponding to the first approximation of the considered solution.

6.1.1 Asymptotic wave propagation into a uniform unperturbed state

In this Subsection we study in the one-dimensional case the asymptotic wave propagation into a uniform unperturbed state, we derive the approximated solution \mathbf{U} , the equation of its wave front and the expression of its velocity along the characteristic rays. To this aim we consider a known uniform unperturbed state defined in (5.1.82):

$$\mathbf{U}^0 = (c^0, 0, r^0, 0),$$

in which the system (5.1.62) is hyperbolic.

We suppose (see [1], [2], [10], [15]) that the solution \mathbf{U} can be developed in the following asymptotic form around the state \mathbf{U}^0 , i.e. we look for the solution of the equations as an asymptotic series of powers of a small parameter, ε , namely with respect to the asymptotic sequence $\{1, \varepsilon^{a+1}, \varepsilon^{a+2}, \dots\}$ or $\{1, \varepsilon^{\frac{1}{p}}, \varepsilon^{\frac{2}{p}}, \dots\}$, as $\varepsilon \rightarrow 0$. In particular we consider $p = 1$ and $\varepsilon = \omega^{-1}$ (see also [5], [7], [8]), such that $\mathbf{U}(x^\alpha, \xi)$ is written as an asymptotic power series of the small parameter ω^{-1} around the initial unperturbed state $\mathbf{U}^0(x^\alpha)$, i.e. with respect to the asymptotic sequence $1, \omega^{-1}, \omega^{-2}, \dots$, as $\omega^{-1} \rightarrow 0$, where \mathbf{U}^i ($i = 1, 2, \dots$) are functions of x^α and ξ ,

$$\mathbf{U} = \mathbf{U}^0 + \frac{1}{\omega} \mathbf{U}^1(x^\alpha, \xi) + \frac{1}{\omega^2} \mathbf{U}^2(x^\alpha, \xi) + \mathcal{O}\left(\frac{1}{\omega^3}\right) \quad (\alpha = 0, 1), \quad (6.1.1)$$

where

$$\xi = \omega \varphi(x^\alpha). \quad (6.1.2)$$

In (6.1.1) and (6.1.2), that are valid also when $\alpha = 0, 1, 2, 3$, ξ is asymptotically fixed, i.e. $\xi = \text{Ord}(1)$ as $\omega^{-1} \rightarrow 0$, ω is a very large real parameter and $\varphi(x^\alpha)$ is the unknown wavefront [11], [15] which is to be determined as well as the vector fields \mathbf{U}^1 and \mathbf{U}^2 (for the sake of simplicity we will determine only \mathbf{U}^1). From (6.1.1) we see that the following relations are valid:

$$\mathbf{A}(\mathbf{U}) = \mathbf{A}^0 + \frac{1}{\omega} (\nabla \mathbf{A})^0 \mathbf{U}^1 + \mathcal{O}\left(\frac{1}{\omega^2}\right), \quad (6.1.3)$$

$$\frac{\partial \mathbf{U}}{\partial x^\alpha} = \frac{\partial \mathbf{U}^1}{\partial \xi} \frac{\partial \varphi}{\partial x^\alpha} + \frac{1}{\omega} \left(\frac{\partial \mathbf{U}^1}{\partial x^\alpha} + \frac{\partial \mathbf{U}^2}{\partial \xi} \frac{\partial \varphi}{\partial x^\alpha} \right) + \mathcal{O}\left(\frac{1}{\omega^2}\right) \quad (\alpha = 0, 1), \quad (6.1.4)$$

$$\mathbf{B}(\mathbf{U}) = \frac{1}{\omega} (\nabla \mathbf{B})^0 \mathbf{U}^1 + \mathcal{O}\left(\frac{1}{\omega^2}\right), \quad (6.1.5)$$

where $\nabla = \frac{\partial}{\partial \mathbf{U}}$ and the superscript “0” denotes that the quantities are calculated in \mathbf{U}^0 (observe that $\mathbf{B}^0 = \mathbf{0}$). Using relations (6.1.3)-(6.1.5), the system (5.1.62) reads

$$\begin{aligned} & \left(\mathbf{A}^0 \frac{\partial \varphi}{\partial x} + \mathbf{I} \frac{\partial \varphi}{\partial t} \right) \frac{\partial \mathbf{U}^1}{\partial \xi} \\ & + \frac{1}{\omega} \left[\left(\mathbf{A}^0 \frac{\partial \varphi}{\partial x} + \mathbf{I} \frac{\partial \varphi}{\partial t} \right) \frac{\partial \mathbf{U}^2}{\partial \xi} + \frac{\partial \mathbf{U}^1}{\partial t} + \mathbf{A}^0 \frac{\partial \mathbf{U}^1}{\partial x} + (\nabla \mathbf{A})^0 \mathbf{U}^1 \frac{\partial \mathbf{U}^1}{\partial \xi} \frac{\partial \varphi}{\partial x} - (\nabla \mathbf{B})^0 \mathbf{U}^1 \right] = \mathbf{0}. \end{aligned} \quad (6.1.6)$$

in which the terms of order greater than $\frac{1}{\omega}$ are been neglected. From equation (6.1.6) we deduce that

$$\left(A^0 \frac{\partial \varphi}{\partial x} + I \frac{\partial \varphi}{\partial t} \right) \frac{\partial \mathbf{U}^1}{\partial \xi} = \mathbf{0}, \quad (6.1.7)$$

$$\left(A^0 \frac{\partial \varphi}{\partial x} + I \frac{\partial \varphi}{\partial t} \right) \frac{\partial \mathbf{U}^2}{\partial \xi} + \frac{\partial \mathbf{U}^1}{\partial t} + A^0 \frac{\partial \mathbf{U}^1}{\partial x} + (\nabla A)^0 \mathbf{U}^1 \frac{\partial \mathbf{U}^1}{\partial \xi} \frac{\partial \varphi}{\partial x} = (\nabla B)^0 \mathbf{U}^1. \quad (6.1.8)$$

Equation (6.1.7) represents a 4×4 system in the unknown $\frac{\partial \mathbf{U}^1}{\partial \xi}$; it admits non trivial solutions if and only if

$$\det \left(A^0 \frac{\partial \varphi}{\partial x} + I \frac{\partial \varphi}{\partial t} \right) = 0, \quad (6.1.9)$$

so $\varphi(x, t)$ is a characteristic surface in the sense of the discontinuity waves theory [1] (see (5.1.11)-(5.1.17)). Now, if we introduce the following quantities (see (5.1.14) and (5.1.16)):

$$\lambda = -\frac{\partial \varphi / \partial t}{|\text{grad } \varphi|}, \quad \mathbf{n} = \frac{\text{grad } \varphi}{|\text{grad } \varphi|},$$

where λ is the velocity normal to the progressive waves and \mathbf{n} is the unit vector normal to the wave front (in this one-dimensional case $\mathbf{n} = (1, 0, 0)$), then, equation (6.1.7) takes the form

$$(A^0 - \lambda I) \frac{\partial \mathbf{U}^1}{\partial \xi} = \mathbf{0}, \quad (6.1.10)$$

and shows that λ is a eigenvalue of A^0 and $\frac{\partial \mathbf{U}^1}{\partial \xi}$ can be taken proportional to the right-eigenvector \mathbf{r} of A^0 , corresponding to λ

$$\frac{\partial \mathbf{U}^1}{\partial \xi} = v^1(x^\alpha, \xi) \mathbf{r}(\mathbf{U}^0) \quad (\alpha = 0, 1), \quad (6.1.11)$$

where v^1 is an arbitrary scalar function supposed integrable with respect to ξ . Analogous expressions are valid in the three-dimensional case. The method to obtain the approximate smooth solutions is valid only for waves propagating with a velocity λ such that $\nabla \lambda \cdot \mathbf{r} \neq 0$, i.e. with a velocity that does not satisfy the Lax-Boillat exceptionality condition [16]. By integrating equation (6.1.11), one obtains

$$\mathbf{U}^1(x^\alpha, \xi) = u^1(x^\alpha, \xi) \mathbf{r}(\mathbf{U}^0) + v^1(x^\alpha) \quad (\alpha = 0, 1), \quad (6.1.12)$$

where $u^1 = \int v^1(x^\alpha, \xi) d\xi$ is still an arbitrary function and v^1 is an arbitrary scalar function of integration which can be taken as zero, without loss of generality (see [2], [6], [10]). It may be observed that in (6.1.12) u^1 gives rise to the phenomenon of the distortion of the signals and this term governs the first-order perturbation obeying a non-linear partial differential equation (the growth equation).

We can introduce, as in Subsection 5.1.1, the quantity (5.1.30)

$$\Psi(\mathbf{U}, \varphi_\alpha) = \varphi_t + |\text{grad } \varphi| \lambda(\mathbf{U}, \mathbf{n}) \quad (\alpha = 0, 1),$$

and we derive the same results (5.1.31)-(5.1.42). The eigenvalues and eigenvectors are given by (5.1.66), (5.1.67) and (5.1.69)-(5.1.71), respectively.

In the next Subsection we will focus our attention on the eigenvalue $\lambda_2^{(+)}$, for which relations (5.1.88)-(5.1.91) are valid, and from (5.1.91) and (6.1.2) we derive

$$\xi(t, x) = \omega \varphi^0 \left(x - \left(\lambda_2^{(+)} \right)^0 t \right). \quad (6.1.13)$$

6.1.2 The growth equation for the first perturbation term

The arbitrariness of u^1 is used to satisfy the condition (6.1.8) following the general theory (see [2]), in the case in which \mathbf{U}^0 is constant, and taking into account (5.1.37) it results that the following transport equation for $u^1(t, \xi)$ can be obtained

$$\frac{\partial u^1}{\partial t} + (\nabla \Psi \cdot \mathbf{r})^0 u^1 \frac{\partial u^1}{\partial \xi} + \frac{1}{\vartheta} \frac{\partial \vartheta}{\partial t} u^1 = \nu^0 u^1. \quad (6.1.14)$$

In (6.1.14) the superscript “0” indicates that the quantities are calculated in \mathbf{U}^0 and we remind that

$$\vartheta = \sqrt{J}, \quad (\nabla \Psi \cdot \mathbf{r})^0 = |\text{grad } \varphi^0| (\nabla \lambda \cdot \mathbf{r})^0,$$

and moreover ν^0 is defined as follows

$$\nu^0 = \frac{\mathbf{l}^0 \cdot [(\nabla \mathbf{B}) \mathbf{r}]^0}{(\mathbf{l} \cdot \mathbf{r})^0}. \quad (6.1.15)$$

Now, we investigate the vector field \mathbf{U}^1 related to the eigenvector $\mathbf{r}_2^{(+)}$ and the eigenvalue $\lambda_2^{(+)}$. From equation (6.1.12) (in which $\nu^1 = 0$) it has the form

$$\mathbf{U}^1(x^\alpha, \xi) = u^1(x^\alpha, \xi) \mathbf{r}_2^{(+)}(\mathbf{U}^0), \quad (6.1.16)$$

where u^1 is scalar function to be determined, that satisfy the partial differential equation (6.1.14).

In our one-dimensional case we have $\vartheta = 1$ and from relation (5.1.87) we can write

$$\left(\nabla \Psi \cdot \mathbf{r}_2^{(+)} \right)^0 = |\varphi_x^0| \frac{\tau^\nu}{2G^0 \mathcal{L}^0} \left[2\rho (\alpha_c^0)^2 \tau^\nu \left(\frac{\partial \alpha_\nu}{\partial c} \right)^0 + \alpha_\nu^0 \mathcal{R}^0 \left(\frac{\partial \alpha_c}{\partial r} \right)^0 \right], \quad (6.1.17)$$

and, the coefficient ν^0 defined by (6.1.15) related to $\mathbf{l}_2^{(+)}$ and $\mathbf{r}_2^{(+)}$, becomes

$$\nu^0 = \frac{\left[\mathbf{l}_2^{(+)} \cdot (\nabla \mathbf{B}) \mathbf{r}_2^{(+)} \right]^0}{\left(\mathbf{l}_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0} = \frac{\tau^\nu \mathcal{S}^0 \mathcal{Q}^0 - 2\rho (\tau^{jc})^2 \mathcal{L}^0}{2\rho \tau^\nu (\tau^{jc})^2 \mathcal{L}^0 + \tau^\nu \tau^{jc} \mathcal{Q}^0 (3\rho D_\nu \tau^{jc} - 3\rho D_c \tau^\nu - G^0)}, \quad (6.1.18)$$

where (see relations (5.1.64), (5.1.84) and (5.1.85))

$$\left[\mathbf{l}_2^{(+)} \cdot (\nabla \mathbf{B}) \mathbf{r}_2^{(+)} \right]^0 = \frac{\mathcal{S}^0 \mathcal{Q}^0}{2\rho (\tau^{jc})^2 \mathcal{L}^0} - \frac{1}{\tau^v}, \quad (6.1.19)$$

and (see (5.1.86))

$$\left(\mathbf{l}_2^{(+)} \cdot \mathbf{r}_2^{(+)} \right)^0 = 1 + \frac{\mathcal{Q}^0 (3\rho D_v \tau^{jc} - 3\rho D_c \tau^v - G^0)}{2\rho \tau^{jc} \mathcal{L}^0}. \quad (6.1.20)$$

Then, in this case the function u^1 satisfies the following equation

$$\frac{\partial u^1}{\partial t} + \left(\nabla \Psi \cdot \mathbf{r}_2^{(+)} \right)^0 u^1 \frac{\partial u^1}{\partial \xi} = \nu^0 u^1. \quad (6.1.21)$$

In [2] and [10] it is seen that from the general equation (6.1.14) (so also equation (6.1.21)) it is possible to derive an equation valid along the characteristic rays, whose solution is well known and is obtained using the following transformation of variables

$$u_2 = u^1 e^{\nu_2}, \quad \nu_2 = \int_0^t \nu^0(s) ds, \quad \tau_2 = \int_0^t \left(\nabla \Psi \cdot \mathbf{r}_2^{(+)} \right)^0 e^{\nu_2} ds, \quad (6.1.22)$$

equation (6.1.21) reduces to the well known non viscous Burger equation

$$\frac{\partial u_2}{\partial \tau_2} + u_2 \frac{\partial u_2}{\partial \xi} = 0, \quad (6.1.23)$$

whose solution, corresponding to the initial value \bar{u}_2 , is implicitly given by

$$u_2 = \bar{u}_2(t, x, \xi - u_2 \tau_2), \quad (6.1.24)$$

so the implicit solution of (6.1.21) is

$$u^1 = \bar{u}_2(t, x, \xi - u_2 \tau_2) e^{\nu_2}. \quad (6.1.25)$$

In conclusion, if we consider (for the sake of simplicity) in (6.1.1) only the terms up to the first order, the asymptotic wave related to the eigenvalue $\lambda_2^{(+)}$ has the form

$$\mathbf{u} = \mathbf{u}^0 + \frac{1}{\omega} \bar{u}_2(x^\alpha, \xi - u_2 \tau_2) e^{\nu_2} \left(\mathbf{r}_2^{(+)} \right)^0. \quad (6.1.26)$$

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Part II

NON-EQUILIBRIUM THERMODYNAMICS OF RIGID BODIES WITH AN INTERNAL TENSORIAL FIELD INFLUENCING THE THERMAL PHENOMENA

7

GENERALIZED BALLISTIC-CONDUCTIVE
HEAT TRANSPORT LAWS IN THREE-
DIMENSIONAL ISOTROPIC MATERIALS

There are several generalisations of classical Fourier law conduction that can also model second-sound phenomena (heat waves) and ballistic propagation. These theories are more and more important in nanostructures and are subjects of various challenging physical, mathematical and numerical researches. For example nonlocal effects and the role of effective temperature is investigated in [40], [42], [43], [44], [45], particular special functions were constructed and exact solutions were calculated for both the hyperbolic and Guyer-Krumhansl heat conduction [58], [59], [60], [61], adapted numerical methods were developed in [14], [26], the role of internal variables in complex media modelling were investigated in [5], [6], [33], the particularities of heat conduction in nanomaterials is discovered in [4], [20], [56]. These investigations are often related to various concepts of non-equilibrium temperature, too.

Second sound, the wavelike propagation of heat, is due to the inertia of internal energy. This property can be modelled by an additional non-equilibrium thermodynamic state variable. A straightforward choice for this additional vectorial state variable is the heat flux [10], [24]. This choice leads to theories of Extended Thermodynamics (ET). There one requires a compatibility with kinetic theory [7], [12], [18], [25], [39], [49], and the structure of the continuum theory will be compatible with the equations derived by moment series expansion of the Boltzmann equation, considering also a Callaway collision integral with two relaxation times. This compatibility with kinetic theory is a necessity for any phenomenology: a universal macroscopic approach must be valid in case of various micro- and mesostructures, in particular, it must be compatible with the theory of rarefied gases.

The key of universality is to introduce only general physical and mathematical requirements and a minimal number of assumptions regarding the structure of the material. In particular, one must use and exploit the second law of thermodynamics and introduce a proper functional characterisation of the deviation from local equilibrium. All these can be accomplished most conveniently with the help of internal variables.

One can achieve the compatibility with kinetic theory if the variables have the same tensorial order than the corresponding moments; therefore, their tensorial order is increasing with every new variable. However, the evolution equations of these fields are direct consequences of the second law, and one can get them solving the inequality of the entropy production. This way, for heat transport one obtains the Maxwell-Cattaneo-Vernotte equation as well as the Guyer-Krumhansl one with a single vectorial internal variable [50], [53]. With an additional tensorial variable, a more general the-

ory can be derived, that correctly describes ballistic propagation and the propagation of heat with the speed of sound, too [15].

Non-Equilibrium Thermodynamics with Internal Variables (NET-IV) can reproduce NaF experiments quantitatively, including the correct ballistic propagation speed [16], [17]. Nevertheless, the universality of the derivation indicates a broader range of validity, beyond rarefied real or phonon gases. This broadened range of validity is a prediction: e.g. one can expect non-Fourier heat transport in heterogeneous materials, too. Really, Guyer-Krumhansl type heat transport has been observed in diverse systems, in various heterogeneous materials with heat pulse experiments at room temperature [3], [55]. Internal variables are powerful for modelling concepts in other continuum theories, like rheology [46], [57], semiconductor crystals with dislocations [13], porous nanocrystals filled by fluid flow [33], [34], [35], [36], and also in the GENERIC framework [30]. Naturally, the relation of NET-IV with theories of ET, and kinetic theory, is not straightforward and its performance is analysed considering the complete theory, not only heat transport [37], [38], [41].

Up to now, the solutions and analyses of wave-like and ballistic propagation are mostly restricted to one spatial dimension. This approach is problematic from the point of view of experimental observations, especially considering the NaF experiments [11], [21]. In the classical experiments, the setup is not one-dimensional, but this fact is not considered in the usual modelling calculations [16], [17]. The related ET theory inherits the dimensional reduction from the particular collision integrals, e.g. the deviatoric and spherical contributions in the evolution equation of the heat flux have the same coefficient in the usual form of the Guyer-Krumhansl equation [25], and this is preserved in nonlinear theories, too [39].

In this Chapter we give the complete three-dimensional form of the equations of a theory of heat transport in isotropic materials, with a second order tensorial internal variable \mathbf{Q} , including the possible Onsager reciprocity relations and second law requirements for the transport coefficients. The cases, where \mathbf{Q} has odd parity and even parity, are developed separately. Since higher-order effects are taken into account, and, since we are considering the full three-dimensional problem, the explicit expressions we provide in the Appendix C are cumbersome. However, they are expected to be useful in computer programming and simulations.

The Chapter is organised as follows. In the Section 7.1 the theoretical framework is outlined and the basic balances and constitutive equations are given in a linear anisotropic form for the media under consideration. In Sections 7.2 and 7.3 the isotropic form of the equations are first treated in general. Then Onsager reciprocity relations are imposed as additional requirements, the entropy production is derived, the conditions of its positive definiteness are discussed and the generalized ballistic-conductive heat transport laws in three-dimensional isotropic materials are worked out. In Section 7.4 the general evolution equations for the heat flux, \mathbf{q} , and for \mathbf{Q} are derived. The same for \mathbf{Q} with odd and even parities together with the one dimensional case is given in Sections 7.5 and 7.6. The general one dimensional form is more general than in

[15], while the obtained special cases of Jeffrey type, Maxwell-Cattaneo-Vernotte and Fourier heat equations are the same. A detailed matrix form of the conductivity matrix is given in the Appendix C, when \mathbf{Q} has odd parity, and the differences with respect to the case where \mathbf{Q} has even parity, are discussed, including the transformation of the sixth-order tensor to a form suitable for the calculation of the positive definiteness of the coefficients.

The studies presented in this Chapter are contained in the article [9]:

A. Famà, L. Restuccia and P. Ván. Generalized ballistic-conductive heat transport laws in three-dimensional isotropic materials. *Continuum Mechanics and Thermodynamics*, 2020.

7.1 BASIC EQUATIONS OF HEAT TRANSPORT COUPLED WITH A TENSORIAL INTERNAL VARIABLE

We consider the balance equations of a rigid heat conductor, i.e. the balance of internal energy and the balance of entropy

$$\rho \dot{e} + q_{i,i} = 0, \quad (7.1.1)$$

$$\rho \dot{s} + J_{i,i} = \sigma^{(s)}. \quad (7.1.2)$$

Here ρ is the density, e the specific internal energy, q_i the current density of the internal energy, the heat flux, s the specific entropy, and J_i denotes the entropy flux. The $\sigma^{(s)}$ entropy production rate plays a central and constructive role in the theory. i, j, k are spatial indices related to Descartes coordinates, but they can also be considered as abstract spatial indices of vectors and tensors in the sense that they do not refer to particular coordinates [32]; however, it is convenient in case of higher than second-order tensors. A comma in lower indices is for spatial derivation, and upper dot denotes the substantial time derivative (e.g. $\dot{e} = \partial_t e + v^i e_{,i}$, where ∂_t is the partial time derivative). In case of rigid conductors at rest, the relative velocity of the continuum is zero; therefore, the substantial time derivative is equal to the partial time derivative. Regarding the general usage of abstract indices in classical nonrelativistic continuum theories see, e.g. in [48], [52].

We introduce an additional internal variable Q_{ij} (a second-order tensor) which will incorporate higher-order effects in heat transport. Its physical meaning is not necessary a priori. However, in order that the reader may set some intuitive feeling of it, it is worth saying that Q_{ij} may be interpreted as the flux of the heat flux (see Ref. [12], [39]) in solids, as the pressure tensor in fluids (see Ref. [12], [17]), or as the gradient of the heat flux, but here we leave open its meaning since it could also have a structural information about the particular material. We assume that Q_{ij} contributes to the entropy and the entropy flux. The entropy flux must be zero if q_i and Q_{ij} are zero, that

is in local thermodynamic equilibrium in the absence of heat flux. Therefore its most general form can be given as

$$J_i = b_{ij}q_j + B_{ijk}Q_{jk}, \quad (7.1.3)$$

where the b_{ij} and B_{ijk} constitutive functions are the Nyíri multipliers, that conveniently represent the deviation from the local equilibrium form of the entropy flux, like their quadratic form in the entropy density [27]. This can be expressed also in an additive form, as the K vector of Müller, [23], if $K_i = (b_{ij} - \delta_{ij}/T)q_j + B_{ijk}Q_{jk}$.

Expanding the entropy function $s(e, q_i, Q_{ij})$ up to second-order approximation around a local equilibrium state, we obtain

$$s(e, q_i, Q_{ij}) = s^{(eq)}(e) - \frac{1}{2\rho}m_{ij}q_iq_j - \frac{1}{2\rho}M_{ijkl}Q_{ij}Q_{kl}. \quad (7.1.4)$$

The coefficients m_{ij} and M_{ijkl} have the following symmetries

$$m_{ij} = m_{ji}, \quad M_{ijkl} = M_{klij}.$$

Note that (7.1.3) and (7.1.4) are valid for anisotropic systems too. For isotropic systems m_{ij} and M_{ijkl} in (7.1.4) would reduce to a scalar and the three scalar components conjugate to the three scalar invariants of tensor Q_{ij} , respectively. Thermodynamic stability requires that the inductivity tensors, m_{ij} , M_{ijkl} (see in [10, 19]), are positive definite and we assume that they are constant. The entropy production $\sigma^{(s)}$, formed by combining (7.1.2), (7.1.3) and (7.1.4), is

$$\begin{aligned} \rho\dot{s} + J_{i,i} &= \sigma^{(s)} \\ &= \rho \frac{ds^{(eq)}}{de} \dot{e} - \frac{1}{2}m_{ij}\dot{q}_i q_j - \frac{1}{2}m_{ij}q_i \dot{q}_j - \frac{1}{2}M_{ijkl}\dot{Q}_{ij}Q_{kl} \\ &\quad - \frac{1}{2}M_{ijkl}Q_{ij}\dot{Q}_{kl} + b_{ij,i}q_j + b_{ij}q_{j,i} + B_{ijk,i}Q_{jk} + B_{ijk}Q_{jk,i} \\ &= \left(b_{ij} - \frac{1}{T}\delta_{ij}\right)q_{j,i} + (b_{ji,j} - m_{ij}\dot{q}_j)q_i + (B_{kij,k} - M_{ijkl}\dot{Q}_{kl})Q_{ij} + B_{ijk}Q_{jk,i} \geq 0. \end{aligned} \quad (7.1.5)$$

Inequality (7.1.5) expresses the second law of thermodynamics. Following the procedures of non-equilibrium thermodynamics we obtain the following *general three-dimensional anisotropic linear relations* between the thermodynamic fluxes $b_{ij} - \frac{1}{T}\delta_{ij}$, $b_{ji,j} - m_{ij}\dot{q}_j$, B_{ijk} , $B_{kij,k} - M_{ijkl}\dot{Q}_{kl}$ and forces q_i , $q_{j,i}$, Q_{ij} , $Q_{jk,i}$

$$b_{ji,j} - m_{ij}\dot{q}_j = L_{ij}^{(1)}q_j + L_{ijk}^{(1,2)}q_{j,k} + L_{ijk}^{(1,3)}Q_{jk} + L_{ijkl}^{(1,4)}Q_{jk,l} \quad (7.1.6)$$

$$b_{ij} - \frac{1}{T}\delta_{ij} = L_{ijk}^{(2,1)}q_k + L_{ijkl}^{(2)}q_{k,l} + L_{ijkl}^{(2,3)}Q_{kl} + L_{ijklm}^{(2,4)}Q_{kl,m} \quad (7.1.7)$$

$$B_{kij,k} - M_{ijkl}\dot{Q}_{kl} = L_{ijk}^{(3,1)}q_k + L_{ijkl}^{(3,2)}q_{k,l} + L_{ijkl}^{(3)}Q_{kl} + L_{ijklm}^{(3,4)}Q_{kl,m} \quad (7.1.8)$$

$$B_{ijk} = L_{ijkl}^{(4,1)}q_l + L_{ijklm}^{(4,2)}q_{l,m} + L_{ijklm}^{(4,3)}Q_{lm} + L_{ijklmn}^{(4)}Q_{lm,n}. \quad (7.1.9)$$

Here the conductivity tensors, $L^{(\alpha,\beta)}$ and $L^{(\gamma)}$, are restricted by material symmetries and by the second law. Furthermore reciprocity relations are also to be considered, as we do in Section 7.2.

7.2 ONSAGER RECIPROCALITY RELATIONS

There are two different justifications of Onsager reciprocity. These are the assumptions regarding microscopic and macroscopic reversibility [22]. The concept of microscopic reversibility goes back to Onsager, [28], [29], and assumes a known microstructure, based on the reversal of microscopic velocities. The principle of macroscopic reversibility assumes a particular parity of the physical quantities regarding time reversal, which is originated in the consistency of the balances, and constitutive equations with a time reversal operation [31], [57]. Then the physical quantities with even parity are called α - and with odd parity as β -type variables. For example density, entropy, energy and all thermostatic state variables are of α -type, the velocity, heat flux, entropy flux are β -type, as one can see from the balances because time derivative changes the parity of the fields (e.g. the time derivative of an α -type variable becomes β -type), but the gradient does not. It is generally assumed, that if the thermodynamic forces are of the same type, then the conductivity tensor is symmetric and when they are of the opposite, then the conductivity tensor becomes antisymmetric.

Several theoretical and experimental results support, that internal variable related thermodynamic fluxes and forces do not have definite parities, and both symmetric and antisymmetric parts of the conductivity tensors can be observed [1], [2], [54]. This is understandable because nothing is assumed about the microscopic structure of the material nor on the physical meaning of Q_{ij} in NET-IV [51]. Therefore the microscopic reversibility conditions of Onsager cannot be applied, and concept of macroscopic reversibility is not violated, if we assume that the internal variable, Q_{ij} , does not have parity. In the following, we start with the general case, without Onsagerian reciprocity and without any assumption on the parity of the Q_{ij} . Then we investigate the parities separately with symmetric and antisymmetric conductivity tensors. Let us remark, that comparison with Extended Thermodynamics identifies Q_{ij} as a pressure tensor or as a flux of the heat flux [41]. In this case, it must have an even character, also because the entropy flux J_i and the heat flux q_i are β -type, odd quantities.

7.2.1 Onsager reciprocity relations

In this Subsection we suppose that the field Q_{ij} (so also $Q_{ij,k}$) is *odd* or *even* functions under time reversal. Then $(B_{kij,k} - M_{ijkl}\dot{Q}_{kl})$ and B_{ijk} have an opposite parity, they are both *even* or both *odd* functions under time reversal. From this assumptions we obtain the following mathematical requirements (Onsager reciprocity relations) for the symmetric part of the conductivity tensor:

$$L_{ik}^{(1)} = L_{ki}^{(1)}, \quad L_{ijk}^{(1,2)} = L_{jki}^{(2,1)}, \quad (7.2.1)$$

$$L_{ijk}^{(1,3)} = \pm L_{jki}^{(3,1)}, \quad L_{ijk}^{(1,4)} = L_{jki}^{(4,1)}, \quad (7.2.2)$$

$$L_{ijkl}^{(2)} = L_{klij}^{(2)}, \quad L_{ijkl}^{(2,3)} = \pm L_{klij}^{(3,2)}, \quad (7.2.3)$$

$$L_{ijklm}^{(2,4)} = \pm L_{klmij}^{(4,2)}, \quad L_{ijkl}^{(3)} = L_{klij}^{(3)}, \quad (7.2.4)$$

$$L_{ijklm}^{(3,4)} = L_{klmij}^{(4,3)}, \quad L_{ijklmn}^{(4)} = L_{lmnijk}^{(4)}. \quad (7.2.5)$$

With the positive sign if Q_{ij} is β -type and with a negative one if it is α -type quantity. The sign is changes only if the parity of the respective thermodynamic forces changes, too. Therefore the the $L^{(\nu)}$ tensors, that is the diagonal hypertensors in (7.1.6)-(7.1.9) do not change sign.

7.3 GENERAL ISOTROPIC CASE WITHOUT ASSUMPTION ON THE PARITY OF Q_{ij}

In the general isotropic case, in which the symmetry properties of the body under consideration are invariant with respect to *all rotations and to inversion of the frame of axes*, but in which Onsager reciprocity relations are not yet imposed, we have [8]

$$m_{ij} = m\delta_{ij}, \quad (7.3.1)$$

$$M_{ijkl} = M_1\delta_{ij}\delta_{kl} + M_2\delta_{ik}\delta_{jl} + M_3\delta_{il}\delta_{jk}, \quad (7.3.2)$$

$$L_{ij}^{(1)} \equiv \mathcal{L}_{ij}^{(1)} = L^{(1)}\delta_{ij}, \quad (7.3.3)$$

$$L_{ijkl}^{(1,4)} \equiv \mathcal{L}_{ijkl}^{(1,4)} = L_1^{(1,4)}\delta_{ij}\delta_{kl} + L_2^{(1,4)}\delta_{ik}\delta_{jl} + L_3^{(1,4)}\delta_{il}\delta_{jk}, \quad (7.3.4)$$

$$L_{ijkl}^{(2)} \equiv \mathcal{L}_{ijkl}^{(2)} = L_1^{(2)}\delta_{ij}\delta_{kl} + L_2^{(2)}\delta_{ik}\delta_{jl} + L_3^{(2)}\delta_{il}\delta_{jk}, \quad (7.3.5)$$

$$L_{ijkl}^{(2,3)} \equiv \mathcal{L}_{ijkl}^{(2,3)} = L_1^{(2,3)}\delta_{ij}\delta_{kl} + L_2^{(2,3)}\delta_{ik}\delta_{jl} + L_3^{(2,3)}\delta_{il}\delta_{jk}, \quad (7.3.6)$$

$$L_{ijkl}^{(3,2)} \equiv \mathcal{L}_{ijkl}^{(3,2)} = L_1^{(3,2)}\delta_{ij}\delta_{kl} + L_2^{(3,2)}\delta_{ik}\delta_{jl} + L_3^{(3,2)}\delta_{il}\delta_{jk}, \quad (7.3.7)$$

$$L_{ijkl}^{(3)} \equiv \mathcal{L}_{ijkl}^{(3)} = L_1^{(3)}\delta_{ij}\delta_{kl} + L_2^{(3)}\delta_{ik}\delta_{jl} + L_3^{(3)}\delta_{il}\delta_{jk}, \quad (7.3.8)$$

$$L_{ijkl}^{(4,1)} \equiv \mathcal{L}_{ijkl}^{(4,1)} = L_1^{(4,1)}\delta_{ij}\delta_{kl} + L_2^{(4,1)}\delta_{ik}\delta_{jl} + L_3^{(4,1)}\delta_{il}\delta_{jk}, \quad (7.3.9)$$

$$\begin{aligned} L_{ijklmn}^{(4)} \equiv \mathcal{L}_{ijklmn}^{(4)} = & L_1^{(4)}\delta_{ij}\delta_{kl}\delta_{mn} + L_2^{(4)}\delta_{ij}\delta_{km}\delta_{ln} + L_3^{(4)}\delta_{ij}\delta_{kn}\delta_{lm} \\ & + L_4^{(4)}\delta_{ik}\delta_{jl}\delta_{mn} + L_5^{(4)}\delta_{ik}\delta_{jm}\delta_{ln} + L_6^{(4)}\delta_{ik}\delta_{jn}\delta_{lm} \\ & + L_7^{(4)}\delta_{il}\delta_{jk}\delta_{mn} + L_8^{(4)}\delta_{im}\delta_{jk}\delta_{ln} + L_9^{(4)}\delta_{in}\delta_{jk}\delta_{lm} \\ & + L_{10}^{(4)}\delta_{il}\delta_{jm}\delta_{kn} + L_{11}^{(4)}\delta_{im}\delta_{jl}\delta_{kn} + L_{12}^{(4)}\delta_{in}\delta_{jl}\delta_{km} \\ & + L_{13}^{(4)}\delta_{in}\delta_{jm}\delta_{kl} + L_{14}^{(4)}\delta_{im}\delta_{jn}\delta_{kl} + L_{15}^{(4)}\delta_{il}\delta_{jn}\delta_{km}. \end{aligned} \quad (7.3.10)$$

The coefficients appearing in the entropy (7.1.4) are (7.3.1) and (7.3.2).

Furthermore, in the isotropic case (where the symmetry properties of the considered body are invariant only with respect to all rotations of the frame of axes) the third

order tensors keep the form $L_{ijk} = L \epsilon_{ijk}$ and the fifth order tensors take the form $L_{ijklm} = A_1 \epsilon_{ijk} \delta_{lm} + A_2 \epsilon_{ijl} \delta_{km} + A_3 \epsilon_{ijm} \delta_{kl} + A_4 \epsilon_{ikl} \delta_{jm} + A_5 \epsilon_{ikm} \delta_{lj} + A_6 \epsilon_{ilm} \delta_{jk}$, where ϵ_{ijk} denotes the Levi Civita tensor and the quantities L and A_i , $i = 1, \dots, 6$, are the independent components of the tensors L_{ijk} and L_{ijklmn} , that vanish when there is also the invariance of the properties with respect to the inversion of the axes. Thus, we obtain

$$L_{ijk}^{(1,2)} = L_{ijk}^{(1,3)} = L_{ijk}^{(2,1)} = L_{ijk}^{(3,1)} = 0, \quad (7.3.11)$$

$$L_{ijklm}^{(2,4)} = L_{ijklm}^{(3,4)} = L_{ijklm}^{(4,2)} = L_{ijklm}^{(4,3)} = 0. \quad (7.3.12)$$

From relations (7.3.1)-(7.3.12), the phenomenological equations (7.1.6)-(7.1.9) in the isotropic case read

$$m\dot{q}_i - b_{ji,j} = -L^{(1)}q_i - L_1^{(1,4)}Q_{ik,k} - L_2^{(1,4)}Q_{ki,k} - L_3^{(1,4)}Q_{kk,i}, \quad (7.3.13)$$

$$b_{ij} - \frac{1}{T}\delta_{ij} = L_1^{(2)}\delta_{ij}q_{k,k} + L_2^{(2)}q_{i,j} + L_3^{(2)}q_{j,i} + L_1^{(2,3)}\delta_{ij}Q_{kk} + L_2^{(2,3)}Q_{ij} + L_3^{(2,3)}Q_{ji}, \quad (7.3.14)$$

$$B_{kij,k} = M_1\delta_{ij}\dot{Q}_{kk} + M_2\dot{Q}_{ij} + M_3\dot{Q}_{ji} + L_1^{(3,2)}\delta_{ij}q_{k,k} + L_2^{(3,2)}q_{i,j} + L_3^{(3,2)}q_{j,i} + L_1^{(3)}\delta_{ij}Q_{kk} + L_2^{(3)}Q_{ij} + L_3^{(3)}Q_{ji}, \quad (7.3.15)$$

$$\begin{aligned} B_{ijk} = & L_1^{(4,1)}\delta_{ij}q_k + L_2^{(4,1)}\delta_{ik}q_j + L_3^{(4,1)}\delta_{jk}q_i \\ & + \delta_{ij}\left(L_1^{(4)}Q_{kl,l} + L_2^{(4)}Q_{lk,l} + L_3^{(4)}Q_{ll,k}\right) \\ & + \delta_{ik}\left(L_4^{(4)}Q_{jl,l} + L_5^{(4)}Q_{lj,l} + L_6^{(4)}Q_{ll,j}\right) \\ & + \delta_{jk}\left(L_7^{(4)}Q_{il,l} + L_8^{(4)}Q_{li,l} + L_9^{(4)}Q_{ll,i}\right) \\ & + L_{10}^{(4)}Q_{ij,k} + L_{11}^{(4)}Q_{ji,k} + L_{12}^{(4)}Q_{jk,i} + L_{13}^{(4)}Q_{kj,i} \\ & + L_{14}^{(4)}Q_{ki,j} + L_{15}^{(4)}Q_{ik,j}. \end{aligned} \quad (7.3.16)$$

In the general isotropy case the number of material coefficients of equations (7.3.13)-(7.3.16) are 38: 4 *static* (m and M_i) and 34 independent *conductivity parameters* ($L^{(\epsilon,\mu)}$ and $L^{(\delta)}$).

7.3.1 Onsager symmetry

Now, we tentatively require Onsager reciprocity relations (7.2.1)-(7.2.5), as additional restrictions on the coefficients, and explore which further reduction this implies on the number of independent conductivity parameters. Then, from (7.2.2)₂ $\mathcal{L}_{ijkl}^{(1,4)} = \mathcal{L}_{jkli}^{(4,1)}$, and being

$$\mathcal{L}_{jkli}^{(4,1)} = L_1^{(4,1)}\delta_{jk}\delta_{li} + L_2^{(4,1)}\delta_{jl}\delta_{ki} + L_3^{(4,1)}\delta_{ji}\delta_{kl}, \quad (7.3.17)$$

we obtain

$$L_1^{(1,4)} = \pm L_3^{(4,1)}, \quad L_2^{(1,4)} = \pm L_2^{(4,1)}, \quad L_3^{(1,4)} = \pm L_1^{(4,1)}. \quad (7.3.18)$$

Furthermore, for each isotropic four tensor \mathcal{L}_{ijkl} we have the following symmetry relation

$$\mathcal{L}_{ijkl} = \mathcal{L}_{klij}, \quad (7.3.19)$$

because of

$$\mathcal{L}_{ijkl} = T_1 \delta_{ij} \delta_{kl} + T_2 \delta_{ik} \delta_{jl} + T_3 \delta_{il} \delta_{jk} = T_1 \delta_{kl} \delta_{ij} + T_2 \delta_{ki} \delta_{lj} + T_3 \delta_{kj} \delta_{li} = \mathcal{L}_{klij}, \quad (7.3.20)$$

where T_1 , T_2 and T_3 indicate the independent components of \mathcal{L}_{ijkl} . Taking into account the property (7.3.19), Onsager relations (7.2.3)₁ and (7.2.4)₂ are verified in the isotropic case and from (7.2.3)₂ we derive $\mathcal{L}_{ijkl}^{(2,3)} = \mathcal{L}_{klij}^{(3,2)} = \mathcal{L}_{ijkl}^{(3,2)}$, from which we have

$$L_i^{(2,3)} = \pm L_i^{(3,2)} \quad (i = 1, 2, 3). \quad (7.3.21)$$

Then, from (7.3.10) we obtain

$$\begin{aligned} \mathcal{L}_{lmnij}^{(4)} = & L_1^{(4)} \delta_{lm} \delta_{ni} \delta_{jk} + L_2^{(4)} \delta_{lm} \delta_{nj} \delta_{ik} + L_3^{(4)} \delta_{lm} \delta_{nk} \delta_{ij} + L_4^{(4)} \delta_{ln} \delta_{mi} \delta_{jk} \\ & + L_5^{(4)} \delta_{ln} \delta_{mj} \delta_{ik} + L_6^{(4)} \delta_{ln} \delta_{mk} \delta_{ij} + L_7^{(4)} \delta_{mn} \delta_{li} \delta_{jk} + L_8^{(4)} \delta_{mn} \delta_{lj} \delta_{ik} \\ & + L_9^{(4)} \delta_{mn} \delta_{lk} \delta_{ij} + L_{10}^{(4)} \delta_{li} \delta_{mj} \delta_{nk} + L_{11}^{(4)} \delta_{lj} \delta_{mi} \delta_{nk} + L_{12}^{(4)} \delta_{lk} \delta_{mi} \delta_{nj} \\ & + L_{13}^{(4)} \delta_{lk} \delta_{mj} \delta_{ni} + L_{14}^{(4)} \delta_{lj} \delta_{mk} \delta_{in} + L_{15}^{(4)} \delta_{li} \delta_{mk} \delta_{nj}. \end{aligned} \quad (7.3.22)$$

Adding (7.3.10) and (7.3.22), using Onsager relation (7.2.5)₂ and dividing by 2, we have

$$\begin{aligned} \mathcal{L}_{ijklmn}^{(4)} = & C_1^{(4)} (\delta_{ij} \delta_{kl} \delta_{mn} + \delta_{in} \delta_{jk} \delta_{lm}) + C_2^{(4)} (\delta_{ij} \delta_{km} \delta_{ln} + \delta_{ik} \delta_{jn} \delta_{lm}) \\ & + C_3^{(4)} \delta_{ij} \delta_{kn} \delta_{lm} + C_4^{(4)} (\delta_{ik} \delta_{jl} \delta_{mn} + \delta_{im} \delta_{jk} \delta_{nl}) + C_5^{(4)} \delta_{ik} \delta_{jm} \delta_{ln} \\ & + C_6^{(4)} \delta_{il} \delta_{jk} \delta_{mn} + C_7^{(4)} \delta_{il} \delta_{jm} \delta_{kn} + C_8^{(4)} \delta_{il} \delta_{jn} \delta_{km} + C_9^{(4)} \delta_{im} \delta_{jl} \delta_{kn} \\ & + C_{10}^{(4)} (\delta_{im} \delta_{jn} \delta_{kl} + \delta_{in} \delta_{jl} \delta_{km}) + C_{11}^{(4)} \delta_{in} \delta_{jm} \delta_{kl}, \end{aligned} \quad (7.3.23)$$

where

$$C_1^{(4)} = \frac{L_1^{(4)} + L_9^{(4)}}{2}, \quad C_2^{(4)} = \frac{L_2^{(4)} + L_6^{(4)}}{2}, \quad C_3^{(4)} = L_3^{(4)}, \quad (7.3.24)$$

$$C_4^{(4)} = \frac{L_4^{(4)} + L_8^{(4)}}{2}, \quad C_5^{(4)} = L_5^{(4)}, \quad C_6^{(4)} = L_7^{(4)}, \quad C_7^{(4)} = L_{10}^{(4)}, \quad (7.3.25)$$

$$C_8^{(4)} = L_{15}^{(4)}, \quad C_9^{(4)} = L_{11}^{(4)}, \quad C_{10}^{(4)} = \frac{L_{12}^{(4)} + L_{14}^{(4)}}{2}, \quad C_{11}^{(4)} = L_{13}^{(4)}. \quad (7.3.26)$$

Thus, from relation $\mathcal{L}_{ijklmn}^{(4)} = \mathcal{L}_{lmnij}^{(4)}$ the significant components of the isotropic tensor \mathcal{L}_{ijklmn} reduce from 15 to 11. Therefore, in case that Onsager reciprocity is imposed, from relations (7.3.18), (7.3.21) and (7.3.23) the number of conductivity parameters are reduced altogether from 34 to 24.

7.3.2 Entropy production

In the general isotropic case, with the aid of relations (7.3.13)-(7.3.16), (7.3.1)-(7.3.9), (7.3.11) and (7.3.12), entropy production (7.1.5) can be written as

$$\begin{aligned} \sigma^{(s)} = & \mathcal{L}_{ik}^{(1)} q_i q_k + \mathcal{L}_{ijkl}^{(2)} q_{j,i} q_{k,l} + \mathcal{L}_{ijkl}^{(3)} Q_{ij} Q_{kl} + \mathcal{L}_{ijklmn}^{(4)} Q_{jk,i} Q_{lm,n} + \\ & + \left(\mathcal{L}_{ijkl}^{(1,4)} + \mathcal{L}_{ljki}^{(4,1)} \right) q_i Q_{jk,l} + \left(\mathcal{L}_{ijkl}^{(2,3)} + \mathcal{L}_{klji}^{(3,2)} \right) q_{j,i} Q_{kl} \geq 0. \end{aligned} \quad (7.3.27)$$

In the case where the internal variable Q_{ij} has odd parity, using Onsager relations and (7.3.21) and (7.3.23), expression (7.3.27) takes the form

$$\begin{aligned} \sigma^{(s)} = & \mathcal{L}_{ik}^{(1)} q_i q_k + \mathcal{L}_{ijkl}^{(2)} q_{j,i} q_{k,l} + \mathcal{L}_{ijkl}^{(3)} Q_{ij} Q_{kl} + \mathcal{L}_{ijklmn}^{(4)} Q_{jk,i} Q_{lm,n} \\ & + \left(\mathcal{L}_{ijkl}^{(1,4)} \pm \mathcal{L}_{iljk}^{(1,4)} \right) q_i Q_{jk,l} + \left(\mathcal{L}_{ijkl}^{(2,3)} \pm \mathcal{L}_{klji}^{(2,3)} \right) q_{j,i} Q_{kl} \geq 0, \end{aligned} \quad (7.3.28)$$

or in extended form

$$\begin{aligned} \sigma^{(s)} = & L^{(1)} \delta_{ik} q_i q_k + \left(L_1^{(2)} \delta_{ji} \delta_{kl} + L_2^{(2)} \delta_{jk} \delta_{il} + L_3^{(2)} \delta_{jl} \delta_{ik} \right) q_{i,j} q_{k,l} \\ & + \left(L_1^{(3)} \delta_{ij} \delta_{kl} + L_2^{(3)} \delta_{ik} \delta_{jl} + L_3^{(3)} \delta_{il} \delta_{jk} \right) Q_{ij} Q_{kl} \\ & + \left[C_1^{(4)} (\delta_{pi} \delta_{jl} \delta_{mn} + \delta_{pn} \delta_{ij} \delta_{lm}) + C_2^{(4)} (\delta_{pi} \delta_{jm} \delta_{ln} + \delta_{pj} \delta_{in} \delta_{lm}) \right. \\ & + C_3^{(4)} \delta_{pi} \delta_{jn} \delta_{lm} + C_4^{(4)} (\delta_{pj} \delta_{il} \delta_{mn} + \delta_{pm} \delta_{ij} \delta_{nl}) + C_5^{(4)} \delta_{pj} \delta_{im} \delta_{ln} \\ & + C_6^{(4)} \delta_{pl} \delta_{ij} \delta_{mn} + C_7^{(4)} \delta_{pl} \delta_{im} \delta_{jn} + C_8^{(4)} \delta_{pl} \delta_{in} \delta_{jm} + C_9^{(4)} \delta_{pm} \delta_{il} \delta_{jn} \\ & \left. + C_{10}^{(4)} (\delta_{pm} \delta_{in} \delta_{jl} + \delta_{pn} \delta_{il} \delta_{jm}) + C_{11}^{(4)} \delta_{pn} \delta_{im} \delta_{jl} \right] Q_{ij,p} Q_{lm,n} \\ & + \left(L_1^{(1,4)} \delta_{il} \delta_{mn} + L_2^{(1,4)} \delta_{im} \delta_{ln} + L_3^{(1,4)} \delta_{in} \delta_{lm} \right) q_i Q_{lm,n} \\ & \pm \left(L_1^{(1,4)} \delta_{kp} \delta_{ij} + L_2^{(1,4)} \delta_{ki} \delta_{pj} + L_3^{(1,4)} \delta_{kj} \delta_{pi} \right) Q_{ij,p} q_k \\ & + \left(L_1^{(2,3)} \delta_{ji} \delta_{kl} + L_2^{(2,3)} \delta_{jk} \delta_{il} + L_3^{(2,3)} \delta_{jl} \delta_{ik} \right) q_{i,j} Q_{kl} \\ & \pm \left(L_1^{(2,3)} \delta_{ij} \delta_{kl} + L_2^{(2,3)} \delta_{ik} \delta_{jl} + L_3^{(2,3)} \delta_{il} \delta_{jk} \right) Q_{ij} q_{k,l} \geq 0. \end{aligned} \quad (7.3.29)$$

From (7.3.29) it is seen that the entropy production is a non-negative bilinear form in the components of the heat flux and its gradient, and in the components of the internal variable and its gradient (see in Appendix C its matrix representation $\sigma^{(s)} = X_\alpha \mathcal{L}_{\alpha\beta} X_\beta$, with X_α , X_β and $\mathcal{L}_{\alpha\beta}$ suitable matrices).

The following inequalities can be obtained for the components of the phenomenological tensors, resulting from the fact that all the elements of the main diagonal of the symbolic matrix $\{\mathcal{L}_{\alpha\beta}\}$ associated to the bilinear form (7.3.29) must be non-negative,

representing a condition (only necessary) for the semi-definiteness of the matrix $\{\mathcal{L}_{\alpha\beta}\}$ (see Appendix C)

$$L^{(1)} \geq 0, \quad L_3^{(2)} \geq 0, \quad L_2^{(3)} \geq 0, \quad (7.3.30)$$

$$L_1^{(2)} + L_2^{(2)} + L_3^{(2)} \geq 0, \quad L_1^{(3)} + L_2^{(3)} + L_3^{(3)} \geq 0, \quad (7.3.31)$$

$$2C_1^{(4)} + 2C_2^{(4)} + C_3^{(4)} + 2C_4^{(4)} + C_5^{(4)} + C_6^{(4)} + C_7^{(4)} + C_8^{(4)} \\ + C_9^{(4)} + 2C_{10}^{(4)} + C_{11}^{(4)} \geq 0, \quad (7.3.32)$$

$$C_2^{(4)} + C_8^{(4)} + C_{10}^{(4)} \geq 0, \quad C_4^{(4)} + C_9^{(4)} + C_{10}^{(4)} \geq 0, \quad (7.3.33)$$

$$C_{10}^{(4)} \geq 0, \quad C_1^{(4)} + C_{10}^{(4)} + C_{11}^{(4)} \geq 0. \quad (7.3.34)$$

Relations (7.3.32)-(7.3.34), come from the non-negativity of the elements of the main diagonal of the sub-matrix $\mathcal{L}_{pijklmn}^{(4)}$.

Moreover, other relations can be obtained from the non-negativity of the major minors P_r ($r = 1, \dots, 48$) of $\{\mathcal{L}_{\alpha\beta}\}$, coming from Sylvester's criterion, that represents a necessary and sufficient condition for the semi-definiteness of the matrix $\{\mathcal{L}_{\alpha\beta}\}$. For instance, the calculation of the major minors up to sixth-order gives the relations (7.3.30)₁, (7.3.30)₂ and (7.3.31)₁.

The non-negativity of the seventh-order major minor of $\{\mathcal{L}_{\alpha\beta}\}$

$$P_7 = \begin{vmatrix} L^{(1)} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & L^{(1)} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & L^{(1)} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & L^{(2)} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & L_3^{(2)} & 0 & L_2^{(2)} \\ 0 & 0 & 0 & 0 & 0 & L_3^{(2)} & 0 \\ 0 & 0 & 0 & 0 & L_2^{(2)} & 0 & L_3^{(2)} \end{vmatrix}, \quad (7.3.35)$$

with $L^{(2)} \equiv L_1^{(2)} + L_2^{(2)} + L_3^{(2)}$, gives the new relation

$$L_2^{(2)} + \left(L_3^{(2)}\right)^2 \geq 0, \quad (7.3.36)$$

and so on. In the Appendix C we give a two-dimensional form of the conductivity matrix $\{\mathcal{L}_{\alpha\beta}\}$, in terms of which the calculation of the conditions of positive definiteness is straightforward.

7.4 RATE EQUATIONS FOR q_i AND Q_{ij} IN THE GENERAL CASE WITHOUT ASSUMPTION ON THE PARITY OF Q_{ij}

Changing indexes i and j in (7.3.14), deriving it with respect to x_j and substituting it into (7.3.13), we deduce

$$m\dot{q}_i + L^{(1)}q_i = \left(L_1^{(2)} + L_2^{(2)}\right)q_{k,ki} + L_3^{(2)}q_{i,kk} + \left(L_1^{(2,3)} - L_3^{(1,4)}\right)Q_{kk,i} + \left(L_3^{(2,3)} - L_1^{(1,4)}\right)Q_{ik,k} + \left(L_2^{(2,3)} - L_2^{(1,4)}\right)Q_{ki,k} + \left(\frac{1}{T}\right)_i. \quad (7.4.1)$$

where

$$m > 0, \quad L^{(1)} > 0, \quad L_1^{(2)} + L_2^{(2)} > 0, \quad L_3^{(2)} > 0. \quad (7.4.2)$$

Equation (7.4.1) can be written as follows

$$\tau\dot{q}_i + q_i = -\lambda T_{,i} + l_1 q_{i,kk} + l_2 q_{k,ki} + l_{12} Q_{kk,i} + l_{13} Q_{ik,k} + l_{14} Q_{ki,k}, \quad (7.4.3)$$

where

$$\tau = \frac{m}{L^{(1)}}, \quad \lambda = \frac{1}{L^{(1)}T^2}, \quad l_1 = \frac{L_3^{(2)}}{L^{(1)}}, \quad l_2 = \frac{L_1^{(2)} + L_2^{(2)}}{L^{(1)}}, \quad (7.4.4)$$

$$l_{12} = \frac{L_1^{(2,3)} - L_3^{(1,4)}}{L^{(1)}}, \quad l_{13} = \frac{L_3^{(2,3)} - L_1^{(1,4)}}{L^{(1)}}, \quad l_{14} = \frac{L_2^{(2,3)} - L_2^{(1,4)}}{L^{(1)}}, \quad (7.4.5)$$

being τ the relaxation time of the heat flux (that, then, has a finite velocity of propagation), λ the heat conductivity and l_i have dimension of square length.

In analogous way, if we change $i \rightarrow k$, $j \rightarrow i$, $k \rightarrow j$ in equation (7.3.16), deriving it with respect to x_k and inserting it into (7.3.15), we have

$$\begin{aligned} & M_1 \delta_{ij} \dot{Q}_{kk} + M_2 \dot{Q}_{ij} + M_3 \dot{Q}_{ji} + L_1^{(3)} \delta_{ij} Q_{kk} + L_2^{(3)} Q_{ij} + L_3^{(3)} Q_{ji} \\ &= \left(L_3^{(4,1)} - L_1^{(3,2)}\right) \delta_{ij} q_{k,k} + \left(L_2^{(4,1)} - L_2^{(3,2)}\right) q_{i,j} + \left(L_1^{(4,1)} - L_3^{(3,2)}\right) q_{j,i} \\ &+ \left(L_3^{(4)} + L_6^{(4)}\right) Q_{kk,ij} + L_{12}^{(4)} Q_{ij,kk} + L_{13}^{(4)} Q_{ji,kk} + \left(L_1^{(4)} + L_{15}^{(4)}\right) Q_{jk,ik} \\ &+ \left(L_2^{(4)} + L_{11}^{(4)}\right) Q_{kj,ik} + \left(L_4^{(4)} + L_{14}^{(4)}\right) Q_{ik,jk} + \left(L_5^{(4)} + L_{10}^{(4)}\right) Q_{ki,jk} \\ &+ \delta_{ij} \left[\left(L_7^{(4)} + L_8^{(4)}\right) Q_{kl,lk} + L_9^{(4)} Q_{ll,kk} \right], \end{aligned} \quad (7.4.6)$$

i.e.

$$\begin{aligned} & \tau_1 \delta_{ij} \dot{Q}_{kk} + \tau_2 \dot{Q}_{ij} + \tau_3 \dot{Q}_{ji} + \delta_{ij} Q_{kk} + l_2^3 Q_{ij} + l_3^3 Q_{ji} = l_{21} \delta_{ij} q_{k,k} + l_{31} q_{i,j} \\ &+ l_{41} q_{j,i} + L_1 Q_{kk,ij} + L_2 Q_{ij,kk} + L_3 Q_{ji,kk} + L_4 Q_{jk,ik} + L_5 Q_{kj,ik} \\ &+ L_6 Q_{ik,jk} + L_7 Q_{ki,jk} + \delta_{ij} (L_8 Q_{kl,kl} + L_9 Q_{ll,kk}), \end{aligned} \quad (7.4.7)$$

where

$$\tau_1 = \frac{M_1}{L_1^{(3)}}, \quad \tau_2 = \frac{M_2}{L_1^{(3)}}, \quad \tau_3 = \frac{M_3}{L_1^{(3)}}, \quad l_2^3 = \frac{L_2^{(3)}}{L_1^{(3)}}, \quad l_3^3 = \frac{L_3^{(3)}}{L_1^{(3)}}, \quad (7.4.8)$$

$$l_{21} = \frac{L_3^{(4,1)} - L_1^{(3,2)}}{L_1^{(3)}}, \quad l_{31} = \frac{L_2^{(4,1)} - L_2^{(3,2)}}{L_1^{(3)}}, \quad l_{41} = \frac{L_1^{(4,1)} - L_3^{(3,2)}}{L_1^{(3)}}, \quad (7.4.9)$$

$$L_1 = \frac{L_3^{(4)} + L_6^{(4)}}{L_1^{(3)}}, \quad L_2 = \frac{L_{12}^{(4)}}{L_1^{(3)}}, \quad L_3 = \frac{L_{13}^{(4)}}{L_1^{(3)}}, \quad (7.4.10)$$

$$L_4 = \frac{L_1^{(4)} + L_{15}^{(4)}}{L_1^{(3)}}, \quad L_5 = \frac{L_2^{(4)} + L_{11}^{(4)}}{L_1^{(3)}}, \quad L_6 = \frac{L_4^{(4)} + L_{14}^{(4)}}{L_1^{(3)}}, \quad (7.4.11)$$

$$L_7 = \frac{L_5^{(4)} + L_{10}^{(4)}}{L_1^{(3)}}, \quad L_8 = \frac{L_7^{(4)} + L_8^{(4)}}{L_1^{(3)}}, \quad L_9 = \frac{L_9^{(4)}}{L_1^{(3)}} \quad (7.4.12)$$

and τ_1 , τ_2 and τ_3 have time dimension.

In the rate equations (7.4.3) and (7.4.7) 24 independent coefficients appear. These equations are the full three-dimensional versions of the one-dimensional equations (12)-(13) in [15]. They represent the *generalized ballistic-conductive heat transport laws in three-dimensional isotropic materials*. Equation (7.4.7) can be rewritten by means three rate equations, splitting the second-order tensor Q_{ij} into its orthogonal components, i.e.

$$Q_{ij} = Q\delta_{ij} + Q_{\langle ij \rangle} + Q_{[ij]}, \quad (7.4.13)$$

where

$$Q = \frac{1}{3}Q_{kk} \quad (\text{scalar part of } Q_{ij}), \quad (7.4.14)$$

$$Q_{\langle ij \rangle} = \frac{1}{2}(Q_{ij} + Q_{ji}) - Q\delta_{ij} \quad (\text{deviator of the symmetric part of } Q_{ij}), \quad (7.4.15)$$

$$Q_{[ij]} = \frac{1}{2}(Q_{ij} - Q_{ji}) \quad (\text{skew-symmetric part of } Q_{ij}). \quad (7.4.16)$$

From equation (7.4.7) we derive the rate equations for Q , $Q_{\langle ij \rangle}$ and $Q_{[ij]}$.

The rate equation for Q is ($i = j$)

$$3(3\tau_1 + \tau_2 + \tau_3)\dot{Q} + 3(3 + l_2^3 + l_3^3)Q = (3l_{21} + l_{31} + l_{41})q_{k,k} + 3(L_1 + L_2 + L_3 + 3L_9)Q_{,kk} + (L_4 + L_5 + L_6 + L_7 + 3L_8)Q_{kl,kl}, \quad (7.4.17)$$

i.e.

$$\tau^0\dot{Q} + Q = l^0q_{k,k} + L_1^0Q_{,kk} + L_2^0Q_{kl,kl}, \quad (7.4.18)$$

where

$$\tau^0 = \frac{3\tau_1 + \tau_2 + \tau_3}{3 + l_2^3 + l_3^3}, \quad l^0 = \frac{3l_{21} + l_{31} + l_{41}}{3(3 + l_2^3 + l_3^3)}, \quad (7.4.19)$$

$$L_1^0 = \frac{L_1 + L_2 + L_3 + 3L_9}{3 + l_2^3 + l_3^3}, \quad L_2^0 = \frac{L_4 + L_5 + L_6 + L_7 + 3L_8}{3(3 + l_2^3 + l_3^3)}, \quad (7.4.20)$$

being τ^0 the relaxation time of Q ;

the rate equation for $Q_{\langle ij \rangle}$ is

$$\hat{\tau} \dot{Q}_{\langle ij \rangle} + Q_{\langle ij \rangle} = \hat{l} q_{\langle i, j \rangle} + \hat{L}_1 Q_{kk, \langle ij \rangle} + \hat{L}_2 Q_{\langle ij \rangle, kk} + \hat{L}_3 Q_{k \langle i, j \rangle k} + \hat{L}_4 Q_{\langle ik, kj \rangle}, \quad (7.4.21)$$

where

$$\hat{\tau} = \frac{\tau_2 + \tau_3}{l_2^3 + l_3^3}, \quad \hat{l} = \frac{l_{31} + l_{41}}{l_2^3 + l_3^3}, \quad \hat{L}_1 = \frac{L_1}{l_2^3 + l_3^3}, \quad (7.4.22)$$

$$\hat{L}_2 = \frac{L_2 + L_3}{l_2^3 + l_3^3}, \quad \hat{L}_3 = \frac{L_5 + L_7}{l_2^3 + l_3^3}, \quad \hat{L}_4 = \frac{L_4 + L_6}{l_2^3 + l_3^3}, \quad (7.4.23)$$

being $\hat{\tau}$ the relaxation time of $Q_{\langle ij \rangle}$;

finally the rate equation for $Q_{[ij]}$ is

$$\check{\tau} \dot{Q}_{[ij]} + Q_{[ij]} = \check{l} q_{[i, j]} + \check{L}_1 Q_{[ij], kk} + \check{L}_2 Q_{k [i, j] k} + \check{L}_3 Q_{[ik, kj]}, \quad (7.4.24)$$

where

$$\check{\tau} = \frac{\tau_2 - \tau_3}{l_2^3 - l_3^3}, \quad \check{l} = \frac{l_{31} - l_{41}}{l_2^3 - l_3^3}, \quad \check{L}_1 = \frac{L_2 - L_3}{l_2^3 - l_3^3}, \quad (7.4.25)$$

$$\check{L}_2 = \frac{L_7 - L_5}{l_2^3 - l_3^3}, \quad \check{L}_3 = \frac{L_6 - L_4}{l_2^3 - l_3^3}, \quad (7.4.26)$$

being $\check{\tau}$ the relaxation time of $Q_{[ij]}$.

7.5 THE RATE EQUATIONS FOR q_i AND Q_{ij} WITH ONSAGER RECIPROCITY IN THE CASE WHERE Q_{ij} HAS ODD PARITY

In Section 7.4 we have obtained the rate equations for q_i and Q_{ij} and for the scalar part, the deviator of the symmetric part and the skew-symmetric part of Q_{ij} (see (7.4.3), (7.4.7) or (7.4.3) and (7.4.18), (7.4.21), (7.4.24), respectively) without assuming reciprocity relations, but only isotropy. In this Section we derive the *heat transport laws in three-dimensional isotropic materials* (7.4.7), (7.4.18), (7.4.21), (7.4.24) in

the form (7.5.9), (7.5.10), (7.5.12) and (7.5.14), by using Onsager reciprocity relations (7.3.18)-(7.3.23), that reduce the number of coefficients in these rate equations from 24 to 21 (when compared to the general isotropic case). The phenomenological equations (7.3.13) and (7.3.14) remain unchanged (thus also the rate equation (7.4.3)), but equations (7.3.15) and (7.3.16) assume the following form

$$B_{kij,k} = M_1 \delta_{ij} \dot{Q}_{kk} + M_2 \dot{Q}_{ij} + M_3 \dot{Q}_{ji} + L_1^{(2,3)} \delta_{ij} q_{k,k} + L_2^{(2,3)} q_{i,j} + L_3^{(2,3)} q_{j,i} + L_1^{(3)} \delta_{ij} Q_{kk} + L_2^{(3)} Q_{ij} + L_3^{(3)} Q_{ji}, \quad (7.5.1)$$

$$B_{ijk} = L_3^{(1,4)} \delta_{ij} q_k + L_2^{(1,4)} \delta_{ik} q_j + L_1^{(1,4)} \delta_{jk} q_i + \delta_{ij} \left(C_1^{(4)} Q_{kl,l} + C_2^{(4)} Q_{lk,l} + C_3^{(4)} Q_{ll,k} \right) + \delta_{ik} \left(C_4^{(4)} Q_{jl,l} + C_5^{(4)} Q_{lj,l} + C_2^{(4)} Q_{ll,j} \right) + \delta_{jk} \left(C_6^{(4)} Q_{il,l} + C_4^{(4)} Q_{li,l} + C_1^{(4)} Q_{ll,i} \right) + C_7^{(4)} Q_{ij,k} + C_8^{(4)} Q_{ik,j} + C_{10}^{(4)} Q_{jk,i} + C_{11}^{(4)} Q_{kj,i} + C_9^{(4)} Q_{ji,k} + C_{10}^{(4)} Q_{ki,j}, \quad (7.5.2)$$

where, with respect to (7.3.15) and (7.3.16) the coefficients $L_i^{(3,2)}$ have been replaced by $L_i^{(2,3)}$ ($i = 1, 2, 3$), and the coefficients $L_i^{(4,1)}$ by $L_i^{(1,4)}$ ($i = 1, 2, 3$). By virtue of (7.5.1) and (7.5.2), (changing $i \rightarrow k$, $j \rightarrow i$, $k \rightarrow j$ in equation (7.5.2), deriving it with respect to x_k , inserting it into (7.5.1) and multiplying the obtained equation by $1/L_1^{(3)}$) we obtain

$$\tau_1 \delta_{ij} \dot{Q}_{kk} + \tau_2 \dot{Q}_{ij} + \tau_3 \dot{Q}_{ji} + \delta_{ij} Q_{kk} + l_2^3 Q_{ij} + l_3^3 Q_{ji} = l_{21} \delta_{ij} q_{k,k} + l_{31} q_{i,j} + l_{41} q_{j,i} + C_1 Q_{kk,ij} + C_2 Q_{ij,kk} + C_3 Q_{ji,kk} + C_4 Q_{jk,ik} + C_5 Q_{kj,ik} + C_6 Q_{ik,jk} + C_7 Q_{ki,jk} + \delta_{ij} (C_8 Q_{kl,kl} + C_9 Q_{ll,kk}), \quad (7.5.3)$$

where

$$C_1 = \frac{C_2^{(4)} + C_3^{(4)}}{L_1^{(3)}}, \quad C_2 = \frac{C_{10}^{(4)}}{L_1^{(3)}}, \quad C_3 = \frac{C_{11}^{(4)}}{L_1^{(3)}}, \quad (7.5.4)$$

$$C_4 = \frac{C_1^{(4)} + C_{10}^{(4)}}{L_1^{(3)}}, \quad C_5 = \frac{C_2^{(4)} + C_8^{(4)}}{L_1^{(3)}}, \quad C_6 = \frac{C_4^{(4)} + C_9^{(4)}}{L_1^{(3)}}, \quad (7.5.5)$$

$$C_7 = \frac{C_5^{(4)} + C_7^{(4)}}{L_1^{(3)}}, \quad C_8 = \frac{C_4^{(4)} + C_6^{(4)}}{L_1^{(3)}}, \quad C_9 = \frac{C_1^{(4)}}{L_1^{(3)}}. \quad (7.5.6)$$

The rate equation (7.5.3) is the same as (7.4.7), but with L_i replaced by C_i ($i = 1 \dots 9$).

We remark that the coefficients l_{21} , l_{31} and l_{41} in (7.5.3) transform according to Onsager relations (7.3.18) and (7.3.21), so that we have

$$l_{21} = \left(L_1^{(1,4)} - L_1^{(2,3)} \right) / L_1^{(3)}, \quad l_{31} = \left(L_2^{(1,4)} - L_2^{(2,3)} \right) / L_1^{(3)}, \quad l_{41} = \left(L_3^{(1,4)} - L_3^{(2,3)} \right) / L_1^{(3)}. \quad (7.5.7)$$

By virtue of (7.5.7) and (7.5.4)₂, (7.5.5)₁ and (7.5.6)₃, the further conditions for the coefficients are worked out:

$$l_{31} = -L^{(1)}l_{14}/L_1^{(3)}, \quad l_{41} = -L^{(1)}(l_{12} + l_{13})/L_1^{(3)} - l_{21}, \quad C_9 = C_4 - C_2. \quad (7.5.8)$$

Thus, using relations (7.5.8), the rate equation (7.5.3) for Q_{ij} takes the form

$$\begin{aligned} \tau_1 \delta_{ij} \dot{Q}_{kk} + \tau_2 \dot{Q}_{ij} + \tau_3 \dot{Q}_{ji} + \delta_{ij} Q_{kk} + l_2^3 Q_{ij} + l_3^3 Q_{ji} &= l_{21} \delta_{ij} q_{k,k} - L^{(1)} l_{14} / L_1^{(3)} q_{i,j} \\ - \left[L^{(1)} (l_{12} + l_{13}) / L_1^{(3)} + l_{21} \right] q_{j,i} + C_1 Q_{kk,ij} + C_2 Q_{ij,kk} + C_3 Q_{ji,kk} + C_4 Q_{jk,ik} & \\ + C_5 Q_{kj,ik} + C_6 Q_{ik,jk} + C_7 Q_{ki,jk} + \delta_{ij} [C_8 Q_{kl,kl} + (C_4 - C_2) Q_{ll,kk}]. & \end{aligned} \quad (7.5.9)$$

As in (7.4.13), we split the second-order tensor Q_{ij} in its orthogonal components Q , $Q_{\langle ij \rangle}$ and $Q_{[ij]}$, its scalar part, the deviator of its symmetric part, its skew-symmetric part (see (7.4.14)-(7.4.16)) that, having Q_{ij} odd parity, have also odd parity. In the following we work out the rate equations for Q , $Q_{\langle ij \rangle}$ and $Q_{[ij]}$.

Thus, from equation (7.5.9) we derive:

the rate equation for Q (obtained when $i = j$)

$$\tau^0 \dot{Q} + Q = c^0 q_{k,k} + C_1^0 Q_{,kk} + C_2^0 Q_{kl,kl}, \quad (7.5.10)$$

where τ^0 is given by (7.4.19)₁ and

$$\begin{aligned} c^0 &= \frac{2L_1^{(3)} l_{21} - L^{(1)} (l_{12} + l_{13} + l_{14})}{3L_1^{(3)} (3 + l_2^3 + l_3^3)}, \quad C_1^0 = \frac{C_1 - 2C_2 + C_3 + 3C_4}{3 + l_2^3 + l_3^3}, \\ C_2^0 &= \frac{C_4 + C_5 + C_6 + C_7 + 3C_8}{3(3 + l_2^3 + l_3^3)}; \end{aligned} \quad (7.5.11)$$

the rate equation for $Q_{\langle ij \rangle}$

$$\hat{\tau} \dot{Q}_{\langle ij \rangle} + Q_{\langle ij \rangle} = \hat{c} q_{\langle i,j \rangle} + \hat{C}_1 Q_{kk,\langle ij \rangle} + \hat{C}_2 Q_{\langle ij \rangle, kk} + \hat{C}_3 Q_{k\langle i,j \rangle k} + \hat{C}_4 Q_{\langle ik,kj \rangle}, \quad (7.5.12)$$

where $\hat{\tau}$ is given by (7.4.22)₁ and

$$\begin{aligned} \hat{c} &= -\frac{L_1^{(3)} l_{21} + L^{(1)} (l_{12} + l_{13} + l_{14})}{L_1^{(3)} (l_2^3 + l_3^3)}, \quad \hat{C}_1 = \frac{C_1}{l_2^3 + l_3^3}, \quad \hat{C}_2 = \frac{C_2 + C_3}{l_2^3 + l_3^3}, \\ \hat{C}_3 &= \frac{C_5 + C_7}{l_2^3 + l_3^3}, \quad \hat{C}_4 = \frac{C_4 + C_6}{l_2^3 + l_3^3}; \end{aligned} \quad (7.5.13)$$

the rate equation for $Q_{[ij]}$

$$\overset{\vee}{\tau}\dot{Q}_{[ij]} + Q_{[ij]} = \overset{\vee}{c}q_{[i,j]} + \overset{\vee}{C}_1Q_{[ij],kk} + \overset{\vee}{C}_2Q_{k[i,j]k} + \overset{\vee}{C}_3Q_{[ik,kj]}, \quad (7.5.14)$$

where $\overset{\vee}{\tau}$ is given by (7.4.25)₁ and

$$\overset{\vee}{c} = \frac{L_1^{(3)}l_{21} + L^{(1)}(l_{12} + l_{13} - l_{14})}{L_1^{(3)}(l_2^3 - l_3^3)}, \quad \overset{\vee}{C}_1 = \frac{C_2 - C_3}{l_2^3 - l_3^3}, \quad \overset{\vee}{C}_2 = \frac{C_7 - C_5}{l_2^3 - l_3^3}, \quad \overset{\vee}{C}_3 = \frac{C_6 - C_4}{l_2^3 - l_3^3}. \quad (7.5.15)$$

7.5.1 One-dimensional heat transport in the case where Q_{ij} has odd parity

In this Subsection we focus on the one-dimensional case, in order to appreciate how the generalization from one dimension to three dimensions analysed in this Chapter is far from trivial. In the one-dimensional case we have that the components of B and Q reduce to

$$B \equiv B_{111} \quad \text{and} \quad Q = Q_{11}, \quad \text{and} \quad \mathbf{q} = (q, 0, 0), \quad \mathbf{Q} = \begin{pmatrix} Q & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \mathbf{b} = \begin{pmatrix} b & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (7.5.16)$$

The system of equations (7.3.13)-(7.3.16) (in which we use the Onsager relations assuming that Q_{ij} has odd parity) becomes

$$m\dot{q} - b_{,x} = -L^{(1)}q - L^{(1,4)}Q_{,x}, \quad (7.5.17)$$

$$b - \frac{1}{T} = L^{(2)}q_{,x} + L^{(2,3)}Q, \quad (7.5.18)$$

$$M\dot{Q} - B_{,x} = -L^{(2,3)}q_{,x} - L^{(3)}Q, \quad (7.5.19)$$

$$B = L^{(1,4)}q + C^{(4)}Q_{,x}, \quad (7.5.20)$$

where $m > 0$, $M > 0$ (see [15]) and

$$L^{(1,4)} = L_1^{(1,4)} + L_2^{(1,4)} + L_3^{(1,4)}, \quad L^{(2)} = L_1^{(2)} + L_2^{(2)} + L_3^{(2)}, \quad (7.5.21)$$

$$L^{(2,3)} = L_1^{(2,3)} + L_2^{(2,3)} + L_3^{(2,3)}, \quad M = M_1 + M_2 + M_3, \quad (7.5.22)$$

$$L^{(3)} = L_1^{(3)} + L_2^{(3)} + L_3^{(3)}, \quad (7.5.23)$$

$$C^{(4)} = 2C_1^{(4)} + 2C_2^{(4)} + C_3^{(4)} + 2C_4^{(4)} + C_5^{(4)} + C_6^{(4)} + C_7^{(4)} + C_8^{(4)} + C_9^{(4)} + 2C_{10}^{(4)} + C_{11}^{(4)}, \quad (7.5.24)$$

with $(\cdot)_{,x}$ indicating the derivative of (\cdot) with respect to x . We observe that the system of equations (7.5.17)-(7.5.20) obtained here is more general of equations (7)-(10)

deduced in [15], because of the presence of the phenomenological constant $L^{(1,4)}$ in (7.5.17) and (7.5.20) and the fact that the coefficients $L^{(1,4)}$, $L^{(2)}$, $L^{(2,3)}$, M , $L^{(3)}$, $C^{(4)}$ have been obtained from a three-dimensional approach.

In this case, the entropy production (7.3.29) assumes the form

$$\sigma^{(s)} = L^{(1)}q^2 + L^{(2)}(q_{,x})^2 + L^{(3)}Q^2 + C^{(4)}(Q_{,x})^2 + 2L^{(1,4)}qQ_{,x} + 2L^{(2,3)}q_{,x}Q \geq 0, \quad (7.5.25)$$

with $C^{(4)} = L_{111111}$ (see matrix (C.0.12) of the Appendix C), or in symbolic matrix notation

$$\sigma^{(s)} = \underbrace{\begin{pmatrix} q & q_{,x} & Q & Q_{,x} \end{pmatrix} \begin{pmatrix} L^{(1)} & 0 & 0 & L^{(1,4)} \\ 0 & L^{(2)} & L^{(2,3)} & 0 \\ 0 & L^{(2,3)} & L^{(3)} & 0 \\ L^{(1,4)} & 0 & 0 & C^{(4)} \end{pmatrix} \begin{pmatrix} q \\ q_{,x} \\ Q \\ Q_{,x} \end{pmatrix}}_{\mathcal{A}} \geq 0. \quad (7.5.26)$$

Because the bilinear form (7.5.25) must be non-negative, the matrix \mathcal{A} (that is symmetric) associated to this form is non-negative semi-definite, so that the elements of its main diagonal and its major minors must be non-negative

$$L^{(1)} \geq 0, \quad L^{(2)} \geq 0, \quad L^{(3)} \geq 0, \quad C^{(4)} \geq 0, \quad (7.5.27)$$

$$L^{(2)}L^{(3)} - (L^{(2,3)})^2 \geq 0, \quad L^{(1)}C^{(4)} - (L^{(1,4)})^2 \geq 0. \quad (7.5.28)$$

Using (7.5.18) and (7.5.20), equations (7.5.17) and (7.5.19) become

$$mq_{,t} + L^{(1)}q - L^{(2)}q_{,xx} = \left(\frac{1}{T}\right)_{,x} - DQ_{,x}, \quad (7.5.29)$$

$$MQ_{,t} + L^{(3)}Q - C^{(4)}Q_{,xx} = Dq_{,x}, \quad (7.5.30)$$

where $D = L^{(1,4)} - L^{(2,3)}$.

In the following we introduce the relaxation time of the internal variable Q , called τ^J :

$$\tau^J = \frac{M}{L^{(3)}}. \quad (7.5.31)$$

Furthermore, we have supposed the body is at rest, so that material derivative coincides with the partial time derivative $(\cdot)_{,t}$.

Equations (7.5.29) and (7.5.30) are analogous to equations (12) and (13) of [15]. For $L^{(2)} = C^{(4)} = 0$, these equations coincide with those provided in [12] or [39] by assuming Q_{ij} as the flux of the heat flux.

In the following we will derive heat transport equations analogous but more general of that obtained in [15], where the finite speed of thermal disturbances and the ballistic and diffusive motion of phonons (heat carriers) are taken into account. Instead, in Fourier equation the velocity of heat propagation is infinite. Differentiating equation (7.5.29) with respect to time, equation (7.5.30) with respect to the spatial variable x and using equation (7.5.29) and its second spatial derivative, we can eliminate Q and work out the following *generalized ballistic-conductive heat transport law*

$$mMq_{,tt} + (ML^{(1)} + mL^{(3)})q_{,t} - (mC^{(4)} + ML^{(2)})q_{,xxt} + C^{(4)}L^{(2)}q_{,xxxx} - (L^{(1)}C^{(4)} + H)q_{,xx} + L^{(3)}L^{(1)}q = M\left(\frac{1}{T}\right)_{,xt} + L^{(3)}\left(\frac{1}{T}\right)_{,x} - C^{(4)}\left(\frac{1}{T}\right)_{,xxx}, \quad (7.5.32)$$

where

$$H = L^{(3)}L^{(2)} - D^2. \quad (7.5.33)$$

Equation (7.5.32) has been obtained via several differentiations of the linear governing equations (7.5.29) and (7.5.30). Hence, equation (7.5.32) is not equivalent to the system of equations (7.5.29) and (7.5.30). In fact (7.5.32) has a larger set of solutions, coming from the larger number of necessary initial conditions.

Thus, we derive

$$\tau\tau^Jq_{,tt} + \tau^q q_{,t} + q - \alpha q_{,xxt} + \beta q_{,xxxx} - \gamma q_{,xx} = \nu\left(\frac{1}{T}\right)_{,xt} - \lambda T_{,x} - \zeta\left(\frac{1}{T}\right)_{,xxx}, \quad (7.5.34)$$

where

$$\tau^q = \tau + \tau^J, \quad \nu = \frac{M}{L^{(1)}L^{(3)}}, \quad (7.5.35)$$

$$\gamma = \frac{L^{(1)}C^{(4)} + H}{L^{(1)}L^{(3)}}, \quad \beta = \frac{C^{(4)}L^{(2)}}{L^{(1)}L^{(3)}}, \quad \alpha = \frac{mC^{(4)} + ML^{(2)}}{L^{(1)}L^{(3)}}, \quad \zeta = \frac{C^{(4)}}{L^{(1)}L^{(3)}}, \quad (7.5.36)$$

H is defined by (7.5.33) and λ is given by (7.4.4)₂.

In (7.5.34) we see that relaxation time $\tau^q = \tau + \tau^J$ is given by two contributions: the first comes from the relaxation time of the heat flux (see (7.4.4)₁) and the second comes from the relaxation time of the internal variable (see (7.5.31)).

7.5.2 Special cases of heat transport equation in the assumption that Q_{ij} has odd parity

From (7.5.32), it is possible to derive as particular case some special equations which have been often analysed in the literature on heat transport.

BALLISTIC-CONDUCTIVE EQUATION. In the case where $C^{(4)} = L^{(2)} = 0$, the heat equation (7.5.32) becomes

$$mMq_{,tt} + (ML^{(1)} + mL^{(3)})q_{,t} - D^2q_{,xx} + L^{(3)}L^{(1)}q = M\left(\frac{1}{T}\right)_{,xt} + L^{(3)}\left(\frac{1}{T}\right)_{,x}. \quad (7.5.37)$$

Thus, we can write

$$\tau\tau^J q_{,tt} + \tau^q q_{,t} + q - \eta q_{,xx} = \nu \left(\frac{1}{T} \right)_{,xt} - \lambda T_{,x}, \quad (7.5.38)$$

where

$$\eta = \frac{D^2}{L^{(1)}L^{(3)}}. \quad (7.5.39)$$

GUYER-KRUMHANSL EQUATION. In the case where $C^{(4)} = M = 0$, the heat equation (7.5.32) becomes

$$mL^{(3)} q_{,t} - Hq_{,xx} + L^{(3)}L^{(1)}q = L^{(3)} \left(\frac{1}{T} \right)_{,x}, \quad (7.5.40)$$

then, we work out

$$\tau q_{,t} - l^2 q_{,xx} + q = -\lambda T_{,x}, \quad (7.5.41)$$

with

$$l^2 = \frac{H}{L^{(1)}L^{(3)}}, \quad (7.5.42)$$

where l , having the dimension of a length which may be interpreted as an average, mean free path of the heat carriers (phonons) i.e. the average length between successive collision amongst them. We observe that only in Guyer-Krumhansl heat equation the coefficient multiplying the field $q_{,xx}$ has the physical meaning of l^2 .

CAHN-HILLIARD TYPE EQUATION. In the case where $C^{(4)} = M = m = 0$, the heat equation (7.5.32) becomes

$$L^{(3)}L^{(1)}q - Hq_{,xx} = L^{(3)} \left(\frac{1}{T} \right)_{,x}, \quad (7.5.43)$$

from which we obtain

$$q - l^2 q_{,xx} = -\lambda T_{,x}. \quad (7.5.44)$$

JEFFREYS TYPE EQUATION (OR DOUBLE-LAG MODEL [47]). In the case where $C^{(4)} = L^{(2)} = m = D = 0$ (then, $H = 0$), the heat equation (7.5.32) becomes

$$ML^{(1)}q_{,t} + L^{(3)}L^{(1)}q = M \left(\frac{1}{T} \right)_{,xt} + L^{(3)} \left(\frac{1}{T} \right)_{,x}, \quad (7.5.45)$$

thus we derive:

$$\tau^J q_{,t} + q = \nu \left(\frac{1}{T} \right)_{,xt} - \lambda T_{,x}. \quad (7.5.46)$$

We note that in the Jeffreys type heat equation τ^J is the relaxation time of q .

MAXWELL-CATTANEO-VERNOTTE EQUATION. In the case where $C^{(4)} = M = L^{(2)} = D = 0$ (then, $H = 0$), the heat equation (7.5.32) becomes

$$mq_{,t} + L^{(1)}q = \left(\frac{1}{T}\right)_{,x}, \quad (7.5.47)$$

from which we have:

$$\tau q_{,t} + q = -\lambda T_{,x}. \quad (7.5.48)$$

FOURIER EQUATION. In the case where $C^{(4)} = M = L^{(2)} = D = m = 0$ (then, $H = 0$), the heat equation (7.5.32) becomes

$$L^{(1)}q = \left(\frac{1}{T}\right)_{,x}, \quad (7.5.49)$$

i.e.

$$q = -\lambda T_{,x}. \quad (7.5.50)$$

What is specially worth in this Subsection is not only the ability to obtain many situations studied up to now, but specially the fact that the coefficients appearing in the one-dimensional case are complicated combinations of the independent coefficients appearing in the three-dimensional case. Thus, measurements in one dimension are not sufficient to give information in the general three-dimensional situation, which is the only one able to exhibit the basic meaning of each coefficient. We emphasize that Jeffrey type, Maxwell-Cattaneo-Vernotte and Fourier equations are the same as in [15].

7.6 RATE EQUATIONS FOR q_i AND Q_{ij} IN THE ISOTROPIC CASE WHERE Q_{ij} HAS EVEN PARITY

In Section 7.4 we have obtained the rate equations (7.4.3) and (7.4.7) for the heat flux q_i and the internal variable Q_{ij} , respectively, in the general isotropic case without assumptions regarding the parity of the internal variable Q_{ij} (q_i is odd and Q_{ij} can be of odd or even type) and then we have not discussed Onsager reciprocity relations. In Section 7.5 we have shown how these rate equations transform supposing the odd parity of Q_{ij} . In this Section we treat the case where Q_{ij} has even parity and it is very easy to see that the rate equation (7.4.3) remains unchanged (as in the odd parity case). Instead, the rate equation (7.4.7) (that takes the form (7.5.9) when we assume the even parity of Q_{ij}) transforms in

$$\begin{aligned} \tau_1 \delta_{ij} \dot{Q}_{kk} + \tau_2 \dot{Q}_{ij} + \tau_3 \dot{Q}_{ji} + \delta_{ij} Q_{kk} + l_2^3 Q_{ij} + l_3^3 Q_{ji} &= l_{21} \delta_{ij} q_{k,k} + L^{(1)} l_{14} / L_1^{(3)} q_{i,j} \\ + \left[L^{(1)} (l_{12} + l_{13}) / L_1^{(3)} - l_{21} \right] q_{j,i} + C_1 Q_{kk,ij} + C_2 Q_{ij,kk} + C_3 Q_{ji,kk} + C_4 Q_{jk,ik} & \quad (7.6.1) \\ + C_5 Q_{kj,ik} + C_6 Q_{ik,jk} + C_7 Q_{ki,jk} + \delta_{ij} [C_8 Q_{kl,kl} + (C_4 - C_2) Q_{ll,kk}], & \end{aligned}$$

where the quantities l_{21} , l_{31} and l_{41} take the following form

$$l_{21} = \frac{L_1^{(2,3)} - L_1^{(1,4)}}{L_1^{(3)}}, \quad l_{31} = \frac{L_2^{(2,3)} - L_2^{(1,4)}}{L_1^{(3)}}, \quad l_{41} = \frac{L_3^{(2,3)} - L_3^{(1,4)}}{L_1^{(3)}}, \quad (7.6.2)$$

in which Onsager symmetry relations (7.3.18) and (7.3.21) have been applied, with negative sign. The other coefficients continue to have the same definitions given in Section 7.4, but the coefficients of $q_{i,j}$ and $q_{j,i}$ have different signs with respect to those in (7.5.9). Furthermore, in this considered case relations (7.5.8)_{1,2} become

$$l_{31} = L^{(1)}l_{14}/L_1^{(3)}, \quad l_{41} = L^{(1)}(l_{12} + l_{13})/L_1^{(3)} - l_{21}. \quad (7.6.3)$$

Finally, the rate equations for the orthogonal components Q , $Q_{\langle ij \rangle}$ and $Q_{[ij]}$, that are still of even type, remain formally unchanged from the equations (7.5.10), (7.5.12), and (7.5.14), valid when Q_{ij} is of odd type. But we have to emphasize that the quantities c^0 , \hat{c} and \check{c} (defined by (7.5.11)₁, (7.5.13)₁ and (7.5.15)₁, respectively) take the following different form

$$c^0 = \frac{2L_1^{(3)}l_{21} + L^{(1)}(l_{12} + l_{13} + l_{14})}{3L_1^{(3)}(3 + l_2^3 + l_3^3)}, \quad \hat{c} = \frac{L^{(1)}(l_{12} + l_{13} + l_{14}) - L_1^{(3)}l_{21}}{L_1^{(3)}(l_2^3 + l_3^3)}, \quad (7.6.4)$$

$$\check{c} = \frac{L_1^{(3)}l_{21} - L^{(1)}(l_{12} + l_{13} + l_{14})}{L_1^{(3)}(l_2^3 - l_3^3)}. \quad (7.6.5)$$

7.6.1 One-dimensional isotropic heat transport in the assumption that Q_{ij} has even parity

Taking into account expressions (7.5.16), using the Onsager relations (7.2.1)-(7.2.5) in the case where the internal variable Q_{ij} has an even parity, the system of equations (7.3.13)-(7.3.16) takes the form

$$m\dot{q} - b_{,x} = -L^{(1)}q - L^{(1,4)}Q_{,x}, \quad (7.6.6)$$

$$b - \frac{1}{T} = L^{(2)}q_{,x} + L^{(2,3)}Q, \quad (7.6.7)$$

$$M\dot{Q} - B_{,x} = L^{(2,3)}q_{,x} - L^{(3)}Q, \quad (7.6.8)$$

$$B = -L^{(1,4)}q + C^{(4)}Q_{,x}, \quad (7.6.9)$$

where only equations (7.6.8) and (7.6.9) are different from (7.5.19) and (7.5.20) because of the signs of the first terms in their right-hand sides. As consequence of this difference we have that the entropy production (7.5.25) takes the new reduced form

$$\sigma^{(s)} = L^{(1)}q^2 + L^{(2)}(q_{,x})^2 + L^{(3)}Q^2 + C^{(4)}(Q_{,x})^2, \quad (7.6.10)$$

so that the associated matrix \mathcal{A} (that is diagonal and thus symmetric) takes the following diagonal form

$$\mathcal{A} = \begin{pmatrix} L^{(1)} & 0 & 0 & 0 \\ 0 & L^{(2)} & 0 & 0 \\ 0 & 0 & L^{(3)} & 0 \\ 0 & 0 & 0 & C^{(4)} \end{pmatrix}, \quad (7.6.11)$$

so that only relations (7.5.27) are still true.

Furthermore, using (7.6.7) and (7.6.9), equations (7.6.6) and (7.6.8) become

$$mq_{,t} + L^{(1)}q - L^{(2)}q_{,xx} = \left(\frac{1}{T}\right)_{,x} - DQ_{,x}, \quad (7.6.12)$$

$$MQ_{,t} + L^{(3)}Q - C^{(4)}Q_{,xx} = -Dq_{,x}, \quad (7.6.13)$$

where $D = L^{(1,4)} - L^{(2,3)}$. Relation (7.6.12) is equal to (7.5.29), while (7.6.13) has opposite sign in its right-hand side with respect to (7.5.30) (D continues to have the same value).

Finally, deriving equation (7.6.12) with respect to time, equation (7.6.13) with respect to the spatial variable x and using equation (7.6.12) and its second spatial derivative, we can eliminate Q and work out the same the heat transport equation (7.5.32) (and than (7.5.34)) where the only difference consist in the fact that the quantity H defined by (7.5.33) takes the new form

$$H = L^{(3)}L^{(2)} + D^2. \quad (7.6.14)$$

Thus, H is always positive in the case of even parity of Q_{ij} .

7.6.2 Special cases of heat transport equation in the assumption that Q_{ij} has even parity

Applying the procedures used in Subsection 7.5.2 to obtain from (7.5.32) (and also (7.5.34)) special cases, we derive the following results:

a) The Ballistic-Conductive heat transport equations (7.5.37) and (7.5.38), being $C^{(4)} = L^{(2)} = 0$ and $H = L^{(3)}L^{(2)} + D^2$, take the following form

$$mMq_{,tt} + (ML^{(1)} + mL^{(3)})q_{,t} + D^2q_{,xx} + L^{(3)}L^{(1)}q = M\left(\frac{1}{T}\right)_{,xt} + L^{(3)}\left(\frac{1}{T}\right)_{,x}, \quad (7.6.15)$$

$$\tau\tau^Jq_{,tt} + \tau^q q_{,t} + q + \eta q_{,xx} = \nu\left(\frac{1}{T}\right)_{,xt} - \lambda T_{,x}, \quad (7.6.16)$$

different from (7.5.37) and (7.5.38) because of the plus sign before D^2 and η . In (7.6.15) and (7.6.16) the definitions (7.4.4)_{1,2}, (7.5.31), (7.5.35) and (7.5.39) and are still valid;

- b) Guyer-Krumhansl heat transport equations, being $C^{(4)} = M = 0$, have the expressions same as (7.5.40) and (7.5.41), but with H (see (7.5.42)) replaced by (7.6.14);
- c) Cahn-Hilliard type heat transport equations (7.5.43) and (7.5.44), being $C^{(4)} = M = m = 0$, remain unchanged, but with H replaced by (7.6.14);
- d) Jeffreys type, Maxwell-Cattaneo-Vernotte, Fourier heat transport equations (where H is not present), remain unchanged.

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CONCLUSIONS REGARDING THE FIRST AND SECOND PART OF THIS THESIS

This Section is dedicated to summarize and discuss the results obtained in the Chapters of the present thesis.

In Chapter 1, a model for porous nanocrystals filled by a fluid flow proposed in the paper [10], in the framework of rational extended irreversible thermodynamics with internal variables, was used to study the thermal, mechanical and transport properties of these materials. It was assumed that the medium under consideration has mass density constant, the body force and heat source distribution are negligible and the structural permeability tensor, its gradient, its flux, the heat flux and the fluid flow are independent variables besides the small strain tensor, the concentration of the fluid and its gradient, the temperature and its gradient. In the linear case, the constitutive equations and the affinities were deduced by the potential method. The rate equations for dissipative fluxes and for the structural permeability tensor, formulated as ansatzes in the form of balance equations describing time-dependent tensorial fields, were worked out and it is seen that porous channels in nanocrystals influence mechanical and transport properties. In particular, the generalized equations Maxwell-Vernotte-Cattaneo and Fick-Nonnenmacher were obtained. Furthermore, in the anisotropic case a generalized telegraph heat equation, with finite velocity for the thermal disturbances, was derived that may have applications in describing the thermal behaviour of the considered nanostructures, where the phenomena are fast and the rate of variation of the properties of the system is faster than the time scale characterizing the relaxation fluxes towards their respective local-equilibrium value. The closure of governing equations system was also discussed. The obtained results have applications in nanotechnology and other fields of applied sciences.

In Chapter 2 we have obtained a description of isotropic and perfect isotropic porous media filled by a fluid flow, in the framework of rational extended irreversible thermodynamics with internal variables, where the structural permeability tensor r_{ij} with its gradient $r_{ij,k}$ and its flux \mathcal{V}_{ijk} were introduced as internal variables in the thermodynamic state vector. Here, the results, obtained in the Chapter 1 for anisotropic porous media, were specialized when the considered media have symmetry properties invariant under orthogonal transformations of the axes frame. It was assumed that the mass density is constant, the body force and heat source are negligible and the constitutive equations, the generalized affinities, the rate equations for dissipative fluxes, presenting a relaxation time, and the closure of system of equations describing the behaviour of the considered media were worked out in the isotropic and perfect isotropic cases. It was seen that porous channels influence mechanical, thermal and transport properties of these media. In particular, when the density of porous defects is higher than its characteristic value the thermal conductivity decreases. The generalized Maxwell-Vernotte-Cattaneo, Fick-Nonnenmacher and telegraph temperature equations were obtained as particular cases. The study of fluid-saturated porous media have a great interest in

applied sciences, like geology, hydrology, pharmaceuticals and nanotechnology, where there are situations of propagation of high-frequency waves.

In Chapter 3 a theory was formulated to describe an incompressible fluid through the channels (rectilinear/curved) of a porous structure. The Darcy-Brinkman-Stokes law was worked out and the erosive/deposition effects of the fluid in a solid matrix were studied and an application of the obtained results to the fluid flow cloaking was illustrated. Practical importance of porous metamaterials in different fields as to mitigate earthquake phenomena, to contrast noise pollution, to analyse particular mechanical properties and to increase ultrasonic imaging, was commented. In the framework of rational thermodynamics a theoretical model was developed completely in accordance with the theory for porous media filled by fluid flow with erosion/deposition, developed in Sections 3.1 and 3.2, when the internal variable influencing the viscous phenomena is interpreted as the symmetric part of the velocity gradient and the results are considered in a first approximation. The constitutive functions were worked out using Liu's theorem and Wang's representations for objective functions for scalar, symmetric tensor and vector functions. The derived theory has a great interest in geophysics, pharmaceuticals, physiology, earthquake engineering, hydrology and other fields.

In Chapter 4 the theoretical approach was used, developed in previous Chapters in the framework of rational extended irreversible thermodynamics. It was supposed that the media with porous channels filled by a fluid can be studied as a mixture of two components. An internal variable, the structural permeability tensor r_{ij} , its gradient $r_{ij,k}$ and its flux \mathcal{V}_{ijk} were introduced in the thermodynamic state vector besides the other classical variables to describe the mechanical, porous and transport properties of these media. Here, the rate equations for the porosity field, its flux, the heat and fluid-concentration fluxes, previously obtained in the anisotropic case, were considered in a special case for perfect isotropic media having symmetry properties invariant under orthogonal transformations. It was assumed that the mass density of the mixture of the porous skeleton and the fluid is constant and the body force, the heat source and the external entropy production source were negligible. The obtained results were applied to the study of the propagation in one direction x of coupled porosity and fluid-concentration waves when the body is supposed occupying the whole space. The dispersion relation was carried out and three possible propagation modes were found, with particular propagation mathematical conditions. The wave propagation velocities as functions of the wavenumber k were represented for a given numerical set of the several coefficients characterizing in an example the porous media under consideration. The study of propagation of these coupled waves has several application fields, such as hydrology, biology, nanotechnology, physiology and seismic waves.

In Chapter 5 we have presented the equations describing porous media considering only the porosity and fluid-concentration fields, and we have derived a quasi-linear hyperbolic PDEs system. Since a thermodynamical model has an added value if possible solutions of the derived theory are found, and because the closed-form solutions

of nonlinear PDEs are rare, we have investigated the propagation of weak discontinuities, as approximated solutions. To this aim we have introduced a new variable related to the surface across which the solutions or/and some of their derivatives undergo a jump, and following a Boillat's methodology for quasi-linear and hyperbolic systems of the first order, we obtained Bernoulli's equation governing the propagation of the amplitude of one of these approximated solutions in the one-dimensional case. Solving this equation, the explicit form of the first approximation of the solution \mathbf{U} of the system has been obtained.

In Chapter 6 we have presented the system of non-linear hyperbolic PDEs describing isotropic porous media of the previous Chapter but we have looked for the solution in a different form, precisely in the form of an asymptotic sequence of powers of some small parameter, which is related to the thickness of internal layers, across which the solutions or/and some of their derivatives varies steeply. To find possible solutions, the theory has an added value. Furthermore the choice to find solutions in power series is also justified from the fact that the achievement of a closed-form solution of nonlinear PDEs is rare. The one-dimensional case has been treated, obtaining the propagation of on of these solutions in a first approximation.

In Chapter 7, ballistic-conductive heat transport in rigid isotropic materials with an internal variable Q_{ij} , influencing thermal phenomena, has been treated in the framework of non-equilibrium thermodynamics with internal variables (NET-IV). Onsager reciprocity has also been considered (in both particular cases in which Q_{ij} have been assumed to be odd or even with respect to macroscopic time reversal) and the consequences were derived. For the sake of fast applicability the explicit expressions for the components of the conductive matrix are given in the Appendix C in the two cases.¹

The approach NET-IV is general and universal. It characterises the deviation from local equilibrium both in the entropy density and in the entropy flux in the simplest possible functional forms. The entropy density depends on the internal variables quadratically, in order to preserve the concavity, that is thermodynamic stability. The entropy flux depends on the internal variables linearly therefore it disappears when they are zero. As long as these two physical conditions and the entropy inequality are valid, the derived consequences are also valid. The generality of the assumptions ensures the universality of the final evolution equations. It was considered a strictly linear theory, when the \mathbf{m} and \mathbf{M} tensors and the conductivity tensors, $\mathbf{L}^{(\alpha,\beta)}$ and $\mathbf{L}^{(\gamma)}$, are constant.

The conditions of positive definiteness of the corresponding conductivity matrix can be calculated directly with the help of computer algebra programs. Though the expressions are very cumbersome, it should be noted that every coefficient appearing in them corresponds in principle to an observable phenomenon. Instead, the much simpler one-dimensional case may grasp essential qualitative features, but its coefficients are a combination of three-dimensional coefficients giving a deeper and more

¹ Remarkable, that for nonlinear, or quasilinear conductivity tensors one can get more restrictions (see [5] and [6]).

complete description. We have obtained a complete set of equations for generalized ballistic-conductive heat transport in three-dimensional isotropic rigid conductors for the variables T , q_i and Q_{ij} . These are the balance of internal energy (7.1.1) with the caloric equation of state $s'_{eq}(e) = 1/T$ and the balance type constitutive equations (7.4.3), (7.4.7) (or (7.4.3), (7.4.18), (7.4.21), (7.4.24)) in the general isotropic case, and (7.4.3), (7.5.9) (or (7.4.3), (7.5.10), (7.5.12), (7.5.14)) with Onsagerian reciprocity as additional constraints.

There are two different aspects of ballistic heat transport in continua. From the point of view of kinetic theory it is the propagation of phonons without collisions with the lattice. Then phonons are reflected only at the boundaries of the medium. This microscopic understanding is the foundation of the so-called ballistic-diffusive integrodifferential model of Chen [2], [3], [13], [14], [15], where kinetic theory and macroscopic considerations are mixed, the distribution function f is split into two parts, one for ballistic phonons and the other referred to diffusive phonons. Also, internal energy and heat flux are decomposed into ballistic and diffusive components. This approach leads to two independent continuum representations. First, it is a particular boundary condition for continuum theories that can also be introduced by second-sound models, like Guyer-Krunhansl equation [1]. On the other hand, for ballistic phonons, the speed of propagation is equal to the speed of 'first' sound, the speed of elastic waves in the medium. The speed of propagation is independent of the boundary conditions in a continuum approach, and this is the meaning of the ballistic terminology in our theory, following Rational Extended Thermodynamics (RET) [4], [9]. It is also remarkable that Chen's model is equivalent to an extended continuum heat transport theory, where the coexistence of two kinds of heat carriers (ballistic and diffusive phonons) is assumed as it was shown by Lebon et al. [7], [8] and investigated in [16].

Theories of Extended Thermodynamics (ET) assume that the constitutive equations are local, and the rate equations are written in a hierarchical series of balances, where the dissipative fluxes appear as densities in the consecutive balance. These assumptions are consequences of the definition of the macroscopic fields as moments of the single-particle phase space probability density and the Boltzmann equation. In our case, with internal variables, this structure is the consequence of the second law and can be observed on the left-hand side of (7.1.6) and (7.1.8). Then essential aspects of ET are well represented. On the other hand, NET-IV has many material coefficients that are missing in ET, in particular in Rational Extended Thermodynamics, where only the two relaxation times of the Callaway collision integral represent the material properties. This property of RET is attractive, but the price is not only that the validity of the theory is connected to the particularities of the microscopic model, but also that the speed of the ballistic propagation, the speed of elastic waves, can be obtained exactly only by considering the complete moment series, or practically by using dozens of evolution equations (with consecutively increasing tensorial orders) [9]. The low number of material coefficients leads to many evolution equations in modelling ballistic propagation of heat.

Giving the three-dimensional structure of ET and NET-IV for heat transport in case of isotropic materials opens the field to build and solve realistic models of two- and three-dimensional experimental setups, where the two theories lead to different predictions. To appreciate some of the original aspects of this Chapter, let us eventually comment the equations (7.3.14) and (7.3.16) for b_{ij} and B_{ijk} and their consequences on the entropy flux. It is well known in the literature [11], [12], that one of the expression of the entropy flux is

$$J_i = \frac{1}{T}q_i + \frac{l^2}{\lambda T^2}q_{i,j}q_j, \quad (7.6.17)$$

Note then that the constitutive equation for the entropy flux (7.1.3), when b_{ij} and B_{ijk} are given by (7.3.14) and (7.3.16), lead to a richer expression than (7.6.17), namely

$$J_i = \frac{1}{T}q_i + L_1^{(2)}q_iq_{k,k} + L_2^{(2)}q_{i,j}q_j + L_3^{(2)}q_jq_{j,i} + L_1^{(2,3)}q_iQ_{kk} + L_2^{(2,3)}Q_{ij}q_j + L_3^{(2,3)}q_jQ_{ji} + f(L_i^{(4,1)}, L_i^{(4)}, q_i, Q_{ij,k}). \quad (7.6.18)$$

Thus, in our analysis the extended entropy flux was more general than (7.6.17), and played an important role in the thermodynamic consistency of couplings with the heat flux q_i and tensorial internal variables as Q_{ij} .

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A

PARTICULAR CASES OF ISOTROPIC AND PERFECT ISOTROPIC TENSORS

In the following Appendix we will consider isotropic tensors of odd order (third and fifth), and isotropic and perfect isotropic tensors of even order (fourth and sixth), having special symmetry properties. We emphasize that the perfect isotropic tensors of odd order (first, third and fifth) are null (see (2.2.1)). Also the isotropic tensors of first order are null (see (2.1.1)₁). The results related to the tensors of odd order are valid only in the isotropic case, when these tensors are invariant in form with respect to all rotations of axes frame (see Section 2.1), while the results related to the tensors of even order are valid both in the isotropic case and in the perfect isotropic case, when these tensors are invariant in form with respect to all rotations and inversions of axes frame, (see Sections 2.1 and 2.2).

A.1 SPECIAL FORM FOR ISOTROPIC TENSORS OF ORDER THREE

In the case where a third order isotropic tensor L_{ijk} has the symmetry

$$L_{ijk} = L_{jik}, \quad (\text{A.1.1})$$

(valid for the third order tensors β_{ijk}^s ($s = 3, 4, 6, 7$) in the rate equation (1.4.1)), we have $L_{ijk} = 0$.

In fact, from relation (2.1.1)₃ we can write

$$L_{jik} = L \epsilon_{jik} = -L \epsilon_{ijk}, \quad (\text{A.1.2})$$

and equating this last relation with (2.1.1)₃ we immediately deduce $L = 0$.

A.2 SPECIAL FORM FOR ISOTROPIC TENSORS OF ORDER FIVE

In the following we study the form of isotropic tensors of order five having special symmetries.

A.2.1 Case where a fifth order isotropic tensor L_{ijklm} has one particular symmetry

In the case when

$$L_{ijklm} = L_{jiklm}, \quad (\text{A.2.1})$$

(valid for the tensor β_{ijklm}^5 in equation (1.4.1)) we show that *the number of the significant independent components of this tensor reduces from 6 to 3.*

In fact, from (2.1.3) we have

$$L_{jiklm} = -L_1 \epsilon_{ijk} \delta_{lm} - L_2 \epsilon_{ijl} \delta_{km} - L_3 \epsilon_{ijm} \delta_{kl} + L_4 \epsilon_{jkl} \delta_{im} + L_5 \epsilon_{jkm} \delta_{li} + L_6 \epsilon_{jlm} \delta_{ik}. \quad (\text{A.2.2})$$

Equating (2.1.3) and (A.2.2) we obtain

$$L_{ijklm} = A_1 (\epsilon_{ikl} \delta_{jm} + \epsilon_{jkl} \delta_{im}) + A_2 (\epsilon_{ikm} \delta_{lj} + \epsilon_{jkm} \delta_{li}) + A_3 (\epsilon_{ilm} \delta_{jk} + \epsilon_{jlm} \delta_{ik}), \quad (\text{A.2.3})$$

where $A_1 = L_4$, $A_2 = L_5$ and $A_3 = L_6$.

A.2.2 Case where a fifth order isotropic tensor L_{ijklm} presents two symmetries

In the case when

$$L_{ijklm} = L_{jiklm}, \quad L_{ijklm} = L_{ijlkm}, \quad (\text{A.2.4})$$

(valid for the tensor β_{ijklm}^8 in equation (1.4.1)) we show that *the significant independent component of this tensor is only one.*

In fact, from (A.2.3) we have

$$L_{ijlkm} = -A_1 (\epsilon_{ikl} \delta_{jm} + \epsilon_{jkl} \delta_{im}) + A_2 (\epsilon_{ilm} \delta_{kj} + \epsilon_{jlm} \delta_{ki}) + A_3 (\epsilon_{ikm} \delta_{jl} + \epsilon_{jkm} \delta_{il}). \quad (\text{A.2.5})$$

Equating (A.2.3) and (A.2.5) we finally work out

$$L_{ijlkm} = L (\epsilon_{ikm} \delta_{lj} + \epsilon_{jkm} \delta_{li} + \epsilon_{ilm} \delta_{jk} + \epsilon_{jlm} \delta_{ik}), \quad (\text{A.2.6})$$

where $L \equiv A_2 = A_3$.

A.3 SPECIAL FORM FOR FOURTH ORDER ISOTROPIC AND PERFECT ISOTROPIC TENSORS

In this Section we will treat special symmetry properties of a fourth order tensor L_{ijkl} and we will demonstrate that L_{ijkl} can be expressed only by *two significant independent components* that will be called A_1 and A_2 .

A.3.1 Case where a fourth order isotropic tensor L_{ijkl} has one particular type of symmetry

In the case when

$$L_{ijkl} = L_{jikl}, \quad (\text{A.3.1})$$

(valid for tensors β_{ijkl}^1 and β_{ijkl}^2 in equation (1.4.1) and the tensor γ_{ijkl}^4 in equation (4.1.10)), from relation (2.1.2) we have

$$L_{jikl} = L_1 \delta_{ji} \delta_{kl} + L_2 \delta_{jk} \delta_{il} + L_3 \delta_{jl} \delta_{ik}. \quad (\text{A.3.2})$$

Adding equations (2.1.2) and (A.3.2), using $L_{ijkl} = L_{jikl}$ and multiplying by 1/2, we obtain

$$L_{ijkl} = A_1 \delta_{ij} \delta_{kl} + A_2 (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}), \quad (\text{A.3.3})$$

where $A_1 = L_1$ and $A_2 = (L_2 + L_3)/2$.

A.3.2 Case where a fourth order isotropic tensor L_{ijkl} has three symmetries

In the case when

$$L_{ijkl} = L_{jikl}, \quad L_{ijkl} = L_{ijlk}, \quad L_{ijkl} = L_{klij}, \quad (\text{A.3.4})$$

that are equivalent to the following chain of equalities

$$L_{ijklm} = L_{jilm} = L_{ijml} = L_{jiml} = L_{lmij} = L_{mlij} = L_{mlji} = L_{lmji}, \quad (\text{A.3.5})$$

(valid for the tensors c_{ijkl} , $\lambda_{ijkl}^{r\epsilon}$ and λ_{ijkl}^{rr} present in equations (1.3.11) and (1.3.13)), from (A.3.3) (that includes the symmetry (A.3.4)₁) we can see that also the symmetry (A.3.4)₂ is true, as well as (A.3.4)₃, because

$$L_{klij} = A_1 \delta_{kl} \delta_{ij} + A_2 (\delta_{ki} \delta_{lj} + \delta_{kj} \delta_{il}) = L_{ijkl}. \quad (\text{A.3.6})$$

The other symmetries in (A.3.5) are also satisfied. Thus, we use for the tensors c_{ijkl} , $\lambda_{ijkl}^{r\epsilon}$ and λ_{ijkl}^{rr} expression (A.3.3) again.

A.3.3 Case where a fourth order isotropic tensor L_{ijkl} has one particular symmetry of another type

In the case when

$$L_{ijkl} = L_{lijk}, \quad (\text{A.3.7})$$

(valid for the coefficients λ_{ijkl}^{vq} and $\lambda_{ijkl}^{vj^c}$ in equations (1.3.15)-(1.3.17)) from relation (2.1.2) we deduce

$$L_{lijk} = L_1 \delta_{li} \delta_{jk} + L_2 \delta_{lj} \delta_{ik} + L_3 \delta_{lk} \delta_{ij}. \quad (\text{A.3.8})$$

Using the same procedure seen in Subsection A.3.2, we obtain

$$L_{ijkl} = A_1 \delta_{ik} \delta_{jl} + A_2 (\delta_{ij} \delta_{kl} + \delta_{il} \delta_{jk}), \quad (\text{A.3.9})$$

where $A_1 = L_2$ and $A_2 = (L_1 + L_3)/2$.

It is useful to emphasize that the same result (A.3.9) is obtained if the symmetries $L_{ijkl} = L_{ilkj}$ and/or $L_{ijkl} = L_{kji l}$ are valid. These results are not used.

A.3.4 Case where a fourth order isotropic tensor L_{ijkl} has the symmetry $L_{ijkl} = L_{ikjl}$

In the case when

$$L_{ijkl} = L_{ikjl}, \quad (\text{A.3.10})$$

(valid for the tensors χ_{ijkl}^6 in equation (1.4.8) and ξ_{ijkl}^6 in equation (1.4.16)), from relation (2.1.2) we have

$$L_{ikjl} = L_1 \delta_{ik} \delta_{jl} + L_2 \delta_{ij} \delta_{kl} + L_3 \delta_{il} \delta_{kj}. \quad (\text{A.3.11})$$

Using the same procedure seen in Subsection A.3.2, we obtain

$$L_{ijkl} = A_1 \delta_{il} \delta_{jk} + A_2 (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl}), \quad (\text{A.3.12})$$

with $A_1 = L_3$ and $A_2 = (L_1 + L_2)/2$.

A.3.5 Case where a fourth order isotropic tensor L_{ijkl} has two symmetries

In the case when

$$L_{ijkl} = L_{ikjl}, \quad L_{ijkl} = L_{ljki}, \quad (\text{A.3.13})$$

that are equivalent to the following chain of equalities

$$L_{ijkl} = L_{ikjl} = L_{ljki} = L_{lkji}, \quad (\text{A.3.14})$$

(valid for the tensor ν_{ijkl}^6 in the temperature equation (1.5.12)), from (A.3.12) (that includes the symmetry (A.3.13)₁) we can see that also the symmetry (A.3.13)₂ is satisfied, so that we use for the tensor ν_{ijkl}^6 expression (A.3.12) again.

A.4 SPECIAL FORM FOR ISOTROPIC AND PERFECT ISOTROPIC TENSORS OF ORDER SIX

In this Section we will treat special symmetry properties of a sixth order tensor L_{ijklmn} and we will demonstrate that the number of its *significant independent components* is reduced.

A.4.1 Case where a sixth order isotropic tensor L_{ijklmn} has one particular symmetry

In the case when

$$L_{ijklmn} = L_{lmnij k}, \quad (\text{A.4.1})$$

(valid for the tensor λ_{ijklmn}^{vv} in equation (1.3.15)) we show that the number of *the significant independent components of this tensor reduce from 15 to 11*.

In fact, writing relation (2.1.4) in the case of $L_{lmnij k}$ (i.e. by exchanging indexes $\{i, j, k\}$ with indexes $\{l, m, n\}$), we obtain

$$\begin{aligned} L_{lmnij k} = & L_1 \delta_{lm} \delta_{ni} \delta_{jk} + L_2 \delta_{lm} \delta_{nj} \delta_{ik} + L_3 \delta_{lm} \delta_{nk} \delta_{ij} + L_4 \delta_{ln} \delta_{mi} \delta_{jk} + L_5 \delta_{ln} \delta_{mj} \delta_{ik} \\ & + L_6 \delta_{ln} \delta_{mk} \delta_{ij} + L_7 \delta_{li} \delta_{mn} \delta_{jk} + L_8 \delta_{li} \delta_{mj} \delta_{nk} + L_9 \delta_{li} \delta_{mk} \delta_{nj} + L_{10} \delta_{lj} \delta_{mn} \delta_{ik} \\ & + L_{11} \delta_{lj} \delta_{mi} \delta_{nk} + L_{12} \delta_{lj} \delta_{mk} \delta_{ni} + L_{13} \delta_{lk} \delta_{mn} \delta_{ij} + L_{14} \delta_{lk} \delta_{mi} \delta_{nj} + L_{15} \delta_{lk} \delta_{mj} \delta_{ni}. \end{aligned} \quad (\text{A.4.2})$$

Adding relation (A.4.2) to (2.1.4) and multiplying by 1/2, we work out

$$\begin{aligned} L_{ijklmn} = & A_1 (\delta_{ij} \delta_{kl} \delta_{mn} + \delta_{in} \delta_{jk} \delta_{lm}) + A_2 (\delta_{ij} \delta_{km} \delta_{ln} + \delta_{ik} \delta_{jn} \delta_{lm}) + A_3 \delta_{ij} \delta_{kn} \delta_{lm} \\ & + A_4 (\delta_{ik} \delta_{jl} \delta_{mn} + \delta_{im} \delta_{jk} \delta_{nl}) + A_5 \delta_{ik} \delta_{jm} \delta_{ln} + A_6 \delta_{il} \delta_{jk} \delta_{mn} + A_7 \delta_{il} \delta_{jm} \delta_{kn} \\ & + A_8 \delta_{il} \delta_{jn} \delta_{km} + A_9 \delta_{im} \delta_{jl} \delta_{kn} + A_{10} (\delta_{im} \delta_{jn} \delta_{kl} + \delta_{in} \delta_{jl} \delta_{km}) + A_{11} \delta_{in} \delta_{jm} \delta_{kl}, \end{aligned} \quad (\text{A.4.3})$$

with $A_1 = (L_1 + L_{13})/2$, $A_2 = (L_2 + L_6)/2$, $A_3 = L_3$, $A_4 = (L_4 + L_{10})/2$, $A_5 = L_5$, $A_6 = L_7$, $A_7 = L_8$, $A_8 = L_9$, $A_9 = L_{11}$, $A_{10} = (L_{12} + L_{14})/2$, $A_{11} = L_{15}$.

A.4.2 Case where a sixth order isotropic tensor L_{ijklmn} has one particular symmetry of another type

In the case when

$$L_{ijklmn} = L_{ijkmln}, \quad (\text{A.4.4})$$

(valid for the tensor γ_{ijklmn}^6 in equation (1.4.16)) we show that the number of *the significant independent components of this tensor reduce from 15 to 9*.

In fact, writing relation (2.1.4) in the case of L_{ijkmln} (i.e. by exchanging index l with index m), we have

$$\begin{aligned} L_{ijkmln} = & L_1 \delta_{ij} \delta_{km} \delta_{ln} + L_2 \delta_{ij} \delta_{kl} \delta_{mn} + L_3 \delta_{ij} \delta_{kn} \delta_{ml} + L_4 \delta_{ik} \delta_{jm} \delta_{ln} + L_5 \delta_{ik} \delta_{jl} \delta_{mn} \\ & + L_6 \delta_{ik} \delta_{jn} \delta_{ml} + L_7 \delta_{im} \delta_{jk} \delta_{ln} + L_8 \delta_{im} \delta_{jl} \delta_{kn} + L_9 \delta_{im} \delta_{jn} \delta_{kl} + L_{10} \delta_{il} \delta_{jk} \delta_{mn} \\ & + L_{11} \delta_{il} \delta_{jm} \delta_{kn} + L_{12} \delta_{il} \delta_{jn} \delta_{km} + L_{13} \delta_{in} \delta_{jk} \delta_{ml} + L_{14} \delta_{in} \delta_{jm} \delta_{kl} + L_{15} \delta_{in} \delta_{jl} \delta_{km}. \end{aligned} \quad (\text{A.4.5})$$

Adding this relation to (2.1.4), using (A.4.4) and multiplying by 1/2, we have

$$\begin{aligned}
L_{ijklmn} = & A_1(\delta_{kl}\delta_{mn} + \delta_{km}\delta_{ln})\delta_{ij} + A_2\delta_{ij}\delta_{kn}\delta_{lm} + A_3(\delta_{jl}\delta_{mn} + \delta_{jm}\delta_{ln})\delta_{ik} + A_4\delta_{ik}\delta_{jn}\delta_{lm} \\
& + A_5(\delta_{il}\delta_{mn} + \delta_{im}\delta_{ln})\delta_{jk} + A_6(\delta_{il}\delta_{jm} + \delta_{im}\delta_{jl})\delta_{kn} + A_7(\delta_{il}\delta_{km} + \delta_{im}\delta_{kl})\delta_{jn} \\
& + A_8\delta_{in}\delta_{jk}\delta_{lm} + A_9(\delta_{jl}\delta_{km} + \delta_{jm}\delta_{kl})\delta_{in},
\end{aligned} \tag{A.4.6}$$

where $A_1 = (L_1 + L_2)/2$, $A_2 = L_3$, $A_3 = (L_4 + L_5)/2$, $A_4 = L_6$, $A_5 = (L_7 + L_{10})/2$, $A_6 = (L_8 + L_{11})/2$, $A_7 = (L_9 + L_{12})/2$, $A_8 = L_{13}$, $A_9 = (L_{14} + L_{15})/2$.

A.4.3 Case where a sixth order isotropic tensor L_{ijklmn} has two particular symmetries

In the case where a sixth order perfect isotropic tensor L_{ijklmn} has the two symmetries

$$L_{ijklmn} = L_{jiklmn}, \quad L_{ijklmn} = L_{ijkmln}, \tag{A.4.7}$$

equivalent to

$$L_{ijklmn} = L_{jiklmn} = L_{ijkmln} = L_{ijkmln}, \tag{A.4.8}$$

(valid for the tensors γ_{ijklmn}^3 and γ_{ijklmn}^6 in equation (4.1.3)) we show that *the number of significant independent components of this tensors reduce from 15 to 6.*

In fact, writing relation (2.1.4) in the case of L_{jiklmn} (i.e. changing the index i with j), we have

$$\begin{aligned}
L_{jiklmn} = & L_1\delta_{ji}\delta_{kl}\delta_{mn} + L_2\delta_{ji}\delta_{km}\delta_{ln} + L_3\delta_{ji}\delta_{kn}\delta_{lm} + L_4\delta_{jk}\delta_{il}\delta_{mn} + L_5\delta_{jk}\delta_{im}\delta_{ln} \\
& + L_6\delta_{jk}\delta_{in}\delta_{lm} + L_7\delta_{jl}\delta_{ik}\delta_{mn} + L_8\delta_{jl}\delta_{im}\delta_{kn} + L_9\delta_{jl}\delta_{in}\delta_{km} + L_{10}\delta_{jm}\delta_{ik}\delta_{ln} \\
& + L_{11}\delta_{jm}\delta_{il}\delta_{kn} + L_{12}\delta_{jm}\delta_{in}\delta_{kl} + L_{13}\delta_{jn}\delta_{ik}\delta_{lm} + L_{14}\delta_{jn}\delta_{il}\delta_{km} + L_{15}\delta_{jn}\delta_{im}\delta_{kl}.
\end{aligned} \tag{A.4.9}$$

Matching expressions (A.4.9) and (2.1.4), by virtue of (A.4.7), we obtain

$$\begin{aligned}
L_{ijklmn} = & B_1\delta_{ij}\delta_{kl}\delta_{mn} + B_2\delta_{ij}\delta_{km}\delta_{ln} + B_3\delta_{ij}\delta_{kn}\delta_{lm} + B_4(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\delta_{mn} \\
& + B_5(\delta_{ik}\delta_{jm} + \delta_{im}\delta_{jk})\delta_{ln} + B_6(\delta_{ik}\delta_{jn} + \delta_{in}\delta_{jk})\delta_{lm} + B_7(\delta_{il}\delta_{jm} + \delta_{im}\delta_{jl})\delta_{kn} \\
& + B_8(\delta_{il}\delta_{jn} + \delta_{in}\delta_{jl})\delta_{km} + B_9(\delta_{im}\delta_{jn} + \delta_{in}\delta_{jm})\delta_{kl};
\end{aligned} \tag{A.4.10}$$

with

$$\begin{aligned}
B_1 = L_1; \quad B_2 = L_2; \quad B_3 = L_3; \quad B_4 = L_4 = L_7; \quad B_5 = L_5 = L_{10}; \\
B_6 = L_6 = L_{13}; \quad B_7 = L_8 = L_{11}; \quad B_8 = L_9 = L_{14}; \quad B_9 = L_{12} = L_{15}.
\end{aligned} \tag{A.4.11}$$

Writing relation (2.1.4) in the case of L_{ijkmln} (i.e. changing the index l with m), we have

$$\begin{aligned}
L_{ijkmln} = & L_1\delta_{ij}\delta_{km}\delta_{ln} + L_2\delta_{ij}\delta_{kl}\delta_{mn} + L_3\delta_{ij}\delta_{kn}\delta_{ml} + L_4\delta_{ik}\delta_{jm}\delta_{ln} + L_5\delta_{ik}\delta_{jl}\delta_{mn} \\
& + L_6\delta_{ik}\delta_{jn}\delta_{ml} + L_7\delta_{im}\delta_{jk}\delta_{ln} + L_8\delta_{im}\delta_{jl}\delta_{kn} + L_9\delta_{im}\delta_{jn}\delta_{kl} + L_{10}\delta_{il}\delta_{jk}\delta_{mn} \\
& + L_{11}\delta_{il}\delta_{jm}\delta_{kn} + L_{12}\delta_{il}\delta_{jn}\delta_{km} + L_{13}\delta_{in}\delta_{jk}\delta_{ml} + L_{14}\delta_{in}\delta_{jm}\delta_{kl} + L_{15}\delta_{in}\delta_{jl}\delta_{km}.
\end{aligned} \tag{A.4.12}$$

Matching relations (A.4.12) and (2.1.4) and using (A.4.8), we obtain

$$\begin{aligned}
L_{ijklmn} = & C_1(\delta_{kl}\delta_{mn} + \delta_{km}\delta_{ln})\delta_{ij} + C_2\delta_{ij}\delta_{kn}\delta_{lm} + C_3(\delta_{jl}\delta_{mn} + \delta_{jm}\delta_{ln})\delta_{ik} + C_4\delta_{ik}\delta_{jn}\delta_{lm} \\
& + C_5(\delta_{il}\delta_{mn} + \delta_{im}\delta_{ln})\delta_{jk} + C_6(\delta_{il}\delta_{jm} + \delta_{im}\delta_{jl})\delta_{kn} + C_7(\delta_{il}\delta_{km} + \delta_{im}\delta_{kl})\delta_{jn} \\
& + C_8\delta_{in}\delta_{jk}\delta_{lm} + C_9(\delta_{jl}\delta_{km} + \delta_{jm}\delta_{kl})\delta_{in},
\end{aligned} \tag{A.4.13}$$

with

$$\begin{aligned}
C_1 = L_1 = L_2; \quad C_2 = L_3; \quad C_3 = L_4 = L_5; \quad C_4 = L_6; \quad C_5 = L_7 = L_{10}; \\
C_6 = L_8 = L_{11}; \quad C_7 = L_9 = L_{12}; \quad C_8 = L_{13}; \quad C_9 = L_{14} = L_{15}.
\end{aligned} \tag{A.4.14}$$

From the match of relations (A.4.10) and (A.4.13), we obtain the special form of a sixth order perfect isotropic tensor having the symmetries (A.4.7)

$$\begin{aligned}
L_{ijklmn} = & D_1(\delta_{kl}\delta_{mn} + \delta_{km}\delta_{ln})\delta_{ij} + D_2\delta_{ij}\delta_{kn}\delta_{lm} + D_3[(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\delta_{mn} + \\
& + (\delta_{ik}\delta_{jm} + \delta_{im}\delta_{jk})\delta_{ln}] + D_4(\delta_{ik}\delta_{jn} + \delta_{in}\delta_{jk})\delta_{lm} + D_5(\delta_{il}\delta_{jm} + \delta_{im}\delta_{jl})\delta_{kn} \\
& + D_6[(\delta_{il}\delta_{jn} + \delta_{in}\delta_{jl})\delta_{km} + (\delta_{im}\delta_{jn} + \delta_{in}\delta_{jm})\delta_{kl}],
\end{aligned} \tag{A.4.15}$$

with

$$\begin{aligned}
D_1 = B_1 = B_2 = C_1 = L_1 = L_2; \quad D_2 = B_3 = C_2 = L_3; \\
D_3 = B_4 = B_5 = C_3 = C_5 = L_4 = L_5 = L_7 = L_{10}; \\
D_4 = B_6 = C_4 = C_8 = L_6 = L_{13}; \quad D_5 = B_7 = C_6 = L_8 = L_{11}; \\
D_6 = B_8 = B_9 = C_7 = C_9 = L_9 = L_{12} = L_{14} = L_{15}.
\end{aligned} \tag{A.4.16}$$

where we have used expressions (A.4.11) and (A.4.14).

B | OBJECTIVE REPRESENTATION OF FUNCTIONS

B.1 OBJECTIVE REPRESENTATION OF SCALAR FUNCTIONS

Following [2], [3] and [4] a scalar objective function f , that depends on m scalar function, namely a_1, a_2, \dots, a_m and l second-order symmetric tensors, namely A_1, A_2, \dots, A_l , is represented as function of the following quantities, called *invariants*

$$a_s, \quad \text{tr} A_i, \quad \text{tr} A_i^2, \quad \text{tr} A_i^3, \quad \text{tr}(A_i A_j), \quad \text{tr}(A_i^2 A_j), \quad \text{tr}(A_i^2 A_j^2), \quad \text{tr}(A_i A_j A_k), \quad (\text{B.1.1})$$

with $s = 1, \dots, m$, $i, j, k = 1, \dots, l$ and $i \neq j \neq k$.

Thus, we have

$$f = f\left(a_s, \text{tr} A_i, \text{tr} A_i^2, \text{tr} A_i^3, \text{tr}(A_i A_j), \text{tr}(A_i^2 A_j), \text{tr}(A_i^2 A_j^2), \text{tr}(A_i A_j A_k)\right), \quad (\text{B.1.2})$$

If we consider the scalar constitutive function $S = S(T, \boldsymbol{\varepsilon}, \mathbf{m}, \mathbf{r})$ of our theoretical model we have $m = 1$, with $a_1 \equiv T$, and $l = 3$, with $A_1 \equiv \boldsymbol{\varepsilon}$, $A_2 \equiv \mathbf{m}$, $A_3 \equiv \mathbf{r}$.

Then, we have $s = 1$, $i, j, k = 1, 2, 3$ and $i \neq j \neq k$ and the invariants for the entropy S are

$$\begin{aligned} T, \quad \text{tr} \boldsymbol{\varepsilon}, \quad \text{tr} \mathbf{m}, \quad \text{tr} \mathbf{r}, \quad \text{tr} \boldsymbol{\varepsilon}^2, \quad \text{tr} \mathbf{m}^2, \quad \text{tr} \mathbf{r}^2, \quad \text{tr} \boldsymbol{\varepsilon}^3, \quad \text{tr} \mathbf{m}^3, \quad \text{tr} \mathbf{r}^3, \quad \text{tr}(\boldsymbol{\varepsilon} \mathbf{m}), \\ \text{tr}(\boldsymbol{\varepsilon} \mathbf{r}), \quad \text{tr}(\mathbf{m} \mathbf{r}), \quad \text{tr}(\boldsymbol{\varepsilon}^2 \mathbf{m}), \quad \text{tr}(\boldsymbol{\varepsilon}^2 \mathbf{r}), \quad \text{tr}(\mathbf{m}^2 \boldsymbol{\varepsilon}), \quad \text{tr}(\mathbf{m}^2 \mathbf{r}), \quad \text{tr}(\mathbf{r}^2 \boldsymbol{\varepsilon}), \quad \text{tr}(\mathbf{r}^2 \mathbf{m}), \\ \text{tr}(\boldsymbol{\varepsilon}^2 \mathbf{m}^2), \quad \text{tr}(\boldsymbol{\varepsilon}^2 \mathbf{r}^2), \quad \text{tr}(\mathbf{m}^2 \mathbf{r}^2), \quad \text{tr}(\boldsymbol{\varepsilon} \mathbf{m} \mathbf{r}), \end{aligned} \quad (\text{B.1.3})$$

or in Cartesian components

$$\begin{aligned} T, \quad \varepsilon_{ii}, \quad m_{ii}, \quad r_{ii}, \quad \varepsilon_{ij} \varepsilon_{ji}, \quad m_{ij} m_{ji}, \quad r_{ij} r_{ji}, \quad \varepsilon_{ij} \varepsilon_{jk} \varepsilon_{ki}, \quad m_{ij} m_{jk} m_{ki}, \quad r_{ij} r_{jk} r_{ki}, \\ \varepsilon_{ij} m_{ji}, \quad \varepsilon_{ij} r_{ji}, \quad m_{ij} r_{ji}, \quad \varepsilon_{ij} \varepsilon_{jk} m_{ki}, \quad \varepsilon_{ij} \varepsilon_{jk} r_{ki}, \quad m_{ij} m_{jk} \varepsilon_{ki}, \quad m_{ij} m_{jk} r_{ki}, \quad r_{ij} r_{jk} \varepsilon_{ki}, \\ r_{ij} r_{jk} m_{ki}, \quad \varepsilon_{ij} \varepsilon_{jk} m_{kl} m_{li}, \quad \varepsilon_{ij} \varepsilon_{jk} r_{kl} r_{li}, \quad m_{ij} m_{jk} r_{kl} r_{li}, \quad \varepsilon_{ij} m_{jk} r_{ki}. \end{aligned} \quad (\text{B.1.4})$$

Being $\boldsymbol{\varepsilon}$, \mathbf{m} and \mathbf{r} symmetric tensors, it is also possible to write, for instance, $\varepsilon_{ij} \varepsilon_{ji} = \varepsilon_{ij} \varepsilon_{ij}$, $m_{ij} r_{ji} = m_{ij} r_{ij}$.

Assuming for S a polynomial form, S may be expressed in the form

$$\begin{aligned} S = S^1 T + S^2 \text{tr} \boldsymbol{\varepsilon} + S^3 \text{tr} \mathbf{m} + S^4 \text{tr} \mathbf{r} + S^5 \text{tr} \boldsymbol{\varepsilon}^2 + S^6 \text{tr} \mathbf{m}^2 + S^7 \text{tr} \mathbf{r}^2 + S^8 \text{tr} \boldsymbol{\varepsilon}^3 + S^9 \text{tr} \mathbf{m}^3 \\ + S^{10} \text{tr} \mathbf{r}^3 + S^{11} \text{tr}(\boldsymbol{\varepsilon} \mathbf{m}) + S^{12} \text{tr}(\boldsymbol{\varepsilon} \mathbf{r}) + S^{13} \text{tr}(\mathbf{m} \mathbf{r}) + S^{14} \text{tr}(\boldsymbol{\varepsilon}^2 \mathbf{m}) + S^{15} \text{tr}(\boldsymbol{\varepsilon}^2 \mathbf{r}) \\ + S^{16} \text{tr}(\mathbf{m}^2 \boldsymbol{\varepsilon}) + S^{17} \text{tr}(\mathbf{m}^2 \mathbf{r}) + S^{18} \text{tr}(\mathbf{r}^2 \boldsymbol{\varepsilon}) + S^{19} \text{tr}(\mathbf{r}^2 \mathbf{m}) + S^{20} \text{tr}(\boldsymbol{\varepsilon}^2 \mathbf{m}^2) \\ + S^{21} \text{tr}(\boldsymbol{\varepsilon}^2 \mathbf{r}^2) + S^{22} \text{tr}(\mathbf{m}^2 \mathbf{r}^2) + S^{23} \text{tr}(\boldsymbol{\varepsilon} \mathbf{m} \mathbf{r}), \end{aligned} \quad (\text{B.1.5})$$

with $S^\alpha = S^\alpha(T, \boldsymbol{\varepsilon}, \mathbf{m}, \mathbf{r})$, $\alpha = 1, \dots, 23$ objective scalar functions, and then depending on the invariants (B.1.3). The expression (3.6.1) is a first approximated form of (B.1.5), being $\mathbf{m} = \dot{\boldsymbol{\varepsilon}}$.

B.2 OBJECTIVE REPRESENTATION OF SYMMETRIC TENSOR FUNCTIONS

In this Section we consider two situations: a) a first case where a second order symmetric objective tensor depends on scalar functions and second order symmetric tensors; b) a second case where a second order symmetric objective tensor depends on scalar functions, second order symmetric tensors and polar vectors.

CASE A). Following [1], [2], [3] and [4] a second order symmetric tensor \mathbf{H} , that depends on m scalar functions, namely a_1, a_2, \dots, a_m (in the case of the pressure tensor \mathbf{P} , $m = 1$ and $a_1 \equiv T$), and l second-order symmetric tensors, namely $\mathbf{A}_1, \mathbf{A}_2, \dots, \mathbf{A}_l$ (in our case $l = 3$ and $\mathbf{A}_1 \equiv \boldsymbol{\varepsilon}$, $\mathbf{A}_2 \equiv \mathbf{m}$, $\mathbf{A}_3 \equiv \mathbf{r}$), is expressed as polynomial form constructed on the following invariants

$$\mathbf{U}, \quad \mathbf{A}_i, \quad \mathbf{A}_i^2, \quad \mathbf{A}_i \mathbf{A}_j + \mathbf{A}_j \mathbf{A}_i, \quad \mathbf{A}_i^2 \mathbf{A}_j + \mathbf{A}_j \mathbf{A}_i^2, \quad \mathbf{A}_i^2 \mathbf{A}_j^2 + \mathbf{A}_j^2 \mathbf{A}_i^2, \quad (\text{B.2.1})$$

with $i, j = 1, \dots, l$ and $i \neq j$, i.e.

$$\mathbf{H} = \sum_{\alpha=1}^r H^\alpha \mathbf{H}_\alpha, \quad (\text{B.2.2})$$

where $H^\alpha = H^\alpha(a_1, a_2, \dots, a_m, \mathbf{A}_1, \mathbf{A}_2, \dots, \mathbf{A}_l)$, $\alpha = 1, \dots, r$, are objective scalar functions (depending on the invariants (B.1.1)) and \mathbf{H}_α are built on the set of invariants of the list (B.2.1).

Thus, for $\mathbf{P} = \mathbf{P}(T, \boldsymbol{\varepsilon}, \mathbf{m}, \mathbf{r})$ they are

$$\begin{aligned} & \mathbf{U}, \quad \boldsymbol{\varepsilon}, \quad \mathbf{m}, \quad \mathbf{r}, \quad \boldsymbol{\varepsilon}^2, \quad \mathbf{m}^2, \quad \mathbf{r}^2, \quad \boldsymbol{\varepsilon} \mathbf{m} + \mathbf{m} \boldsymbol{\varepsilon}, \quad \boldsymbol{\varepsilon} \mathbf{r} + \mathbf{r} \boldsymbol{\varepsilon}, \quad \mathbf{m} \mathbf{r} + \mathbf{r} \mathbf{m}, \\ & \boldsymbol{\varepsilon}^2 \mathbf{m} + \mathbf{m} \boldsymbol{\varepsilon}^2, \quad \boldsymbol{\varepsilon}^2 \mathbf{r} + \mathbf{r} \boldsymbol{\varepsilon}^2, \quad \mathbf{m}^2 \mathbf{r} + \mathbf{r} \mathbf{m}^2, \quad \mathbf{m}^2 \boldsymbol{\varepsilon} + \boldsymbol{\varepsilon} \mathbf{m}^2, \quad \mathbf{r}^2 \mathbf{m} + \mathbf{m} \mathbf{r}^2, \\ & \mathbf{r}^2 \boldsymbol{\varepsilon} + \boldsymbol{\varepsilon} \mathbf{r}^2, \quad \boldsymbol{\varepsilon}^2 \mathbf{m}^2 + \mathbf{m}^2 \boldsymbol{\varepsilon}^2, \quad \boldsymbol{\varepsilon}^2 \mathbf{r}^2 + \mathbf{r}^2 \boldsymbol{\varepsilon}^2, \quad \mathbf{m}^2 \mathbf{r}^2 + \mathbf{r}^2 \mathbf{m}^2, \end{aligned} \quad (\text{B.2.3})$$

where, for instance $\boldsymbol{\varepsilon}^2 \mathbf{m} + \mathbf{m} \boldsymbol{\varepsilon}^2 \equiv (\varepsilon_{ik} \varepsilon_{kl} m_{lj} + m_{ik} \varepsilon_{kl} \varepsilon_{lj})$, $\boldsymbol{\varepsilon}^2 \mathbf{m}^2 + \mathbf{m}^2 \boldsymbol{\varepsilon}^2 \equiv (\varepsilon_{ik} \varepsilon_{kl} m_{lp} m_{pj} + m_{ik} m_{kl} \varepsilon_{lp} \varepsilon_{pj})$. Thus, according to (B.2.2) the general form of \mathbf{P} is

$$\begin{aligned} \mathbf{P} = & P^1 \mathbf{U} + P^2 \boldsymbol{\varepsilon} + P^3 \mathbf{m} + P^4 \mathbf{r} + P^5 \boldsymbol{\varepsilon}^2 + P^6 \mathbf{m}^2 + P^7 \mathbf{r}^2 + P^8 (\boldsymbol{\varepsilon} \mathbf{m} + \mathbf{m} \boldsymbol{\varepsilon}) + P^9 (\boldsymbol{\varepsilon} \mathbf{r} + \mathbf{r} \boldsymbol{\varepsilon}) \\ & + P^{10} (\mathbf{m} \mathbf{r} + \mathbf{r} \mathbf{m}) + P^{11} (\boldsymbol{\varepsilon}^2 \mathbf{m} + \mathbf{m} \boldsymbol{\varepsilon}^2) + P^{12} (\boldsymbol{\varepsilon}^2 \mathbf{r} + \mathbf{r} \boldsymbol{\varepsilon}^2) + P^{13} (\mathbf{m}^2 \mathbf{r} + \mathbf{r} \mathbf{m}^2) \\ & + P^{14} (\mathbf{m}^2 \boldsymbol{\varepsilon} + \boldsymbol{\varepsilon} \mathbf{m}^2) + P^{15} (\mathbf{r}^2 \mathbf{m} + \mathbf{m} \mathbf{r}^2) + P^{16} (\mathbf{r}^2 \boldsymbol{\varepsilon} + \boldsymbol{\varepsilon} \mathbf{r}^2) + P^{17} (\boldsymbol{\varepsilon}^2 \mathbf{m}^2 + \mathbf{m}^2 \boldsymbol{\varepsilon}^2) \\ & + P^{18} (\boldsymbol{\varepsilon}^2 \mathbf{r}^2 + \mathbf{r}^2 \boldsymbol{\varepsilon}^2) + P^{19} (\mathbf{m}^2 \mathbf{r}^2 + \mathbf{r}^2 \mathbf{m}^2), \end{aligned} \quad (\text{B.2.4})$$

where $P^\alpha = P^\alpha(T, \boldsymbol{\varepsilon}, \mathbf{m}, \mathbf{r})$, $\alpha = 1, \dots, 19$, are objective scalar functions (and than depending on the invariants (B.1.3)). The expression (3.6.2) is a first approximated form of (B.2.4), with $\mathbf{m} = \dot{\boldsymbol{\varepsilon}}$.

CASE B). Following [1], [2], [3] and [4] in the case where the second-order symmetric tensor \mathbf{H} depends also on a vector \mathbf{w} (as in the case of \mathcal{M} and $\mathcal{R}^{(i)}$, with $\mathbf{w} \equiv \nabla T$), it is expressed as polynomial of the form (B.2.2), with \mathbf{H}^α the following invariants

$$\begin{aligned} & \mathbf{U}, \quad A_i, \quad A_i^2, \quad A_i A_j + A_j A_i, \quad A_i^2 A_j + A_j A_i^2, \quad A_i^2 A_j^2 + A_j^2 A_i^2, \\ & \mathbf{w} \otimes \mathbf{w}, \quad \mathbf{w} \otimes (A_i \mathbf{w}) + (A_i \mathbf{w}) \otimes \mathbf{w}, \quad \mathbf{w} \otimes (A_i^2 \mathbf{w}) + (A_i^2 \mathbf{w}) \otimes \mathbf{w} \end{aligned} \quad (\text{B.2.5})$$

and the objective scalar functions $H^\alpha(a_1, a_2, \dots, a_m, A_1, A_2, \dots, A_l, \mathbf{w})$ depending on the invariants

$$\begin{aligned} & a_s, \quad \text{tr} A_i, \quad \text{tr} A_i^2, \quad \text{tr} A_i^3, \quad \text{tr}(A_i A_j), \quad \text{tr}(A_i^2 A_j), \quad \text{tr}(A_i^2 A_j^2), \quad \text{tr}(A_i A_j A_k), \\ & \mathbf{w} \cdot \mathbf{w}, \quad \mathbf{w} \cdot (A_i \mathbf{w}), \quad \mathbf{w} \cdot (A_i^2 \mathbf{w}), \quad (A_i \mathbf{w}) \cdot (A_j \mathbf{w}), \end{aligned} \quad (\text{B.2.6})$$

with $s = 1, \dots, m$, $i, j = 1, \dots, l$ and $i \neq j$.

In the case of \mathcal{M} and $\mathcal{R}^{(i)}$ we have $m = 1$ and $a_1 \equiv T$, $l = 3$ and $A_1 \equiv \boldsymbol{\varepsilon}$, $A_2 \equiv \mathbf{m}$, $A_3 \equiv \mathbf{r}$, and $\mathbf{w} \equiv \nabla T$. Then, the second order symmetric tensors $\mathcal{M}(T, \nabla T, \boldsymbol{\varepsilon}, \mathbf{m}, \mathbf{r})$ and $\mathcal{R}^{(i)}(T, \nabla T, \boldsymbol{\varepsilon}, \mathbf{m}, \mathbf{r})$ are built on the following invariants

$$\begin{aligned} & \mathbf{U}, \quad \boldsymbol{\varepsilon}, \quad \mathbf{m}, \quad \mathbf{r}, \quad \boldsymbol{\varepsilon}^2, \quad \mathbf{m}^2, \quad \mathbf{r}^2, \quad \boldsymbol{\varepsilon} \mathbf{m} + \mathbf{m} \boldsymbol{\varepsilon}, \quad \boldsymbol{\varepsilon} \mathbf{r} + \mathbf{r} \boldsymbol{\varepsilon}, \quad \mathbf{m} \mathbf{r} + \mathbf{r} \mathbf{m}, \\ & \boldsymbol{\varepsilon}^2 \mathbf{m} + \mathbf{m} \boldsymbol{\varepsilon}^2, \quad \boldsymbol{\varepsilon}^2 \mathbf{r} + \mathbf{r} \boldsymbol{\varepsilon}^2, \quad \mathbf{m}^2 \mathbf{r} + \mathbf{r} \mathbf{m}^2, \quad \mathbf{m}^2 \boldsymbol{\varepsilon} + \boldsymbol{\varepsilon} \mathbf{m}^2, \quad \mathbf{r}^2 \mathbf{m} + \mathbf{m} \mathbf{r}^2, \\ & \mathbf{r}^2 \boldsymbol{\varepsilon} + \boldsymbol{\varepsilon} \mathbf{r}^2, \quad \boldsymbol{\varepsilon}^2 \mathbf{m}^2 + \mathbf{m}^2 \boldsymbol{\varepsilon}^2, \quad \boldsymbol{\varepsilon}^2 \mathbf{r}^2 + \mathbf{r}^2 \boldsymbol{\varepsilon}^2, \quad \mathbf{m}^2 \mathbf{r}^2 + \mathbf{r}^2 \mathbf{m}^2, \\ & \nabla T \otimes \nabla T, \quad \nabla T \otimes (\boldsymbol{\varepsilon} \nabla T) + (\boldsymbol{\varepsilon} \nabla T) \otimes \nabla T, \quad \nabla T \otimes (\mathbf{m} \nabla T) + (\mathbf{m} \nabla T) \otimes \nabla T, \\ & \nabla T \otimes (\mathbf{r} \nabla T) + (\mathbf{r} \nabla T) \otimes \nabla T, \quad \nabla T \otimes (\boldsymbol{\varepsilon}^2 \nabla T) + (\boldsymbol{\varepsilon}^2 \nabla T) \otimes \nabla T, \\ & \nabla T \otimes (\mathbf{m}^2 \nabla T) + (\mathbf{m}^2 \nabla T) \otimes \nabla T, \quad \nabla T \otimes (\mathbf{r}^2 \nabla T) + (\mathbf{r}^2 \nabla T) \otimes \nabla T., \end{aligned} \quad (\text{B.2.7})$$

where, for instance, $\nabla T \otimes \nabla T \equiv (T_{,i} T_{,j})$, $\nabla T \otimes (\boldsymbol{\varepsilon} \nabla T) + (\boldsymbol{\varepsilon} \nabla T) \otimes \nabla T \equiv (T_{,i} \boldsymbol{\varepsilon}_{jk} T_{,k} + \boldsymbol{\varepsilon}_{ik} T_{,k} T_{,j})$ and $\nabla T \otimes (\boldsymbol{\varepsilon}^2 \nabla T) + (\boldsymbol{\varepsilon}^2 \nabla T) \otimes \nabla T \equiv (T_{,i} \boldsymbol{\varepsilon}_{jl} \boldsymbol{\varepsilon}_{lk} T_{,k} + \boldsymbol{\varepsilon}_{il} \boldsymbol{\varepsilon}_{lk} T_{,k} T_{,j})$.

Thus, we have for \mathcal{M} and $\mathcal{R}^{(i)}$, according to (B.2.2), the following expressions

$$\begin{aligned} \mathcal{M} = & M^1 \mathbf{U} + M^2 \boldsymbol{\varepsilon} + M^3 \mathbf{m} + M^4 \mathbf{r} + M^5 \boldsymbol{\varepsilon}^2 + M^6 \mathbf{m}^2 + M^7 \mathbf{r}^2 + M^8 (\boldsymbol{\varepsilon} \mathbf{m} + \mathbf{m} \boldsymbol{\varepsilon}) \\ & + M^9 (\boldsymbol{\varepsilon} \mathbf{r} + \mathbf{r} \boldsymbol{\varepsilon}) + M^{10} (\mathbf{m} \mathbf{r} + \mathbf{r} \mathbf{m}) + M^{11} (\boldsymbol{\varepsilon}^2 \mathbf{m} + \mathbf{m} \boldsymbol{\varepsilon}^2) + M^{12} (\boldsymbol{\varepsilon}^2 \mathbf{r} + \mathbf{r} \boldsymbol{\varepsilon}^2) \\ & + M^{13} (\mathbf{m}^2 \mathbf{r} + \mathbf{r} \mathbf{m}^2) + M^{14} (\mathbf{m}^2 \boldsymbol{\varepsilon} + \boldsymbol{\varepsilon} \mathbf{m}^2) + M^{15} (\mathbf{r}^2 \mathbf{m} + \mathbf{m} \mathbf{r}^2) + M^{16} (\mathbf{r}^2 \boldsymbol{\varepsilon} + \boldsymbol{\varepsilon} \mathbf{r}^2) \\ & + M^{17} (\boldsymbol{\varepsilon}^2 \mathbf{m}^2 + \mathbf{m}^2 \boldsymbol{\varepsilon}^2) + M^{18} (\boldsymbol{\varepsilon}^2 \mathbf{r}^2 + \mathbf{r}^2 \boldsymbol{\varepsilon}^2) + M^{19} (\mathbf{m}^2 \mathbf{r}^2 + \mathbf{r}^2 \mathbf{m}^2) + M^{20} (\nabla T \otimes \nabla T) \\ & + M^{21} [\nabla T \otimes (\boldsymbol{\varepsilon} \nabla T) + (\boldsymbol{\varepsilon} \nabla T) \otimes \nabla T] + M^{22} [\nabla T \otimes (\mathbf{m} \nabla T) + (\mathbf{m} \nabla T) \otimes \nabla T] \\ & + M^{23} [\nabla T \otimes (\mathbf{r} \nabla T) + (\mathbf{r} \nabla T) \otimes \nabla T] + M^{24} [\nabla T \otimes (\boldsymbol{\varepsilon}^2 \nabla T) + (\boldsymbol{\varepsilon}^2 \nabla T) \otimes \nabla T] \\ & + M^{25} [\nabla T \otimes (\mathbf{m}^2 \nabla T) + (\mathbf{m}^2 \nabla T) \otimes \nabla T] + M^{26} [\nabla T \otimes (\mathbf{r}^2 \nabla T) + (\mathbf{r}^2 \nabla T) \otimes \nabla T], \end{aligned} \quad (\text{B.2.8})$$

and

$$\begin{aligned}
 \mathcal{R}^{(i)} = & R^1 \mathbf{U} + R^2 \boldsymbol{\varepsilon} + R^3 \mathbf{m} + R^4 \mathbf{r} + R^5 \boldsymbol{\varepsilon}^2 + R^6 \mathbf{m}^2 + R^7 \mathbf{r}^2 + R^8 (\boldsymbol{\varepsilon} \mathbf{m} + \mathbf{m} \boldsymbol{\varepsilon}) + R^9 (\boldsymbol{\varepsilon} \mathbf{r} + \mathbf{r} \boldsymbol{\varepsilon}) \\
 & + R^{10} (\mathbf{m} \mathbf{r} + \mathbf{r} \mathbf{m}) + R^{11} (\boldsymbol{\varepsilon}^2 \mathbf{m} + \mathbf{m} \boldsymbol{\varepsilon}^2) + R^{12} (\boldsymbol{\varepsilon}^2 \mathbf{r} + \mathbf{r} \boldsymbol{\varepsilon}^2) + R^{13} (\mathbf{m}^2 \mathbf{r} + \mathbf{r} \mathbf{m}^2) \\
 & + R^{14} (\mathbf{m}^2 \boldsymbol{\varepsilon} + \boldsymbol{\varepsilon} \mathbf{m}^2) + R^{15} (\mathbf{r}^2 \mathbf{m} + \mathbf{m} \mathbf{r}^2) + R^{16} (\mathbf{r}^2 \boldsymbol{\varepsilon} + \boldsymbol{\varepsilon} \mathbf{r}^2) + R^{17} (\boldsymbol{\varepsilon}^2 \mathbf{m}^2 + \mathbf{m}^2 \boldsymbol{\varepsilon}^2) \\
 & + R^{18} (\boldsymbol{\varepsilon}^2 \mathbf{r}^2 + \mathbf{r}^2 \boldsymbol{\varepsilon}^2) + R^{19} (\mathbf{m}^2 \mathbf{r}^2 + \mathbf{r}^2 \mathbf{m}^2) + R^{20} (\nabla T \otimes \nabla T) \\
 & + R^{21} [\nabla T \otimes (\boldsymbol{\varepsilon} \nabla T) + (\boldsymbol{\varepsilon} \nabla T) \otimes \nabla T] + R^{22} [\nabla T \otimes (\mathbf{m} \nabla T) + (\mathbf{m} \nabla T) \otimes \nabla T] \\
 & + R^{23} [\nabla T \otimes (\mathbf{r} \nabla T) + (\mathbf{r} \nabla T) \otimes \nabla T] + R^{24} [\nabla T \otimes (\boldsymbol{\varepsilon}^2 \nabla T) + (\boldsymbol{\varepsilon}^2 \nabla T) \otimes \nabla T] \\
 & + R^{25} [\nabla T \otimes (\mathbf{m}^2 \nabla T) + (\mathbf{m}^2 \nabla T) \otimes \nabla T] + R^{26} [\nabla T \otimes (\mathbf{r}^2 \nabla T) + (\mathbf{r}^2 \nabla T) \otimes \nabla T],
 \end{aligned} \tag{B.2.9}$$

where $M^\alpha(T, \nabla T, \boldsymbol{\varepsilon}, \mathbf{m}, \mathbf{r})$ and $R^\alpha(T, \nabla T, \boldsymbol{\varepsilon}, \mathbf{m}, \mathbf{r})$, $\alpha = 1, \dots, 26$, are scalar objective functions, that depend on the following invariants

$$\begin{aligned}
 & T, \quad \text{tr} \boldsymbol{\varepsilon}, \quad \text{tr} \mathbf{m}, \quad \text{tr} \mathbf{r}, \quad \text{tr} \boldsymbol{\varepsilon}^2, \quad \text{tr} \mathbf{m}^2, \quad \text{tr} \mathbf{r}^2, \quad \text{tr} \boldsymbol{\varepsilon}^3, \quad \text{tr} \mathbf{m}^3, \quad \text{tr} \mathbf{r}^3, \quad \text{tr} (\boldsymbol{\varepsilon} \mathbf{m}), \\
 & \text{tr} (\boldsymbol{\varepsilon} \mathbf{r}), \quad \text{tr} (\mathbf{m} \mathbf{r}), \quad \text{tr} (\boldsymbol{\varepsilon}^2 \mathbf{m}), \quad \text{tr} (\boldsymbol{\varepsilon}^2 \mathbf{r}), \quad \text{tr} (\mathbf{m}^2 \boldsymbol{\varepsilon}), \quad \text{tr} (\mathbf{m}^2 \mathbf{r}), \quad \text{tr} (\mathbf{r}^2 \boldsymbol{\varepsilon}), \quad \text{tr} (\mathbf{r}^2 \mathbf{m}), \\
 & \text{tr} (\boldsymbol{\varepsilon}^2 \mathbf{m}^2), \quad \text{tr} (\boldsymbol{\varepsilon}^2 \mathbf{r}^2), \quad \text{tr} (\mathbf{m}^2 \mathbf{r}^2), \quad \text{tr} (\boldsymbol{\varepsilon} \mathbf{m} \mathbf{r}), \\
 & \nabla T \cdot \nabla T, \quad \nabla T \cdot (\boldsymbol{\varepsilon} \nabla T), \quad \nabla T \cdot (\mathbf{m} \nabla T), \quad \nabla T \cdot (\mathbf{r} \nabla T), \quad \nabla T \cdot (\boldsymbol{\varepsilon}^2 \nabla T), \quad \nabla T \cdot (\mathbf{m}^2 \nabla T), \\
 & \nabla T \cdot (\mathbf{r}^2 \nabla T), \quad (\boldsymbol{\varepsilon} \nabla T) \cdot (\mathbf{m} \nabla T), \quad (\boldsymbol{\varepsilon} \nabla T) \cdot (\mathbf{r} \nabla T), \quad (\mathbf{m} \nabla T) \cdot (\mathbf{r} \nabla T).
 \end{aligned} \tag{B.2.10}$$

where, for instance, $\nabla T \cdot (\boldsymbol{\varepsilon}^2 \nabla T) \equiv (T_{,i} \varepsilon_{il} \varepsilon_{lk} T_{,k})$. Notice that the invariants of the first three lines of (B.2.10) are those of (B.1.3). Relations (3.6.4) and (3.6.5) are a first approximation of (B.2.8) and (B.2.9), respectively, being $\mathbf{m} = \dot{\boldsymbol{\varepsilon}}$.

B.3 OBJECTIVE REPRESENTATION OF VECTOR FUNCTIONS

Following [1], [2], [3] and [4] a vector function \mathbf{g} , that depends on m scalar function, namely a_1, a_2, \dots, a_m , (in the case of the heat flux \mathbf{q} , $m = 1$ and $a_1 \equiv T$), and l second-order symmetric tensors, namely A_1, A_2, \dots, A_l (in our case $l = 3$ and $A_1 \equiv \boldsymbol{\varepsilon}$, $A_2 \equiv \mathbf{m}$, $A_3 \equiv \mathbf{r}$) and on a vector \mathbf{w} (in our case $\mathbf{w} \equiv \nabla T$), is expressed as polynomial of the invariants

$$\mathbf{w}, \quad A_i \mathbf{w}, \quad A_i^2 \mathbf{w}, \quad A_i A_j \mathbf{w}, \quad A_j A_i \mathbf{w}, \tag{B.3.1}$$

with $i, j = 1, \dots, l$ and $i \neq j$, having the form

$$\mathbf{g} = \sum_{\beta=1}^n g^\beta \mathbf{g}_\beta, \tag{B.3.2}$$

where $g^\beta = g^\beta(a_1, a_2, \dots, a_m, A_1, A_2, \dots, A_l, \mathbf{w})$, $\beta = 1, \dots, n$, are objective scalar functions (and then depending on the invariants (B.2.10)) and \mathbf{g}_β are building on the set of the invariants of the list (B.3.1).

Thus, the invariants of the vector-value function $q(T, \nabla T, \boldsymbol{\varepsilon}, \mathbf{m}, \mathbf{r})$ are

$$\begin{aligned} &\nabla T, \quad \boldsymbol{\varepsilon} \nabla T, \quad \mathbf{m} \nabla T, \quad \mathbf{r} \nabla T, \quad \boldsymbol{\varepsilon}^2 \nabla T, \quad \mathbf{m}^2 \nabla T, \quad \mathbf{r}^2 \nabla T, \quad \boldsymbol{\varepsilon} \mathbf{m} \nabla T, \quad \boldsymbol{\varepsilon} \mathbf{r} \nabla T, \quad \mathbf{m} \mathbf{r} \nabla T, \\ &\mathbf{m} \boldsymbol{\varepsilon} \nabla T, \quad \mathbf{r} \boldsymbol{\varepsilon} \nabla T, \quad \mathbf{r} \mathbf{m} \nabla T, \end{aligned} \tag{B.3.3}$$

and, according to (B.3.2) (with $n = 13$), q has the form

$$\begin{aligned} q = &q^1 \nabla T + q^2 \boldsymbol{\varepsilon} \nabla T + q^3 \mathbf{m} \nabla T + q^4 \mathbf{r} \nabla T + q^5 \boldsymbol{\varepsilon}^2 \nabla T + q^6 \mathbf{m}^2 \nabla T + q^7 \mathbf{r}^2 \nabla T + q^8 \boldsymbol{\varepsilon} \mathbf{m} \nabla T \\ &+ q^9 \boldsymbol{\varepsilon} \mathbf{r} \nabla T + q^{10} \mathbf{m} \mathbf{r} \nabla T + q^{11} \mathbf{m} \boldsymbol{\varepsilon} \nabla T + q^{12} \mathbf{r} \boldsymbol{\varepsilon} \nabla T + q^{13} \mathbf{r} \mathbf{m} \nabla T, \end{aligned} \tag{B.3.4}$$

where $q^\beta = q^\beta(T, \nabla T, \boldsymbol{\varepsilon}, \mathbf{m}, \mathbf{r})$, $\beta = 1, \dots, 13$, are objective scalar functions, that depend on the invariants (B.2.10). Relation (3.6.10), $q = q^1 \nabla T$, is a first approximated form of (B.3.4), with $\mathbf{m} = \dot{\boldsymbol{\varepsilon}}$.

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C | MATRIX REPRESENTATION

Here, we give a two-dimensional symmetric explicit representation of the conductivity matrix $\{\mathcal{L}_{\alpha\beta}\}$ that appears in the entropy production (7.3.28) of Chapter 7. This form is useful when the conditions of positive definiteness have to be calculated. Though the explicit writing is cumbersome, it is especially useful when an abstract notation is not sufficient, but explicit calculations must be done, or when a computer program for solving equations or carrying out numerical simulations must be implemented.

Representation of the conductivity matrix $\{\mathcal{L}_{\alpha\beta}\}$ in the case where the internal variable Q has odd parity

Entropy production (7.3.28) of Subsection 7.3.2, can be written in the symbolic matrix notation

$$X_\alpha \mathcal{L}_{\alpha\beta} X_\beta \geq 0 \quad (\alpha, \beta = 1, \dots, 48), \quad (\text{C.0.1})$$

where

$$\begin{aligned} \{X_\alpha\} &= \{q_i ; q_{i,j} ; Q_{ij} ; Q_{ij,p}\} = \\ &= \{q_1 ; q_2 ; q_3 ; q_{1,1} ; q_{1,2} ; q_{1,3} ; q_{2,1} ; q_{2,2} ; q_{2,3} ; q_{3,1} ; q_{3,2} ; q_{3,3} ; \\ &\quad Q_{11,1} ; Q_{11,2} ; Q_{11,3} ; Q_{12,1} ; Q_{12,2} ; Q_{12,3} ; Q_{13,1} ; Q_{13,2} ; Q_{13,3} ; \\ &\quad Q_{21,1} ; Q_{21,2} ; Q_{21,3} ; Q_{22,1} ; Q_{22,2} ; Q_{22,3} ; Q_{23,1} ; Q_{23,2} ; Q_{23,3} ; \\ &\quad Q_{31,1} ; Q_{31,2} ; Q_{31,3} ; Q_{32,1} ; Q_{32,2} ; Q_{32,3} ; Q_{33,1} ; Q_{33,2} ; Q_{33,3}\}, \end{aligned} \quad (\text{C.0.2})$$

$$\{X_\beta\} = \{q_k ; q_{k,l} ; Q_{kl} ; Q_{lm,n}\}^T. \quad (\text{C.0.3})$$

For $\mathcal{L}_{\alpha\beta}$ we introduce the following notation

$$\{\mathcal{L}_{\alpha\beta}\} = \begin{pmatrix} \begin{array}{c|c|c|c} 3 \times 3 & 3 \times 9 & 3 \times 9 & 3 \times 27 \\ \mathcal{L}_{ik}^{(1)} & 0 & 0 & \mathcal{L}_{ilmn}^{(1,4)} \end{array} \\ \hline \begin{array}{c|c|c|c} 9 \times 3 & 9 \times 9 & 9 \times 9 & 9 \times 27 \\ 0 & \mathcal{L}_{jkl}^{(2)} & \mathcal{L}_{jkl}^{(2,3)} & 0 \end{array} \\ \hline \begin{array}{c|c|c|c} 9 \times 3 & 9 \times 9 & 9 \times 9 & 9 \times 27 \\ 0 & \mathcal{L}_{ijkl}^{(3,2)} & \mathcal{L}_{ijkl}^{(3)} & 0 \end{array} \\ \hline \begin{array}{c|c|c|c} 27 \times 3 & 27 \times 9 & 27 \times 9 & 27 \times 27 \\ \mathcal{L}_{kpij}^{(4,1)} & 0 & 0 & \mathcal{L}_{pijlmn}^{(4)} \end{array} \end{pmatrix} \quad (\alpha, \beta = 1, \dots, 48), \quad (\text{C.0.4})$$

in which 0 is the symbolic null matrix of dimension $n \times m$. This matrix is symmetric by virtue of Onsager relations (7.2.2)₂ and (7.2.3)₂.

In the following we write the sub-matrices that appear in (C.0.4)

$$\mathcal{L}_{ik}^{(1)} = \begin{pmatrix} L^{(1)} & 0 & 0 \\ 0 & L^{(1)} & 0 \\ 0 & 0 & L^{(1)} \end{pmatrix}, \quad (\text{C.0.5})$$

$$\mathcal{L}_{ijkl}^{(2)} = \begin{pmatrix} \mathcal{L}_{1111}^{(2)} & \mathcal{L}_{1112}^{(2)} & \mathcal{L}_{1113}^{(2)} & \mathcal{L}_{1121}^{(2)} & \mathcal{L}_{1122}^{(2)} & \mathcal{L}_{1123}^{(2)} & \mathcal{L}_{1131}^{(2)} & \mathcal{L}_{1132}^{(2)} & \mathcal{L}_{1133}^{(2)} \\ \mathcal{L}_{2111}^{(2)} & \mathcal{L}_{2112}^{(2)} & \mathcal{L}_{2113}^{(2)} & \mathcal{L}_{2121}^{(2)} & \mathcal{L}_{2122}^{(2)} & \mathcal{L}_{2123}^{(2)} & \mathcal{L}_{2131}^{(2)} & \mathcal{L}_{2132}^{(2)} & \mathcal{L}_{2133}^{(2)} \\ \mathcal{L}_{3111}^{(2)} & \mathcal{L}_{3112}^{(2)} & \mathcal{L}_{3113}^{(2)} & \mathcal{L}_{3121}^{(2)} & \mathcal{L}_{3122}^{(2)} & \mathcal{L}_{3123}^{(2)} & \mathcal{L}_{3131}^{(2)} & \mathcal{L}_{3132}^{(2)} & \mathcal{L}_{3133}^{(2)} \\ \mathcal{L}_{1211}^{(2)} & \mathcal{L}_{1212}^{(2)} & \mathcal{L}_{1213}^{(2)} & \mathcal{L}_{1221}^{(2)} & \mathcal{L}_{1222}^{(2)} & \mathcal{L}_{1223}^{(2)} & \mathcal{L}_{1231}^{(2)} & \mathcal{L}_{1232}^{(2)} & \mathcal{L}_{1233}^{(2)} \\ \mathcal{L}_{2211}^{(2)} & \mathcal{L}_{2212}^{(2)} & \mathcal{L}_{2213}^{(2)} & \mathcal{L}_{2221}^{(2)} & \mathcal{L}_{2222}^{(2)} & \mathcal{L}_{2223}^{(2)} & \mathcal{L}_{2231}^{(2)} & \mathcal{L}_{2232}^{(2)} & \mathcal{L}_{2233}^{(2)} \\ \mathcal{L}_{3211}^{(2)} & \mathcal{L}_{3212}^{(2)} & \mathcal{L}_{3213}^{(2)} & \mathcal{L}_{3221}^{(2)} & \mathcal{L}_{3222}^{(2)} & \mathcal{L}_{3223}^{(2)} & \mathcal{L}_{3231}^{(2)} & \mathcal{L}_{3232}^{(2)} & \mathcal{L}_{3233}^{(2)} \\ \mathcal{L}_{1311}^{(2)} & \mathcal{L}_{1312}^{(2)} & \mathcal{L}_{1313}^{(2)} & \mathcal{L}_{1321}^{(2)} & \mathcal{L}_{1322}^{(2)} & \mathcal{L}_{1323}^{(2)} & \mathcal{L}_{1331}^{(2)} & \mathcal{L}_{1332}^{(2)} & \mathcal{L}_{1333}^{(2)} \\ \mathcal{L}_{2311}^{(2)} & \mathcal{L}_{2312}^{(2)} & \mathcal{L}_{2313}^{(2)} & \mathcal{L}_{2321}^{(2)} & \mathcal{L}_{2322}^{(2)} & \mathcal{L}_{2323}^{(2)} & \mathcal{L}_{2331}^{(2)} & \mathcal{L}_{2332}^{(2)} & \mathcal{L}_{2333}^{(2)} \\ \mathcal{L}_{3311}^{(2)} & \mathcal{L}_{3312}^{(2)} & \mathcal{L}_{3313}^{(2)} & \mathcal{L}_{3321}^{(2)} & \mathcal{L}_{3322}^{(2)} & \mathcal{L}_{3323}^{(2)} & \mathcal{L}_{3331}^{(2)} & \mathcal{L}_{3332}^{(2)} & \mathcal{L}_{3333}^{(2)} \end{pmatrix} = \quad (\text{C.0.6})$$

$$= \begin{pmatrix} L^{(2)} & 0 & 0 & 0 & L_1^{(2)} & 0 & 0 & 0 & L_1^{(2)} \\ 0 & L_3^{(2)} & 0 & L_2^{(2)} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & L_3^{(2)} & 0 & 0 & 0 & L_2^{(2)} & 0 & 0 \\ 0 & L_2^{(2)} & 0 & L_3^{(2)} & 0 & 0 & 0 & 0 & 0 \\ L_1^{(2)} & 0 & 0 & 0 & L^{(2)} & 0 & 0 & 0 & L_1^{(2)} \\ 0 & 0 & 0 & 0 & 0 & L_3^{(2)} & 0 & L_2^{(2)} & 0 \\ 0 & 0 & L_2^{(2)} & 0 & 0 & 0 & L_3^{(2)} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & L_2^{(2)} & 0 & L_3^{(2)} & 0 \\ L_1^{(2)} & 0 & 0 & 0 & L_1^{(2)} & 0 & 0 & 0 & L^{(2)} \end{pmatrix},$$

where $L^{(2)} \equiv L_1^{(2)} + L_2^{(2)} + L_3^{(2)}$.

$$\mathcal{L}_{ilmn}^{(1,4)} = \begin{pmatrix} \mathcal{L}_{1111}^{(1,4)} & \mathcal{L}_{2111}^{(1,4)} & \mathcal{L}_{3111}^{(1,4)} \\ \mathcal{L}_{1112}^{(1,4)} & \mathcal{L}_{2112}^{(1,4)} & \mathcal{L}_{3112}^{(1,4)} \\ \mathcal{L}_{1113}^{(1,4)} & \mathcal{L}_{2113}^{(1,4)} & \mathcal{L}_{3113}^{(1,4)} \\ \mathcal{L}_{1121}^{(1,4)} & \mathcal{L}_{2121}^{(1,4)} & \mathcal{L}_{3121}^{(1,4)} \\ \mathcal{L}_{1122}^{(1,4)} & \mathcal{L}_{2122}^{(1,4)} & \mathcal{L}_{3122}^{(1,4)} \\ \mathcal{L}_{1123}^{(1,4)} & \mathcal{L}_{2123}^{(1,4)} & \mathcal{L}_{3123}^{(1,4)} \\ \mathcal{L}_{1131}^{(1,4)} & \mathcal{L}_{2131}^{(1,4)} & \mathcal{L}_{3131}^{(1,4)} \\ \mathcal{L}_{1132}^{(1,4)} & \mathcal{L}_{2132}^{(1,4)} & \mathcal{L}_{3132}^{(1,4)} \\ \mathcal{L}_{1133}^{(1,4)} & \mathcal{L}_{2133}^{(1,4)} & \mathcal{L}_{3133}^{(1,4)} \\ \mathcal{L}_{1211}^{(1,4)} & \mathcal{L}_{2211}^{(1,4)} & \mathcal{L}_{3211}^{(1,4)} \\ \mathcal{L}_{1212}^{(1,4)} & \mathcal{L}_{2212}^{(1,4)} & \mathcal{L}_{3212}^{(1,4)} \\ \mathcal{L}_{1213}^{(1,4)} & \mathcal{L}_{2213}^{(1,4)} & \mathcal{L}_{3213}^{(1,4)} \\ \mathcal{L}_{1221}^{(1,4)} & \mathcal{L}_{2221}^{(1,4)} & \mathcal{L}_{3221}^{(1,4)} \\ \mathcal{L}_{1222}^{(1,4)} & \mathcal{L}_{2222}^{(1,4)} & \mathcal{L}_{3222}^{(1,4)} \\ \mathcal{L}_{1223}^{(1,4)} & \mathcal{L}_{2223}^{(1,4)} & \mathcal{L}_{3223}^{(1,4)} \\ \mathcal{L}_{1231}^{(1,4)} & \mathcal{L}_{2231}^{(1,4)} & \mathcal{L}_{3231}^{(1,4)} \\ \mathcal{L}_{1232}^{(1,4)} & \mathcal{L}_{2232}^{(1,4)} & \mathcal{L}_{3232}^{(1,4)} \\ \mathcal{L}_{1233}^{(1,4)} & \mathcal{L}_{2233}^{(1,4)} & \mathcal{L}_{3233}^{(1,4)} \\ \mathcal{L}_{1311}^{(1,4)} & \mathcal{L}_{2311}^{(1,4)} & \mathcal{L}_{3311}^{(1,4)} \\ \mathcal{L}_{1312}^{(1,4)} & \mathcal{L}_{2312}^{(1,4)} & \mathcal{L}_{3312}^{(1,4)} \\ \mathcal{L}_{1313}^{(1,4)} & \mathcal{L}_{2313}^{(1,4)} & \mathcal{L}_{3313}^{(1,4)} \\ \mathcal{L}_{1321}^{(1,4)} & \mathcal{L}_{2321}^{(1,4)} & \mathcal{L}_{3321}^{(1,4)} \\ \mathcal{L}_{1322}^{(1,4)} & \mathcal{L}_{2322}^{(1,4)} & \mathcal{L}_{3322}^{(1,4)} \\ \mathcal{L}_{1323}^{(1,4)} & \mathcal{L}_{2323}^{(1,4)} & \mathcal{L}_{3323}^{(1,4)} \\ \mathcal{L}_{1331}^{(1,4)} & \mathcal{L}_{2331}^{(1,4)} & \mathcal{L}_{3331}^{(1,4)} \\ \mathcal{L}_{1332}^{(1,4)} & \mathcal{L}_{2332}^{(1,4)} & \mathcal{L}_{3332}^{(1,4)} \\ \mathcal{L}_{1333}^{(1,4)} & \mathcal{L}_{2333}^{(1,4)} & \mathcal{L}_{3333}^{(1,4)} \end{pmatrix}^T = \begin{pmatrix} L^{(1,4)} & 0 & 0 \\ 0 & L_3^{(1,4)} & 0 \\ 0 & 0 & L_3^{(1,4)} \\ 0 & L_2^{(1,4)} & 0 \\ L_1^{(1,4)} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & L_2^{(1,4)} \\ 0 & 0 & 0 \\ L_1^{(1,4)} & 0 & 0 \\ 0 & L_1^{(1,4)} & 0 \\ L_2^{(1,4)} & 0 & 0 \\ 0 & 0 & 0 \\ L_3^{(1,4)} & 0 & 0 \\ 0 & L^{(1,4)} & 0 \\ 0 & 0 & L_3^{(1,4)} \\ 0 & 0 & 0 \\ 0 & 0 & L_2^{(1,4)} \\ 0 & L_1^{(1,4)} & 0 \\ 0 & 0 & L_1^{(1,4)} \\ 0 & 0 & 0 \\ L_2^{(1,4)} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & L_1^{(1,4)} \\ 0 & L_2^{(1,4)} & 0 \\ L_3^{(1,4)} & 0 & 0 \\ 0 & L_3^{(1,4)} & 0 \\ 0 & 0 & L^{(1,4)} \end{pmatrix}^T, \quad (\text{C.0.7})$$

where $L^{(1,4)} \equiv L_1^{(1,4)} + L_2^{(1,4)} + L_3^{(1,4)}$.

$$\mathcal{L}_{ijkl}^{(2,3)} = \begin{pmatrix} \mathcal{L}_{1111}^{(2,3)} & \mathcal{L}_{1112}^{(2,3)} & \mathcal{L}_{1113}^{(2,3)} & \mathcal{L}_{1121}^{(2,3)} & \mathcal{L}_{1122}^{(2,3)} & \mathcal{L}_{1123}^{(2,3)} & \mathcal{L}_{1131}^{(2,3)} & \mathcal{L}_{1132}^{(2,3)} & \mathcal{L}_{1133}^{(2,3)} \\ \mathcal{L}_{2111}^{(2,3)} & \mathcal{L}_{2112}^{(2,3)} & \mathcal{L}_{2113}^{(2,3)} & \mathcal{L}_{2121}^{(2,3)} & \mathcal{L}_{2122}^{(2,3)} & \mathcal{L}_{2123}^{(2,3)} & \mathcal{L}_{2131}^{(2,3)} & \mathcal{L}_{2132}^{(2,3)} & \mathcal{L}_{2133}^{(2,3)} \\ \mathcal{L}_{3111}^{(2,3)} & \mathcal{L}_{3112}^{(2,3)} & \mathcal{L}_{3113}^{(2,3)} & \mathcal{L}_{3121}^{(2,3)} & \mathcal{L}_{3122}^{(2,3)} & \mathcal{L}_{3123}^{(2,3)} & \mathcal{L}_{3131}^{(2,3)} & \mathcal{L}_{3132}^{(2,3)} & \mathcal{L}_{3133}^{(2,3)} \\ \mathcal{L}_{1211}^{(2,3)} & \mathcal{L}_{1212}^{(2,3)} & \mathcal{L}_{1213}^{(2,3)} & \mathcal{L}_{1221}^{(2,3)} & \mathcal{L}_{1222}^{(2,3)} & \mathcal{L}_{1223}^{(2,3)} & \mathcal{L}_{1231}^{(2,3)} & \mathcal{L}_{1232}^{(2,3)} & \mathcal{L}_{1233}^{(2,3)} \\ \mathcal{L}_{2211}^{(2,3)} & \mathcal{L}_{2212}^{(2,3)} & \mathcal{L}_{2213}^{(2,3)} & \mathcal{L}_{2221}^{(2,3)} & \mathcal{L}_{2222}^{(2,3)} & \mathcal{L}_{2223}^{(2,3)} & \mathcal{L}_{2231}^{(2,3)} & \mathcal{L}_{2232}^{(2,3)} & \mathcal{L}_{2233}^{(2,3)} \\ \mathcal{L}_{3211}^{(2,3)} & \mathcal{L}_{3212}^{(2,3)} & \mathcal{L}_{3213}^{(2,3)} & \mathcal{L}_{3221}^{(2,3)} & \mathcal{L}_{3222}^{(2,3)} & \mathcal{L}_{3223}^{(2,3)} & \mathcal{L}_{3231}^{(2,3)} & \mathcal{L}_{3232}^{(2,3)} & \mathcal{L}_{3233}^{(2,3)} \\ \mathcal{L}_{1311}^{(2,3)} & \mathcal{L}_{1312}^{(2,3)} & \mathcal{L}_{1313}^{(2,3)} & \mathcal{L}_{1321}^{(2,3)} & \mathcal{L}_{1322}^{(2,3)} & \mathcal{L}_{1323}^{(2,3)} & \mathcal{L}_{1331}^{(2,3)} & \mathcal{L}_{1332}^{(2,3)} & \mathcal{L}_{1333}^{(2,3)} \\ \mathcal{L}_{2311}^{(2,3)} & \mathcal{L}_{2312}^{(2,3)} & \mathcal{L}_{2313}^{(2,3)} & \mathcal{L}_{2321}^{(2,3)} & \mathcal{L}_{2322}^{(2,3)} & \mathcal{L}_{2323}^{(2,3)} & \mathcal{L}_{2331}^{(2,3)} & \mathcal{L}_{2332}^{(2,3)} & \mathcal{L}_{2333}^{(2,3)} \\ \mathcal{L}_{3311}^{(2,3)} & \mathcal{L}_{3312}^{(2,3)} & \mathcal{L}_{3313}^{(2,3)} & \mathcal{L}_{3321}^{(2,3)} & \mathcal{L}_{3322}^{(2,3)} & \mathcal{L}_{3323}^{(2,3)} & \mathcal{L}_{3331}^{(2,3)} & \mathcal{L}_{3332}^{(2,3)} & \mathcal{L}_{3333}^{(2,3)} \end{pmatrix} = \quad (C.0.8)$$

$$= \begin{pmatrix} L^{(2,3)} & 0 & 0 & 0 & L_1^{(2,3)} & 0 & 0 & 0 & L_1^{(2,3)} \\ 0 & L_3^{(2,3)} & 0 & L_2^{(2,3)} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & L_3^{(2,3)} & 0 & 0 & 0 & L_2^{(2,3)} & 0 & 0 \\ 0 & L_2^{(2,3)} & 0 & L_3^{(2,3)} & 0 & 0 & 0 & 0 & 0 \\ L_1^{(2,3)} & 0 & 0 & 0 & L^{(2,3)} & 0 & 0 & 0 & L_1^{(2,3)} \\ 0 & 0 & 0 & 0 & 0 & L_3^{(2,3)} & 0 & L_2^{(2,3)} & 0 \\ 0 & 0 & L_2^{(2,3)} & 0 & 0 & 0 & L_3^{(2,3)} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & L_2^{(2,3)} & 0 & L_3^{(2,3)} & 0 \\ L_1^{(2,3)} & 0 & 0 & 0 & L_1^{(2,3)} & 0 & 0 & 0 & L^{(2,3)} \end{pmatrix},$$

where $L^{(2,3)} \equiv L_1^{(2,3)} + L_2^{(2,3)} + L_3^{(2,3)}$.

$$\mathcal{L}_{ijkl}^{(3)} = \begin{pmatrix} \mathcal{L}_{1111}^{(3)} & \mathcal{L}_{1112}^{(3)} & \mathcal{L}_{1113}^{(3)} & \mathcal{L}_{1121}^{(3)} & \mathcal{L}_{1122}^{(3)} & \mathcal{L}_{1123}^{(3)} & \mathcal{L}_{1131}^{(3)} & \mathcal{L}_{1132}^{(3)} & \mathcal{L}_{1133}^{(3)} \\ \mathcal{L}_{1211}^{(3)} & \mathcal{L}_{1212}^{(3)} & \mathcal{L}_{1213}^{(3)} & \mathcal{L}_{1221}^{(3)} & \mathcal{L}_{1222}^{(3)} & \mathcal{L}_{1223}^{(3)} & \mathcal{L}_{1231}^{(3)} & \mathcal{L}_{1232}^{(3)} & \mathcal{L}_{1233}^{(3)} \\ \mathcal{L}_{1311}^{(3)} & \mathcal{L}_{1312}^{(3)} & \mathcal{L}_{1313}^{(3)} & \mathcal{L}_{1321}^{(3)} & \mathcal{L}_{1322}^{(3)} & \mathcal{L}_{1323}^{(3)} & \mathcal{L}_{1331}^{(3)} & \mathcal{L}_{1332}^{(3)} & \mathcal{L}_{1333}^{(3)} \\ \mathcal{L}_{2111}^{(3)} & \mathcal{L}_{2112}^{(3)} & \mathcal{L}_{2113}^{(3)} & \mathcal{L}_{2121}^{(3)} & \mathcal{L}_{2122}^{(3)} & \mathcal{L}_{2123}^{(3)} & \mathcal{L}_{2131}^{(3)} & \mathcal{L}_{2132}^{(3)} & \mathcal{L}_{2133}^{(3)} \\ \mathcal{L}_{2211}^{(3)} & \mathcal{L}_{2212}^{(3)} & \mathcal{L}_{2213}^{(3)} & \mathcal{L}_{2221}^{(3)} & \mathcal{L}_{2222}^{(3)} & \mathcal{L}_{2223}^{(3)} & \mathcal{L}_{2231}^{(3)} & \mathcal{L}_{2232}^{(3)} & \mathcal{L}_{2233}^{(3)} \\ \mathcal{L}_{2311}^{(3)} & \mathcal{L}_{2312}^{(3)} & \mathcal{L}_{2313}^{(3)} & \mathcal{L}_{2321}^{(3)} & \mathcal{L}_{2322}^{(3)} & \mathcal{L}_{2323}^{(3)} & \mathcal{L}_{2331}^{(3)} & \mathcal{L}_{2332}^{(3)} & \mathcal{L}_{2333}^{(3)} \\ \mathcal{L}_{3111}^{(3)} & \mathcal{L}_{3112}^{(3)} & \mathcal{L}_{3113}^{(3)} & \mathcal{L}_{3121}^{(3)} & \mathcal{L}_{3122}^{(3)} & \mathcal{L}_{3123}^{(3)} & \mathcal{L}_{3131}^{(3)} & \mathcal{L}_{3132}^{(3)} & \mathcal{L}_{3133}^{(3)} \\ \mathcal{L}_{3211}^{(3)} & \mathcal{L}_{3212}^{(3)} & \mathcal{L}_{3213}^{(3)} & \mathcal{L}_{3221}^{(3)} & \mathcal{L}_{3222}^{(3)} & \mathcal{L}_{3223}^{(3)} & \mathcal{L}_{3231}^{(3)} & \mathcal{L}_{3232}^{(3)} & \mathcal{L}_{3233}^{(3)} \\ \mathcal{L}_{3311}^{(3)} & \mathcal{L}_{3312}^{(3)} & \mathcal{L}_{3313}^{(3)} & \mathcal{L}_{3321}^{(3)} & \mathcal{L}_{3322}^{(3)} & \mathcal{L}_{3323}^{(3)} & \mathcal{L}_{3331}^{(3)} & \mathcal{L}_{3332}^{(3)} & \mathcal{L}_{3333}^{(3)} \end{pmatrix} = \quad (C.0.9)$$

$$= \begin{pmatrix} L^{(3)} & 0 & 0 & 0 & L_1^{(3)} & 0 & 0 & 0 & L_1^{(3)} \\ 0 & L_2^{(3)} & 0 & L_3^{(3)} & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & L_2^{(3)} & 0 & 0 & 0 & L_3^{(3)} & 0 & 0 \\ 0 & L_3^{(3)} & 0 & L_2^{(3)} & 0 & 0 & 0 & 0 & 0 \\ L_1^{(3)} & 0 & 0 & 0 & L^{(3)} & 0 & 0 & 0 & L_1^{(3)} \\ 0 & 0 & 0 & 0 & 0 & L_2^{(3)} & 0 & L_3^{(3)} & 0 \\ 0 & 0 & L_3^{(3)} & 0 & 0 & 0 & L_2^{(3)} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & L_3^{(3)} & 0 & L_2^{(3)} & 0 \\ L_1^{(3)} & 0 & 0 & 0 & L_1^{(3)} & 0 & 0 & 0 & L^{(3)} \end{pmatrix},$$

where $L^{(3)} \equiv L_1^{(3)} + L_2^{(3)} + L_3^{(3)}$.

$$\begin{aligned}
 \mathcal{L}_{ijkl}^{(3,2)} &= \begin{pmatrix}
 \mathcal{L}_{1111}^{(2,3)} & \mathcal{L}_{1112}^{(2,3)} & \mathcal{L}_{1113}^{(2,3)} & \mathcal{L}_{1121}^{(2,3)} & \mathcal{L}_{1122}^{(2,3)} & \mathcal{L}_{1123}^{(2,3)} & \mathcal{L}_{1131}^{(2,3)} & \mathcal{L}_{1132}^{(2,3)} & \mathcal{L}_{1133}^{(2,3)} \\
 \mathcal{L}_{1211}^{(2,3)} & \mathcal{L}_{1212}^{(2,3)} & \mathcal{L}_{1213}^{(2,3)} & \mathcal{L}_{1221}^{(2,3)} & \mathcal{L}_{1222}^{(2,3)} & \mathcal{L}_{1223}^{(2,3)} & \mathcal{L}_{1231}^{(2,3)} & \mathcal{L}_{1232}^{(2,3)} & \mathcal{L}_{1233}^{(2,3)} \\
 \mathcal{L}_{1311}^{(2,3)} & \mathcal{L}_{1312}^{(2,3)} & \mathcal{L}_{1313}^{(2,3)} & \mathcal{L}_{1321}^{(2,3)} & \mathcal{L}_{1322}^{(2,3)} & \mathcal{L}_{1323}^{(2,3)} & \mathcal{L}_{1331}^{(2,3)} & \mathcal{L}_{1332}^{(2,3)} & \mathcal{L}_{1333}^{(2,3)} \\
 \mathcal{L}_{2111}^{(2,3)} & \mathcal{L}_{2112}^{(2,3)} & \mathcal{L}_{2113}^{(2,3)} & \mathcal{L}_{2121}^{(2,3)} & \mathcal{L}_{2122}^{(2,3)} & \mathcal{L}_{2123}^{(2,3)} & \mathcal{L}_{2131}^{(2,3)} & \mathcal{L}_{2132}^{(2,3)} & \mathcal{L}_{2133}^{(2,3)} \\
 \mathcal{L}_{2211}^{(2,3)} & \mathcal{L}_{2212}^{(2,3)} & \mathcal{L}_{2213}^{(2,3)} & \mathcal{L}_{2221}^{(2,3)} & \mathcal{L}_{2222}^{(2,3)} & \mathcal{L}_{2223}^{(2,3)} & \mathcal{L}_{2231}^{(2,3)} & \mathcal{L}_{2232}^{(2,3)} & \mathcal{L}_{2233}^{(2,3)} \\
 \mathcal{L}_{2311}^{(2,3)} & \mathcal{L}_{2312}^{(2,3)} & \mathcal{L}_{2313}^{(2,3)} & \mathcal{L}_{2321}^{(2,3)} & \mathcal{L}_{2322}^{(2,3)} & \mathcal{L}_{2323}^{(2,3)} & \mathcal{L}_{2331}^{(2,3)} & \mathcal{L}_{2332}^{(2,3)} & \mathcal{L}_{2333}^{(2,3)} \\
 \mathcal{L}_{3111}^{(2,3)} & \mathcal{L}_{3112}^{(2,3)} & \mathcal{L}_{3113}^{(2,3)} & \mathcal{L}_{3121}^{(2,3)} & \mathcal{L}_{3122}^{(2,3)} & \mathcal{L}_{3123}^{(2,3)} & \mathcal{L}_{3131}^{(2,3)} & \mathcal{L}_{3132}^{(2,3)} & \mathcal{L}_{3133}^{(2,3)} \\
 \mathcal{L}_{3211}^{(2,3)} & \mathcal{L}_{3212}^{(2,3)} & \mathcal{L}_{3213}^{(2,3)} & \mathcal{L}_{3221}^{(2,3)} & \mathcal{L}_{3222}^{(2,3)} & \mathcal{L}_{3223}^{(2,3)} & \mathcal{L}_{3231}^{(2,3)} & \mathcal{L}_{3232}^{(2,3)} & \mathcal{L}_{3233}^{(2,3)} \\
 \mathcal{L}_{3311}^{(2,3)} & \mathcal{L}_{3312}^{(2,3)} & \mathcal{L}_{3313}^{(2,3)} & \mathcal{L}_{3321}^{(2,3)} & \mathcal{L}_{3322}^{(2,3)} & \mathcal{L}_{3323}^{(2,3)} & \mathcal{L}_{3331}^{(2,3)} & \mathcal{L}_{3332}^{(2,3)} & \mathcal{L}_{3333}^{(2,3)}
 \end{pmatrix} = \\
 &= \begin{pmatrix}
 L^{(2,3)} & 0 & 0 & 0 & L_1^{(2,3)} & 0 & 0 & 0 & L_1^{(2,3)} \\
 0 & L_2^{(2,3)} & 0 & L_3^{(2,3)} & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & L_2^{(2,3)} & 0 & 0 & 0 & L_3^{(2,3)} & 0 & 0 \\
 0 & L_3^{(2,3)} & 0 & L_2^{(2,3)} & 0 & 0 & 0 & 0 & 0 \\
 L_1^{(2,3)} & 0 & 0 & 0 & L^{(2,3)} & 0 & 0 & 0 & L_1^{(2,3)} \\
 0 & 0 & 0 & 0 & 0 & L_2^{(2,3)} & 0 & L_3^{(2,3)} & 0 \\
 0 & 0 & L_3^{(2,3)} & 0 & 0 & 0 & L_2^{(2,3)} & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & L_3^{(2,3)} & 0 & L_2^{(2,3)} & 0 \\
 L_1^{(2,3)} & 0 & 0 & 0 & L_1^{(2,3)} & 0 & 0 & 0 & L^{(2,3)}
 \end{pmatrix}, \tag{C.0.10}
 \end{aligned}$$

where we have used the Onsager relations (7.2.3)₂.

$$\mathcal{L}_{kpij}^{(4,1)} = \begin{pmatrix} \mathcal{L}_{1111}^{(1,4)} & \mathcal{L}_{2111}^{(1,4)} & \mathcal{L}_{3111}^{(1,4)} \\ \mathcal{L}_{1211}^{(1,4)} & \mathcal{L}_{2211}^{(1,4)} & \mathcal{L}_{3211}^{(1,4)} \\ \mathcal{L}_{1311}^{(1,4)} & \mathcal{L}_{2311}^{(1,4)} & \mathcal{L}_{3311}^{(1,4)} \\ \mathcal{L}_{1112}^{(1,4)} & \mathcal{L}_{2112}^{(1,4)} & \mathcal{L}_{3112}^{(1,4)} \\ \mathcal{L}_{1212}^{(1,4)} & \mathcal{L}_{2212}^{(1,4)} & \mathcal{L}_{3212}^{(1,4)} \\ \mathcal{L}_{1312}^{(1,4)} & \mathcal{L}_{2312}^{(1,4)} & \mathcal{L}_{3312}^{(1,4)} \\ \mathcal{L}_{1113}^{(1,4)} & \mathcal{L}_{2113}^{(1,4)} & \mathcal{L}_{3113}^{(1,4)} \\ \mathcal{L}_{1213}^{(1,4)} & \mathcal{L}_{2213}^{(1,4)} & \mathcal{L}_{3213}^{(1,4)} \\ \mathcal{L}_{1313}^{(1,4)} & \mathcal{L}_{2313}^{(1,4)} & \mathcal{L}_{3313}^{(1,4)} \\ \mathcal{L}_{1121}^{(1,4)} & \mathcal{L}_{2121}^{(1,4)} & \mathcal{L}_{3121}^{(1,4)} \\ \mathcal{L}_{1221}^{(1,4)} & \mathcal{L}_{2221}^{(1,4)} & \mathcal{L}_{3221}^{(1,4)} \\ \mathcal{L}_{1321}^{(1,4)} & \mathcal{L}_{2321}^{(1,4)} & \mathcal{L}_{3321}^{(1,4)} \\ \mathcal{L}_{1122}^{(1,4)} & \mathcal{L}_{2122}^{(1,4)} & \mathcal{L}_{3122}^{(1,4)} \\ \mathcal{L}_{1222}^{(1,4)} & \mathcal{L}_{2222}^{(1,4)} & \mathcal{L}_{3222}^{(1,4)} \\ \mathcal{L}_{1322}^{(1,4)} & \mathcal{L}_{2322}^{(1,4)} & \mathcal{L}_{3322}^{(1,4)} \\ \mathcal{L}_{1123}^{(1,4)} & \mathcal{L}_{2123}^{(1,4)} & \mathcal{L}_{3123}^{(1,4)} \\ \mathcal{L}_{1223}^{(1,4)} & \mathcal{L}_{2223}^{(1,4)} & \mathcal{L}_{3223}^{(1,4)} \\ \mathcal{L}_{1323}^{(1,4)} & \mathcal{L}_{2323}^{(1,4)} & \mathcal{L}_{3323}^{(1,4)} \\ \mathcal{L}_{1131}^{(1,4)} & \mathcal{L}_{2131}^{(1,4)} & \mathcal{L}_{3131}^{(1,4)} \\ \mathcal{L}_{1231}^{(1,4)} & \mathcal{L}_{2231}^{(1,4)} & \mathcal{L}_{3231}^{(1,4)} \\ \mathcal{L}_{1331}^{(1,4)} & \mathcal{L}_{2331}^{(1,4)} & \mathcal{L}_{3331}^{(1,4)} \\ \mathcal{L}_{1132}^{(1,4)} & \mathcal{L}_{2132}^{(1,4)} & \mathcal{L}_{3132}^{(1,4)} \\ \mathcal{L}_{1232}^{(1,4)} & \mathcal{L}_{2232}^{(1,4)} & \mathcal{L}_{3232}^{(1,4)} \\ \mathcal{L}_{1332}^{(1,4)} & \mathcal{L}_{2332}^{(1,4)} & \mathcal{L}_{3332}^{(1,4)} \\ \mathcal{L}_{1133}^{(1,4)} & \mathcal{L}_{2133}^{(1,4)} & \mathcal{L}_{3133}^{(1,4)} \\ \mathcal{L}_{1233}^{(1,4)} & \mathcal{L}_{2233}^{(1,4)} & \mathcal{L}_{3233}^{(1,4)} \\ \mathcal{L}_{1333}^{(1,4)} & \mathcal{L}_{2333}^{(1,4)} & \mathcal{L}_{3333}^{(1,4)} \end{pmatrix} = \begin{pmatrix} L^{(1,4)} & 0 & 0 \\ 0 & L_1^{(1,4)} & 0 \\ 0 & 0 & L_1^{(1,4)} \\ 0 & L_3^{(1,4)} & 0 \\ L_2^{(1,4)} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & L_3^{(1,4)} \\ 0 & 0 & 0 \\ L_2^{(1,4)} & 0 & 0 \\ 0 & L_2^{(1,4)} & 0 \\ L_3^{(1,4)} & 0 & 0 \\ 0 & 0 & 0 \\ L_1^{(1,4)} & 0 & 0 \\ 0 & L^{(1,4)} & 0 \\ 0 & 0 & L_1^{(1,4)} \\ 0 & 0 & 0 \\ 0 & 0 & L_3^{(1,4)} \\ 0 & L_2^{(1,4)} & 0 \\ 0 & 0 & L_2^{(1,4)} \\ 0 & 0 & 0 \\ L_3^{(1,4)} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & L_2^{(1,4)} \\ 0 & L_3^{(1,4)} & 0 \\ L_1^{(1,4)} & 0 & 0 \\ 0 & L_1^{(1,4)} & 0 \\ 0 & 0 & L^{(1,4)} \end{pmatrix}, \quad (\text{C.0.11})$$

where $L^{(1,4)} \equiv L_1^{(1,4)} + L_2^{(1,4)} + L_3^{(1,4)}$ and we have used the Onsager relations (7.2.2)₂.

where

$$\begin{aligned}
C^{(4)} &= 2C_1^{(4)} + 2C_2^{(4)} + C_3^{(4)} + 2C_4^{(4)} + C_5^{(4)} + C_6^{(4)} + C_7^{(4)} + C_8^{(4)} + C_9^{(4)} + 2C_{10}^{(4)} + C_{11}^{(4)}, \\
\Lambda_1 &= C_1^{(4)} + C_4^{(4)} + C_6^{(4)}, \quad \Lambda_2 = C_2^{(4)} + C_4^{(4)} + C_5^{(4)}, \quad \Lambda_3 = C_1^{(4)} + C_2^{(4)} + C_3^{(4)}, \\
\Lambda_4 &= C_1^{(4)} + C_{10}^{(4)} + C_{11}^{(4)}, \quad \Lambda_5 = C_4^{(4)} + C_9^{(4)} + C_{10}^{(4)}, \quad \Lambda_6 = C_6^{(4)} + C_7^{(4)} + C_8^{(4)}, \\
\Lambda_7 &= C_3^{(4)} + C_7^{(4)} + C_9^{(4)}, \quad \Lambda_8 = C_2^{(4)} + C_8^{(4)} + C_{10}^{(4)}, \quad \Lambda_9 = C_5^{(4)} + C_7^{(4)} + C_{11}^{(4)}.
\end{aligned}$$

Representation of the conductivity matrix $\{\mathcal{L}_{\alpha\beta}\}$ in the case where Q has even parity

When the internal variable Q has even parity the expressions (C.0.1)-(C.0.4) and the results (C.0.5)-(C.0.9) and (C.0.12) of this Appendix remain unchanged. The phenomenological tensors $\mathcal{L}_{ijkl}^{(3,2)}$ and $\mathcal{L}_{kpij}^{(4,1)}$ are defined in the same way, but in the last terms of (C.0.10) and (C.0.11) before their matrix representation a minus sign appears because of in the calculations we take into account Onsager symmetry relations (7.2.2)₂ (7.2.3)₂. Thus, we have obtained that in the case where Q has odd parity the matrix $\{\mathcal{L}_{\alpha\beta}\}$ is symmetric, but in the case where Q has even parity the matrix $\{\mathcal{L}_{\alpha\beta}\}$ is not symmetric because of Onsager relations (7.2.2)₂ and (7.2.3)₂.