

DERIVATION OF EQUATIONS FOR CONTINUUM MECHANICS AND THERMODYNAMICS OF FLUIDS

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Dedicated to professor K. R. Rajagopal on the occasion of his 65th birthday.

ABSTRACT. The chapter starts with overview of the derivation of the balance equations for mass, momentum, angular momentum and total energy, which is followed by a detailed discussion of the concept of entropy and entropy production. While the balance laws are universal for any continuous medium, the particular behaviour of the material of interest must be described by an extra set of material specific equations. These equations relating for example the Cauchy stress tensor and the kinematical quantities are called the constitutive relations.

The core part of the chapter is devoted to the presentation of a modern thermodynamically based phenomenological theory of constitutive relations. The key feature of the theory is that the constitutive relations stem from the choice of two scalar quantities, the internal energy and the entropy production. This is tantamount to the proposition that the material behaviour is fully characterised by the way it stores the energy and produces the entropy.

The general theory is documented by several examples of increasing complexity. It is shown how to derive the constitutive relations for compressible and incompressible viscous heat conducting fluids (Navier–Stokes–Fourier fluid), Korteweg fluids and compressible and incompressible heat conducting viscoelastic fluids (Oldroyd-B and Maxwell fluid).

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1. INTRODUCTION

Continuum mechanics and thermodynamics are based on the idea of continuously distributed matter and other physical quantities. Originally, continuum mechanics was equated with hydrodynamics, aerodynamics and elasticity. The scope of the study was the motion of water and air and the deformation of some special solid substances. However, the concept of continuous medium has been shown to be useful and extremely viable even in the modelling of the behaviour of much more complex systems such as polymeric solutions, granular materials, rock and land masses, special alloys and many others. Moreover, the range of physical processes modelled in the continuum framework nowadays goes beyond purely mechanical processes. Processes such as phase transitions or growth and remodelling of biological tissues are routinely approached in the setting of continuum thermodynamics. Finally, the systems studied in continuum thermodynamics range from the very small ones studied in microfluidics, see for example Squires and Quake [89], up to the gigantic ones studied in planetary science, see for example Karato and Wu [48].

It seems that the laws governing the motion of a continuous medium must be extremely complicated in order to capture such a wide range of physical systems and phenomena of interest. This is only partially true. In principle, the laws governing the motion of a continuous medium can be seen as reformulations and generalizations/counterparts of the classical physical laws. (The laws of Newtonian physics of point particles and the laws of classical thermodynamics.) Surprisingly, the continuum counterparts of the classical laws are relatively easy to derive. These laws are—in the case of a single continuum medium—the *balance equations* for the mass, momentum, angular momentum, energy and the evolution equation for the entropy. The balance equations are supposed to be universally valid for any continuous medium, and their derivation is briefly discussed in Section 2.

The critical and the most difficult part in formulating the system of governing equations for a given material is the specification of the response of the material to the given stimuli. The sought stimulus–response relation can be, for example, a relation between the deformation and the stress or a relation between the heat flux and the temperature gradient. The task of finding a description of the material response is the task of finding the so-called *constitutive relations*.

Apparently, the need to specify the constitutive relation for a given material calls for an investigation of the microscopic structure of the material. The reader who is interested in examples of the derivation of constitutive relations from microscopic theories is referred to Bird et al [4] or Larson [52] to name a few. However, the investigation of the microscopic structure of the material is not the only option.

The constitutive relations can be specified staying entirely at the phenomenological level. Here the phenomenological level means that it is possible to deal only with phenomena directly accessible to the experience and measurement without trying to interpret the phenomena in terms of ostensibly more fundamental (microscopic) physical theories. Indeed, the possible class of constitutive relations is in fact severely restricted by physical requirements stemming for example from the requirement on Galilean invariance of the governing equations, perceived symmetry of the material, or the second law of thermodynamics. As it is apparent from the discussion in Section 4 such restrictions allow one to successfully specify constitutive relations.

2. BALANCE EQUATIONS

Before discussing the theory of constitutive relations it will be convenient to briefly recall the fundamental balance equations for a continuous medium. The reader who is not yet familiar with the field of continuum mechanics and thermodynamics is referred to Truesdell and Toupin [93], Müller [62], Truesdell and Rajagopal [92] or Gurtin et al [35] for a detailed treatment of balance equations and kinematics of continuous medium. Note that the same formalism can be applied even for several interacting continuous media which constitutes the continuum approach to the theory of mixtures, see for example Samohýl [84] and Rajagopal and Tao [81].

The continuous body \mathcal{B} is assumed to be a part of Euclidean space \mathbb{R}^3 . The motion of the body is described by the function χ that maps the positions \mathbf{X} of points at time t_0 to their respective positions \mathbf{x} at a later time instant t , such that $\mathbf{x} = \chi(\mathbf{X}, t)$. Concerning a suitable framework for the description of processes in a continuous medium, one can, in principle, choose from two alternatives.

Either one expresses the quantities of interest as functions of time and the initial position \mathbf{X} , or as functions of time and the chosen position \mathbf{x} in space \mathbb{R}^3 . The former alternative is called the Lagrangian description, while the latter is referred to as the Eulerian description.

The Lagrangian description is especially suitable for the description of change of form or shape, since in order to describe the change a reference point is needed. (Change with respect to some initial state.) As such, the Lagrangian description is a popular choice for studying the motion of solids.

On the other hand, the Eulerian description is not primarily focused on change with respect to some initial state, but on the rate of change. Naturally, the rate of change (the time derivative) can be captured by referring to the state of the material at the current time and in its infinitesimally small time neighborhood. In other words, if one is interested in the instantaneous velocity field, then there is no need to know complete trajectories of the individual points from the possibly distant initial state. As such, the Eulerian approach is useful for the description of the motion of fluids, where one is primarily interested in the velocity field, and the knowledge of the motion (individual trajectories) is of secondary importance. (Note, however, that the Eulerian description can be advantageous even in the description of solids, in particular in problems that involve phenomena like fluid-structure interaction or growth, see for example Frei et al [29, 30].) In what follows a theory for fluids is of primary interest, hence the Eulerian description is used.

The balance laws are derived by applying the classical laws of Newtonian physics and classical thermodynamics to a volume of the moving material $V(t) =_{\text{def}} \chi(V(t_0), t)$, where $V(t_0)$ is an arbitrarily chosen part of the continuous body \mathcal{B} . The main mathematical tool is the Reynolds transport theorem, see for example Truesdell and Toupin [93].

Theorem 1 (Reynolds transport theorem). *Let $\chi(\mathbf{x}, t)$ be a sufficiently smooth function describing the motion of the body \mathcal{B} , and let $V(t_0)$ be an arbitrary part of \mathcal{B} at the initial time t_0 . Let $\phi(\mathbf{x}, t)$ be a sufficiently smooth scalar Eulerian field, and let $V(t) = \chi(V(t_0), t)$ be the volume transported by the motion χ . Then*

$$\frac{d}{dt} \int_{V(t)} \phi(\mathbf{x}, t) \, dv = \int_{V(t)} \left(\frac{d\phi(\mathbf{x}, t)}{dt} + \phi(\mathbf{x}, t) \operatorname{div} \mathbf{v}(\mathbf{x}, t) \right) \, dv,$$

where

$$\frac{d\phi(\mathbf{x}, t)}{dt} =_{\text{def}} \frac{\partial \phi(\mathbf{x}, t)}{\partial t} + \mathbf{v}(\mathbf{x}, t) \cdot \nabla \phi(\mathbf{x}, t) \quad (2.1)$$

denotes the material time derivative, and $\mathbf{v}(\mathbf{x}, t)$ is the Eulerian velocity field, $\mathbf{v}(\mathbf{x}, t) =_{\text{def}} \left. \frac{\partial \chi(\mathbf{X}, t)}{\partial t} \right|_{\mathbf{X}=\chi^{-1}(\mathbf{x}, t)}$.

2.1. Balance of mass, momentum and angular momentum.

2.1.1. *Balance of mass.* Classical Newtonian physics assumes conservation of mass m , which can be written as $\frac{dm}{dt} = 0$. The balance of mass is a generalization of this equation to the continuum mechanics setting. The mass $m_{V(t)}$ of volume $V(t)$ is expressed in terms of the Eulerian density field $\rho(\mathbf{x}, t)$ as $m_{V(t)} =_{\text{def}} \int_{V(t)} \rho(\mathbf{x}, t) \, dv$. Using the notion of the density field, the Reynolds transport theorem and the requirement

$$\frac{dm_{V(t)}}{dt} = 0 \quad (2.2)$$

then immediately yield the integral form of the balance of mass

$$\int_{V(t)} \left(\frac{d\rho(\mathbf{x}, t)}{dt} + \rho(\mathbf{x}, t) \operatorname{div} \mathbf{v}(\mathbf{x}, t) \right) \, dv = 0, \quad (2.3)$$

where $V(t)$ is an arbitrary volume in the sense that it is the volume obtained by tracking an arbitrarily chosen initial volume $V(t_0)$. Since the volume in (2.3) is arbitrary, and the considered physical quantities are assumed to be sufficiently smooth, the integral form of the balance of mass leads to the pointwise evolution equation

$$\frac{d\rho(\mathbf{x}, t)}{dt} + \rho(\mathbf{x}, t) \operatorname{div} \mathbf{v}(\mathbf{x}, t) = 0. \quad (2.4)$$

Having (2.4), it follows that Reynolds transport theorem for the quantity $\phi(\mathbf{x}, t) =_{\text{def}} \rho(\mathbf{x}, t) \mathbf{w}(\mathbf{x}, t)$, where \mathbf{w} is an arbitrary Eulerian field, in fact reads

$$\frac{d}{dt} \int_{V(t)} \rho(\mathbf{x}, t) \mathbf{w}(\mathbf{x}, t) \, dv = \int_{V(t)} \rho(\mathbf{x}, t) \frac{d\mathbf{w}(\mathbf{x}, t)}{dt} \, dv. \quad (2.5)$$

This simple identity will be useful in the derivation of the remaining balance equations.

Note that the integral form of the balance of mass and the other balance equations as well can be reformulated in a weak form without the need to use the pointwise equation (2.4) as an intermediate step. See Feireisl [27] or Bulíček et al [8] for details.

2.1.2. *Balance of momentum.* Balance of momentum is the counterpart of Newton second law $\frac{d\mathbf{p}}{dt} = \mathbf{F}$ for point particles, where $\mathbf{p} = m\mathbf{v}$ is the momentum of particle with mass m moving with velocity \mathbf{v} . In continuum setting the momentum $\mathbf{p}_{V(t)}$ of volume $V(t)$ is expressed in terms of the Eulerian density and the velocity field as $\mathbf{p}_{V(t)} =_{\text{def}} \int_{V(t)} \rho(\mathbf{x}, t) \mathbf{v}(\mathbf{x}, t) \, dv$. The balance of momentum for $V(t)$ then reads

$$\frac{d\mathbf{p}_{V(t)}}{dt} = \mathbf{F}. \quad (2.6)$$

The force \mathbf{F} on the right hand side of the continuum counterpart of the Newton second law consists of two contributions,

$$\mathbf{F} = \mathbf{F}_{\text{volume}} + \mathbf{F}_{\text{contact}}. \quad (2.7)$$

The first physical mechanism that contributes to the force acting on the volume $V(t)$ is the specific body force \mathbf{b} . This is the force that acts on every part of $V(t)$, hence the specific body force contributes to the total force \mathbf{F} via the volume integral

$$\mathbf{F}_{\text{volume}} =_{\text{def}} \int_{V(t)} \rho(\mathbf{x}, t) \mathbf{b}(\mathbf{x}, t) \, dv. \quad (2.8)$$

A particular example of specific body force is the electrostatic force or the gravitational force.

The second contribution to the force \mathbf{F} acting on the volume $V(t)$ is the force $\mathbf{F}_{\text{contact}}$ due to the resistance of the material surrounding the volume $V(t)$. Since this force contribution arises due to wading of the volume $V(t)$ through the surrounding material, it acts on the surface of the volume $V(t)$. Consequently, it is referred to as the contact or surface force. The contact force contribution is a new physical mechanism that goes beyond the concept of forces between point particles, and it is the key concept in mechanics of continuous media.

The total contact force $\mathbf{F}_{\text{contact}}$ acting on $V(t)$ is assumed to take the form

$$\mathbf{F}_{\text{contact}} =_{\text{def}} \int_{\partial V(t)} \mathbf{t}(\mathbf{x}, t, \mathbf{n}(\mathbf{x}, t)) \, ds, \quad (2.9)$$

where \mathbf{t} is the contact force density and \mathbf{n} denotes the unit outward normal to the surface of volume $V(t)$. It is worth emphasising that the formula for the contact force is a *fundamental and nontrivial assumption concerning the nature of the forces acting in a continuous medium*.

Assuming that the contact force is given in terms of the contact force density $\mathbf{t}(\mathbf{x}, t, \mathbf{n}(\mathbf{x}, t))$, one can proceed further and prove that the contact force density is in fact given by the formula

$$\mathbf{t}(\mathbf{x}, t, \mathbf{n}(\mathbf{x}, t)) = \mathbb{T}(\mathbf{x}, t)\mathbf{n}(\mathbf{x}, t), \quad (2.10)$$

where $\mathbb{T}(\mathbf{x}, t)$ is a tensorial quantity that is referred to as the Cauchy stress tensor. The corresponding theorem is referred to as the Cauchy stress theorem, and the interested reader will find the proof for example in the classical treatise by Truesdell and Toupin [93]. Note that the proof of the Cauchy stress theorem could be rather subtle if one wants to work with functions that lack smoothness, see for example Šilhavý [87] and references therein for the discussion of this issue.

Using (2.10) and the formulae for the body force and the contact force, the equality $\frac{d\mathbf{p}_{V(t)}}{dt} = \mathbf{F}_{\text{volume}} + \mathbf{F}_{\text{contact}}$ that holds for arbitrary volume $V(t)$ can be rewritten in the form

$$\frac{d}{dt} \int_{V(t)} \rho(\mathbf{x}, t) \mathbf{v}(\mathbf{x}, t) dv = \int_{V(t)} \rho(\mathbf{x}, t) \mathbf{b}(\mathbf{x}, t) dv + \int_{\partial V(t)} \mathbb{T}(\mathbf{x}, t) \mathbf{n}(\mathbf{x}, t) ds, \quad (2.11)$$

which upon using the Reynolds transport theorem, the Stokes theorem and the identity (2.4) reduces to

$$\int_{V(t)} \rho(\mathbf{x}, t) \frac{d\mathbf{v}(\mathbf{x}, t)}{dt} dv = \int_{V(t)} [\text{div } \mathbb{T}(\mathbf{x}, t) + \rho(\mathbf{x}, t) \mathbf{b}(\mathbf{x}, t)] dv, \quad (2.12)$$

where $\frac{d\mathbf{v}(\mathbf{x}, t)}{dt}$ denotes the material time derivative of the Eulerian velocity field. (The divergence of the tensor field is defined as the operator that satisfies $(\text{div } \mathbb{A}) \cdot \mathbf{w} = \text{div}(\mathbb{A}^\top \mathbf{w})$ for an arbitrary constant vector field \mathbf{w} .) Since the considered physical quantities are assumed to be sufficiently smooth and the volume $V(t)$ can be chosen arbitrarily, the integral form of the balance of momentum (2.12) reduces to the pointwise equality

$$\rho(\mathbf{x}, t) \frac{d\mathbf{v}(\mathbf{x}, t)}{dt} = \text{div } \mathbb{T}(\mathbf{x}, t) + \rho(\mathbf{x}, t) \mathbf{b}(\mathbf{x}, t). \quad (2.13)$$

2.1.3. Balance of angular momentum. Balance of angular momentum is for a single point particle a simple consequence of Newton laws of motion, and it is in fact redundant. In the context of a continuous medium the balance of angular momentum however provides a nontrivial piece of information concerning the structure of the Cauchy stress tensor. In the simplest setting it reduces to the requirement on the symmetry of the Cauchy stress tensor

$$\mathbb{T}(\mathbf{x}, t) = \mathbb{T}^\top(\mathbf{x}, t), \quad (2.14)$$

see for example Truesdell and Toupin [93] for details.

2.2. Balance of total energy. The need to work with thermal effects inevitably calls for reformulating the laws of classical thermodynamics in continuum setting. Classical thermodynamics is essentially a theory applicable to a volume of a material wherein the physical fields are homogeneous and undergo only infinitesimal (slow in time) changes. This is clearly insufficient for the description of the behaviour of a moving continuous medium. In particular, the concepts of energy and entropy as introduced in classical thermodynamics, see for example Callen [15], need to be revisited.

A good demonstration of the (in)applicability of classical thermodynamics and its continuum counterpart is the analysis of the famous Joule experiment, see Joule [46]. In the experiment concerning the mechanical equivalence of heat Joule studied the rise of temperature due to the motion of a paddle-wheel rotating in a vessel filled with a fluid. The motion of the paddle-wheel was driven by the descent of weights connected via a system of pulleys to the paddle-wheel axis, see Figure 1. The potential energy of the weights is in this experiment transformed to the kinetic energy of the paddle-wheel and due to the resistance of the fluid in the vessel also to the kinetic and thermal energy of the fluid.

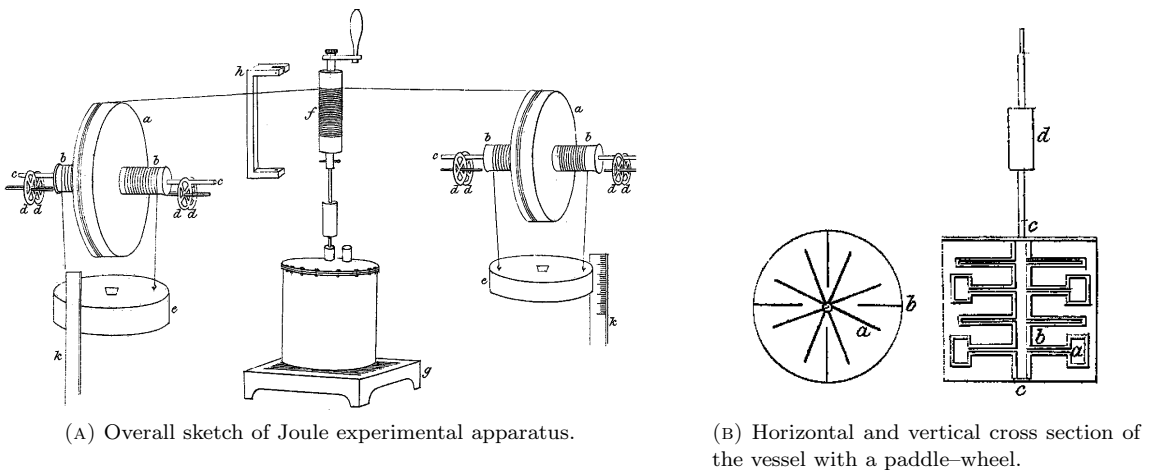


FIGURE 1. Joule experiment. (Original figures from Joule [47] with edits.)

Classical thermodynamics is restricted to the description of the initial and final state where the weights are at rest. At the beginning, the temperature is constant all over the vessel. This is the initial state. As the weights descend, the fluid moves and its temperature rises. Once the weights are stopped the temperature reaches, after some time, homogeneous distribution in the vessel. This is the final state. In the classical setting it is impossible to say anything about the intermediate states since the descent of the weight induces substantial motion in the fluid and inhomogeneous distribution of the temperature in the vessel. (Recall that the energy, entropy and temperature are in the classical setting defined only for the whole vessel.)

On the other hand the ambition of continuum thermodynamics is to describe the whole process and *the time evolution of the spatial distribution of the physical quantities of interest*. In order to describe the spatial distribution of the physical quantities of interest, one obviously needs to talk about specific internal energy $e(\mathbf{x}, t)$ and the specific entropy $\eta(\mathbf{x}, t)$. The internal energy or the entropy of the volume $V(t)$ of the material are then obtained by volume integration of the corresponding densities.

Besides the introduction of the specific internal energy $e(\mathbf{x}, t)$ and the specific entropy $\eta(\mathbf{x}, t)$, it is necessary to identify the energy exchange mechanisms in the continuous medium. Naturally, one part of the energy exchange is due to processes of mechanical origin.

In order to identify the energy exchange due to mechanical processes, it suffices to recall the same concept in classical Newtonian physics. The energy balance for a single particle of constant mass m is in the classical setting obtained via the multiplication of the Newton's second law $\frac{d}{dt}(m\mathbf{v}) = \mathbf{F}$ by the particle velocity \mathbf{v} , which yields $\frac{d}{dt}\left(\frac{1}{2}m|\mathbf{v}|^2\right) = \mathbf{F} \cdot \mathbf{v}$. Repeating the same steps in the setting of continuum mechanics—see the pointwise equality (2.13)—yields

$$\int_{V(t)} \rho(\mathbf{x}, t) \frac{d\mathbf{v}(\mathbf{x}, t)}{dt} \cdot \mathbf{v}(\mathbf{x}, t) dv = \int_{V(t)} [\operatorname{div} \mathbb{T}(\mathbf{x}, t) + \rho(\mathbf{x}, t)\mathbf{b}(\mathbf{x}, t)] \cdot \mathbf{v}(\mathbf{x}, t) dv, \quad (2.15)$$

where $\mathbf{v}(\mathbf{x}, t)$ is the Eulerian velocity field.

Further, one needs to introduce a quantity describing the non-mechanical part of the energy exchange between the given volume of the material and its surroundings. It is assumed that this part of the energy exchange can be described using the energy flux \mathbf{j}_e , and that the energy exchange through the volume boundary is then given by the means of a surface integral

$$- \int_{\partial V(t)} \mathbf{j}_e(\mathbf{x}, t) \cdot \mathbf{n}(\mathbf{x}, t) ds, \quad (2.16)$$

where \mathbf{n} denotes the unit outward normal to the surface of the volume. (The minus sign is due to the standard sign convention. If the energy flux vector \mathbf{j}_e points into the volume $V(t)$ —that is in the opposite direction to the unit outward normal—then the energy is transferred from the surrounding into the volume, and the surface integral is positive.) The energy flux \mathbf{j}_e is, in the simplest setting, tantamount to the heat flux $\mathbf{j}_q(\mathbf{x}, t)$. Consequently, *for the sake of clarity and specificity of the presentation*, it is henceforward assumed that $\mathbf{j}_e \equiv \mathbf{j}_q$. Using the heat flux \mathbf{j}_q , the non-mechanical energy exchange—the transferred heat—between the volume $V(t)$ and its surrounding is given by the surface integral

$$- \int_{\partial V(t)} \mathbf{j}_q(\mathbf{x}, t) \cdot \mathbf{n}(\mathbf{x}, t) ds. \quad (2.17)$$

Alternatively, one can also introduce volumetric heat source contribution to the energy exchange,

$$\int_{V(t)} \rho(\mathbf{x}, t) q(\mathbf{x}, t) dv, \quad (2.18)$$

but the volumetric contribution shall not be considered here for the sake of simplicity of presentation. (Similarly, volumetric contribution is not considered in the discussion on the concept of entropy and entropy production.)

Now one is ready to formulate the total energy balance for the volume $V(t)$. The total energy of the continuous medium in the volume $V(t)$ is assumed to be given by the volume integral $\int_{V(t)} \rho(\mathbf{x}, t) e_{\text{tot}}(\mathbf{x}, t) dv$ of the specific total energy e_{tot} . Further, the specific total energy is assumed to be given as the sum of the specific kinetic energy of the macroscopic motion $\frac{1}{2}|\mathbf{v}|^2$ and the specific internal energy e ,

$$\rho(\mathbf{x}, t) e_{\text{tot}}(\mathbf{x}, t) =_{\text{def}} \rho(\mathbf{x}, t) e(\mathbf{x}, t) + \frac{1}{2} \rho(\mathbf{x}, t) |\mathbf{v}(\mathbf{x}, t)|^2. \quad (2.19)$$

(In the simplest setting the internal energy represents the thermal energy, that is the energy of the microscopic motion, see Clausius [17].) The integral form of the balance law then reads

$$\begin{aligned} & \frac{d}{dt} \int_{V(t)} \rho(\mathbf{x}, t) e_{\text{tot}}(\mathbf{x}, t) dv \\ &= \int_{V(t)} \rho(\mathbf{x}, t) \mathbf{b}(\mathbf{x}, t) \cdot \mathbf{v}(\mathbf{x}, t) dv + \int_{\partial V(t)} [\mathbb{T}(\mathbf{x}, t) \mathbf{n}(\mathbf{x}, t)] \cdot \mathbf{v}(\mathbf{x}, t) ds - \int_{\partial V(t)} \mathbf{j}_q(\mathbf{x}, t) \cdot \mathbf{n}(\mathbf{x}, t) ds, \end{aligned} \quad (2.20)$$

where the right hand side contains all possible contributions to the energy exchange, namely the mechanical ones, see the right hand side of (2.15), and the non-mechanical ones, see (2.17).

If the physical quantities of interest are sufficiently smooth, then (2.20) can be in virtue of the Reynolds theorem, the Stokes theorem and the symmetry of the Cauchy stress tensor (2.14) reduced to the pointwise equation

$$\rho(\mathbf{x}, t) \frac{de_{\text{tot}}(\mathbf{x}, t)}{dt} = \rho(\mathbf{x}, t) \mathbf{b}(\mathbf{x}, t) \cdot \mathbf{v}(\mathbf{x}, t) + \operatorname{div} [\mathbb{T}(\mathbf{x}, t) \mathbf{v}(\mathbf{x}, t)] - \operatorname{div} \mathbf{j}_q(\mathbf{x}, t). \quad (2.21)$$

Equation (2.21) can be further manipulated in order to get an evolution equation for the specific internal energy e only. Multiplying the balance of momentum (2.13) by \mathbf{v} and subtracting the arising equation from the balance of total energy (2.21) yields, in virtue of the identity $\operatorname{div}(\mathbb{A}^\top \mathbf{a}) = (\operatorname{div} \mathbb{A}) \cdot \mathbf{a} + \mathbb{A} : \nabla \mathbf{a}$, the equation

$$\rho(\mathbf{x}, t) \frac{de(\mathbf{x}, t)}{dt} = \mathbb{T}(\mathbf{x}, t) : \mathbb{D}(\mathbf{x}, t) - \operatorname{div} \mathbf{j}_q(\mathbf{x}, t), \quad (2.22)$$

where the symmetry of the Cauchy stress tensor has been used. The symbol \mathbb{D} stands for the symmetric part of the velocity gradient, $\mathbb{D} =_{\text{def}} \frac{1}{2}(\nabla \mathbf{v} + \nabla \mathbf{v}^\top)$, and $\mathbb{A} : \mathbb{B} =_{\text{def}} \operatorname{Tr}(\mathbb{A} \mathbb{B}^\top)$. The term $\mathbb{T}(\mathbf{x}, t) : \mathbb{D}(\mathbf{x}, t)$ in (2.22) is called the stress power and plays a fundamental role in thermodynamics of continuous medium. A few hints on its relevance are given in Section 3. Later, in the discussion concerning constitutive relations for viscous fluids, it is shown that the stress power is one of the terms in the entropy production.

Note that although equations (2.22) and (2.21) are, in virtue of the balance of momentum (2.13), equivalent for sufficiently smooth functions, they are different from the perspective of a weak solution, see Feireisl and Málek [28], Bulíček et al [8] and Bulíček et al [9] for details.

2.3. Entropy. Concerning the concept of entropy in the setting of continuum mechanics, two assumptions must be made.

First, it is assumed, following the classical setting, that an energetic equation of state holds even for the *specific* internal energy and the *specific* entropy. Note that the particular form of the energetic equation of state depends on the given material, hence the energetic equation of state is in fact a constitutive relation.

In the simplest setting, the energetic equation of state reads

$$e(\mathbf{x}, t) = e(\eta(\mathbf{x}, t), \rho(\mathbf{x}, t)), \quad (2.23)$$

which is clearly a straightforward generalization of the classical relation $E = E(S, V)$, see for example Callen [15]. A general energetic equation of state can however take a more complex form

$$e(\mathbf{x}, t) = e(\eta(\mathbf{x}, t), y_1(\mathbf{x}, t), \dots, y_m(\mathbf{x}, t)), \quad (2.24)$$

where y_1, \dots, y_m , $m \in \mathbb{N}$, $m \geq 1$ are other state variables.

If the energetic equation of state is obtained as a direct analogue of a classical equilibrium energetic equation of state, then it is said that the system under consideration satisfies the assumption of *local equilibrium*, and that the system is studied in the framework of classical irreversible thermodynamics. However, if one wants to describe the phenomena that go beyond the classical setting, see for example Section 4, then the energetic equation of state must be more complex. In particular, the energetic equation of state can contain the spatial gradients as variables. In such a case it is said that the system is studied in the framework of *extended irreversible thermodynamics*.

Second, the energetic equation of state is assumed to *hold at every time instant in the given class of processes of interest*. This is again a departure from the classical setting, where the relations of type $E = E(S, V)$ hold only in equilibrium or in quasistatic (infinitesimally slow) processes. In particular, in the current setting it is assumed that one can take the time derivative of the equation of state. For example, if the equation of state is (2.23) then

$$\frac{de(\mathbf{x}, t)}{dt} = \left. \frac{\partial e(\eta, \rho)}{\partial \rho} \right|_{\eta=\eta(\mathbf{x}, t), \rho=\rho(\mathbf{x}, t)} \frac{d\rho(\mathbf{x}, t)}{dt} + \left. \frac{\partial e(\eta, \rho)}{\partial \eta} \right|_{\eta=\eta(\mathbf{x}, t), \rho=\rho(\mathbf{x}, t)} \frac{d\eta(\mathbf{x}, t)}{dt} \quad (2.25)$$

is assumed to be valid in the *given class of processes* of interest, no matter how rapid the time changes are or how large the spatial inhomogeneities are.

2.3.1. Thermodynamic temperature. Besides the energetic equation of the state one can, following classical equilibrium thermodynamics, specify the entropy as a function of the internal energy e and the other state variables y_1, \dots, y_m , $m \in \mathbb{N}$, $m \geq 1$, which leads to the entropic equation of state

$$\eta(\mathbf{x}, t) = \eta(e(\mathbf{x}, t), y_1(\mathbf{x}, t), \dots, y_m(\mathbf{x}, t)). \quad (2.26)$$

The specific entropy η is assumed to be a differentiable function, and further it is assumed that

$$\left. \frac{\partial \eta}{\partial e}(e, y_1, \dots, y_m) \right|_{e=e(\mathbf{x}, t), y_1=y_1(\mathbf{x}, t), \dots, y_m=y_m(\mathbf{x}, t)} > 0 \quad (2.27)$$

holds for any fixed m -tuple y_1, \dots, y_m and point (\mathbf{x}, t) . This allows one to invert (2.26) and get the energetic equation of state

$$e(\mathbf{x}, t) = e(\eta(\mathbf{x}, t), y_1(\mathbf{x}, t), \dots, y_m(\mathbf{x}, t)). \quad (2.28)$$

Further, following classical equilibrium thermodynamics, the thermodynamic temperature θ is defined as

$$\theta(\mathbf{x}, t) =_{\text{def}} \left. \frac{\partial e}{\partial \eta}(\eta, y_1, \dots, y_m) \right|_{\eta=\eta(\mathbf{x}, t), y_1=y_1(\mathbf{x}, t), \dots, y_m=y_m(\mathbf{x}, t)}. \quad (2.29)$$

2.3.2. *Clausius–Duhem inequality.* The last ingredient one needs in the development of thermodynamics of continuous medium is a counterpart of the classical Clausius inequality

$$dS \geq \frac{dQ}{\theta}, \quad (2.30)$$

where θ is the thermodynamic temperature, see Clausius [18]. Recall that in the ideal situation of reversible processes the inequality reduces to the equality

$$dS = \frac{dQ}{\theta}. \quad (2.31)$$

The generalisation of the Clausius inequality is the Clausius–Duhem inequality

$$\frac{d}{dt} \int_{V(t)} \rho(\mathbf{x}, t) \eta(\mathbf{x}, t) dv \geq - \int_{\partial V(t)} \frac{\mathbf{j}_q(\mathbf{x}, t)}{\theta(\mathbf{x}, t)} \cdot \mathbf{n} ds + \int_{V(t)} \rho(\mathbf{x}, t) \frac{q(\mathbf{x}, t)}{\theta(\mathbf{x}, t)} dv, \quad (2.32)$$

which can be obtained from (2.30) by appealing to the same arguments as in the discussion of the concept of the energy. (Recall that the transferred heat is expressed in terms of the surface integral (2.17).) The last term in (2.32) accounts for entropy changes due to volumetric heat sources. As before, see the discussion in Section 2.2, the volumetric term shall not be henceforward considered for the sake of simplicity of presentation. In what follows, the Clausius–Duhem inequality is therefore considered in the form

$$\frac{d}{dt} \int_{V(t)} \rho(\mathbf{x}, t) \eta(\mathbf{x}, t) dv \geq - \int_{\partial V(t)} \frac{\mathbf{j}_q(\mathbf{x}, t)}{\theta(\mathbf{x}, t)} \cdot \mathbf{n} ds, \quad (2.33)$$

where $V(t)$ is again an arbitrary volume in the sense that it is the volume obtained by tracking an arbitrarily chosen initial volume $V(t_0)$.

Since the classical Clausius (in)equality (2.30) is the mathematical formalisation of the second law of thermodynamics, the Clausius–Duhem inequality (2.33) can be understood as the *reinterpretation of the second law of thermodynamics in the setting of continuum thermodynamics*. As such the Clausius–Duhem inequality can be expected to play a crucial role in the theory which is indeed the case.

It is convenient, for the sake of later reference, to rewrite the inequality in a slightly different form. Using the Stokes theorem, the Reynolds transport theorem and identity (2.5), the inequality (2.33) can be rewritten in the form

$$\int_{V(t)} \left[\rho(\mathbf{x}, t) \frac{d\eta}{dt}(\mathbf{x}, t) + \operatorname{div} \left(\frac{\mathbf{j}_q(\mathbf{x}, t)}{\theta(\mathbf{x}, t)} \right) \right] dv \geq 0. \quad (2.34)$$

The first term in (2.34) is the change of the net entropy,

$$\frac{dS_{V(t)}}{dt} =_{\text{def}} \left[\frac{d}{dt} \int_{V(t)} \rho(\mathbf{x}, t) \eta(\mathbf{x}, t) dv \right], \quad (2.35)$$

while the other term is the entropy exchange—the entropy flux—with the surrounding of volume $V(t)$,

$$J_{\partial V(t)} =_{\text{def}} \int_{\partial V(t)} \frac{\mathbf{j}_q(\mathbf{x}, t)}{\theta(\mathbf{x}, t)} \cdot \mathbf{n} ds. \quad (2.36)$$

The general statement of a balance law in continuum mechanics and thermodynamics is that the time change of the given quantity in the volume $V(t)$ plus the flux $J_{\partial V(t)}$ of the quantity through the boundary of $V(t)$ is equal to the production of the given quantity in the volume $V(t)$,

$$\frac{dS_{V(t)}}{dt} + J_{\partial V(t)} = \Xi_{V(t)}. \quad (2.37)$$

Using this nomenclature, it follows that the left hand side of (2.34) deserves to be denoted as the *net entropy production* in the volume $V(t)$.

Further, it is assumed that the net entropy production can be obtained via a volume integral of the corresponding spatially distributed quantity $\xi(\mathbf{x}, t)$,

$$\Xi_{V(t)} =_{\text{def}} \int_{V(t)} \xi(\mathbf{x}, t) dv. \quad (2.38)$$

In such a case the Clausius–Duhem inequality can be rewritten as

$$\Xi_{V(t)} = \frac{dS_{V(t)}}{dt} + J_{\partial V(t)} \geq 0. \quad (2.39)$$

Now it is clear that the Clausius–Duhem inequality in fact states that the net entropy production in the volume $V(t)$ is nonnegative,

$$\Xi_{V(t)} \geq 0. \quad (2.40)$$

Note that if the heat flux \mathbf{j}_q vanishes on the boundary of $V(t)$, then the flux term in (2.39) vanishes, and it follows that the net entropy of the volume $V(t)$ increases in time. This is the classical statement concerning the behaviour of isolated systems.

Finally, using the concept of entropy production density (2.38) it follows that the localised version of (2.34) reads

$$\xi(\mathbf{x}, t) = \rho(\mathbf{x}, t) \frac{d\eta}{dt}(\mathbf{x}, t) + \operatorname{div} \left(\frac{\mathbf{j}_q(\mathbf{x}, t)}{\theta(\mathbf{x}, t)} \right) \geq 0. \quad (2.41)$$

The fact that (2.33) is indeed a generalization of (2.30) is best seen in the case of a vessel filled with a fluid with “almost” constant uniform temperature distribution $\theta(\mathbf{x}, t) =_{\text{def}} \theta$ that is subject to heat exchange with its surrounding. In such a case time integration of (2.33) from t_1 to t_2 yields

$$\int_{V(t_2)} \rho(\mathbf{x}, t_2) \eta(\mathbf{x}, t_2) \, dv - \int_{V(t_1)} \rho(\mathbf{x}, t_1) \eta(\mathbf{x}, t_1) \, dv \geq -\frac{1}{\theta} \int_{t_1}^{t_2} \left(\int_{\partial V(t)} \mathbf{j}_q(\mathbf{x}, t) \cdot \mathbf{n} \, ds \right) dt. \quad (2.42)$$

The left hand side is the difference between the net entropy of the fluid in the vessel at times t_2 and t_1 , and the right hand side is the heat exchanged with the surrounding in the time interval $[t_1, t_2]$, hence one gets

$$S(t_2) - S(t_1) \geq \frac{\Delta Q}{\theta}, \quad (2.43)$$

which is tantamount to (2.30).

2.3.3. Entropy production. In the setting of continuum mechanics it is assumed that the energetic equation of state is known, which means that a relation of the type (2.25) holds for the time derivative of the entropy. The knowledge of the energetic equation of state for the given material allows one to identify the entropy production mechanisms in the material, that is the quantity $\xi(\mathbf{x}, t)$ in (2.41). In other words one can rewrite the left hand side of (2.41) in terms of more convenient quantities than the entropy. Indeed, inspecting carefully (2.25) it is easy to see that (2.25) is in fact a formula for the material time derivative of the specific entropy $\frac{d\eta(\mathbf{x}, t)}{dt}$,

$$\frac{d\eta(\mathbf{x}, t)}{dt} = \frac{1}{\theta(\mathbf{x}, t)} \left[\frac{de(\mathbf{x}, t)}{dt} - \frac{p_{\text{th}}(\mathbf{x}, t)}{[\rho(\mathbf{x}, t)]^2} \frac{d\rho(\mathbf{x}, t)}{dt} \right], \quad (2.44)$$

where the thermodynamic temperature $\theta(\mathbf{x}, t)$ and the thermodynamic pressure $p_{\text{th}}(\mathbf{x}, t)$ have been defined by formulae

$$\theta(\mathbf{x}, t) =_{\text{def}} \left. \frac{\partial e(\eta, \rho)}{\partial \eta} \right|_{\eta=\eta(\mathbf{x}, t), \rho=\rho(\mathbf{x}, t)}, \quad (2.45a)$$

$$p_{\text{th}}(\mathbf{x}, t) =_{\text{def}} [\rho(\mathbf{x}, t)]^2 \left. \frac{\partial e(\eta, \rho)}{\partial \rho} \right|_{\eta=\eta(\mathbf{x}, t), \rho=\rho(\mathbf{x}, t)}. \quad (2.45b)$$

(These relations are counterparts of the well known classical relations, see for example Callen [15].)

The time derivatives $\frac{de(\mathbf{x}, t)}{dt}$ and $\frac{d\rho(\mathbf{x}, t)}{dt}$ are known from the balance laws (2.22) and (2.4), and using the balance laws in (2.44) yields

$$\rho(\mathbf{x}, t) \frac{d\eta(\mathbf{x}, t)}{dt} = \frac{1}{\theta(\mathbf{x}, t)} [\mathbb{T}(\mathbf{x}, t) : \mathbb{D}(\mathbf{x}, t) - \text{div } \mathbf{j}_q(\mathbf{x}, t) + p_{\text{th}}(\mathbf{x}, t) \text{div } \mathbf{v}(\mathbf{x}, t)]. \quad (2.46)$$

Finally, using (2.46) in (2.41) leads one, after some manipulation, to

$$\frac{1}{\theta(\mathbf{x}, t)} [\mathbb{T}(\mathbf{x}, t) : \mathbb{D}(\mathbf{x}, t) + p_{\text{th}}(\mathbf{x}, t) \text{div } \mathbf{v}(\mathbf{x}, t)] - \frac{1}{[\theta(\mathbf{x}, t)]^2} \mathbf{j}_q(\mathbf{x}, t) \cdot \nabla \theta(\mathbf{x}, t) = \rho(\mathbf{x}, t) \frac{d\eta}{dt}(\mathbf{x}, t) + \text{div} \left(\frac{\mathbf{j}_q(\mathbf{x}, t)}{\theta(\mathbf{x}, t)} \right) \geq 0. \quad (2.47)$$

The expression on the left hand side of (2.47) that is

$$\xi(\mathbf{x}, t) =_{\text{def}} \frac{1}{\theta(\mathbf{x}, t)} [\mathbb{T}(\mathbf{x}, t) : \mathbb{D}(\mathbf{x}, t) + p_{\text{th}}(\mathbf{x}, t) \text{div } \mathbf{v}(\mathbf{x}, t)] - \frac{1}{[\theta(\mathbf{x}, t)]^2} \mathbf{j}_q(\mathbf{x}, t) \cdot \nabla \theta(\mathbf{x}, t) \quad (2.48)$$

determines the *entropy production* in the given material, see the local version of the Clausius–Duhem inequality (2.41). In other words, in the continuum setting one is able to explicitly evaluate, for the given material, the “uncompensated transformation”

$$N =_{\text{def}} dS - \frac{dQ}{\theta} \quad (2.49)$$

introduced by Clausius [18].

The Clausius–Duhem inequality (2.41) requires $\xi(\mathbf{x}, t)$ to be nonnegative, hence (2.47) can be expected to impose some restrictions on the form of the constitutive relations. This is indeed the case, and this observation is the key concept exploited in the theory of constitutive relations discussed in Section 4.

Furthermore, relations of the type (2.47) provide one an explicit criterion for the validity of the Clausius *equality* (2.31). In particular, a process in a material with energetic equation of state of the type (2.23) is reversible, that is (2.31) holds, if the entropy production (2.48) vanishes. From (2.48) it follows that the entropy production vanishes if there are no temperature and velocity gradients in the material. This means that the process in the material is very close to an ideal reversible process if the gradients $\nabla \theta$ and \mathbb{D} are during the whole process kept extremely small. The other possibility is that the entropy production identically vanishes because of the particular choice of the constitutive relation for \mathbb{T} and \mathbf{j}_q , see Section 4.2.2 for details.

3. STRESS POWER AND ITS IMPORTANCE

The second law of thermodynamics requires the entropy production to be a nonnegative quantity. However, such statement concerning the entropy production does not seem to be very intuitive. In what follows it is shown that the nonnegativity of the entropy production is in fact closely related to some fundamental direct observations concerning the qualitative behaviour of real materials.

Let us for example consider the entropy production for an *incompressible* homogeneous viscous heat non-conducting fluid. The incompressibility means that $\operatorname{div} \mathbf{v} = 0$ is required to hold in the class of considered processes, while the fact that a heat non-conducting fluid is considered translates into the requirement $\mathbf{j}_q = \mathbf{0}$. In such a case the entropy production (2.48) reduces to

$$\xi(\mathbf{x}, t) = \frac{1}{\theta(\mathbf{x}, t)} \mathbb{T}(\mathbf{x}, t) : \mathbb{D}(\mathbf{x}, t). \quad (3.1)$$

(Details concerning the derivation of the entropy production in an incompressible fluid can be found in Section 4. Note that for an incompressible fluid one gets $\mathbb{T} : \mathbb{D} = \mathbb{T}_\delta : \mathbb{D}_\delta$, see the discussion in Section 4.2.3, in particular formula (4.53).) Since the thermodynamic temperature in (3.1) is a positive quantity, it follows that the requirement on the nonnegativity of the entropy production simplifies to

$$\mathbb{T} : \mathbb{D} \geq 0. \quad (3.2)$$

This means that the second law is satisfied provided that the *stress power* is a pointwise nonnegative quantity.

The importance of the requirement concerning the nonnegativity of the stress power term $\mathbb{T} : \mathbb{D}$ —and consequently the nonnegativity of the entropy production—is documented below by means of two simple *mechanical examples*. These two examples show that the seemingly esoteric requirement on the nonnegativity of entropy production leads to very natural consequences. First, it is shown that the pointwise *positivity* of the stress power is sufficient for establishing the fact that the *drag force* acting on a rigid body moving through an incompressible fluid decelerates the moving body, see Section 3.1. Second, it is shown that the pointwise positivity of the stress power is sufficient to establish the *stability of the rest state* of an incompressible fluid, see Section 3.2.

3.1. Drag. Let us first consider the setting shown in Figure 2. A rigid body \mathcal{B} moves with *constant velocity* \mathbf{U} in an infinite domain, and it is assumed that no body force is acting on the surrounding fluid. Further, it is assumed that the velocity field in the fluid that is generated by the motion of the body decays sufficiently fast at infinity, and that the fluid adheres to the surface of the body, that is $\mathbf{v}|_{\partial\mathcal{B}} = \mathbf{U}$.

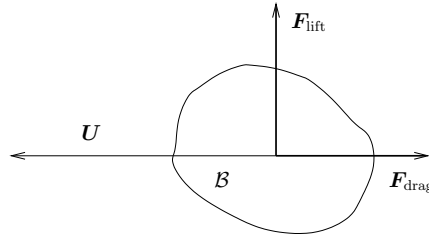


FIGURE 2. Body moving in a fluid.

The drag force is the projection of the force acting on the body to the direction parallel to the velocity \mathbf{U} ,

$$\mathbf{F}_{\text{drag}} =_{\text{def}} \frac{\mathbf{U} \otimes \mathbf{U}}{|\mathbf{U}|^2} \left(\int_{\partial\mathcal{B}} \mathbb{T} \mathbf{n} \, ds \right). \quad (3.3)$$

The key observation is that if the fluid is assumed to be a homogeneous incompressible fluid with symmetric Cauchy stress tensor, then the formula for the drag force (3.3) can be rewritten in the form

$$\mathbf{F}_{\text{drag}} = - \left(\int_{\text{exterior of } \mathcal{B}} \mathbb{T} : \mathbb{D} \, dv \right) \frac{\mathbf{U}}{|\mathbf{U}|^2}. \quad (3.4)$$

The derivation of (3.4) proceeds as follows. The balance of momentum (2.13) and the balance of mass (2.5) for the motion of the fluid outside the body \mathcal{B} are

$$\rho \frac{d\mathbf{v}}{dt} = \operatorname{div} \mathbb{T}, \quad (3.5a)$$

$$\operatorname{div} \mathbf{v} = 0, \quad (3.5b)$$

and the boundary conditions read

$$\mathbf{v}|_{\partial\mathcal{B}} = \mathbf{U}, \quad (3.5c)$$

$$\mathbf{v}(\mathbf{x}, t) \rightarrow \mathbf{0} \text{ as } |\mathbf{x}| \rightarrow +\infty. \quad (3.5d)$$

Note that the velocity field is considered to be a steady velocity field, hence the material time derivative is $\frac{d\mathbf{v}}{dt} = [\nabla \mathbf{v}] \mathbf{v}$.

Let $\Omega = \{\mathbf{x} \in \mathbb{R}^3, |\mathbf{x}| < R\} \setminus \overline{\mathcal{B}}$ denote the ball centered at origin with radius R (large number) with excluded body \mathcal{B} and its boundary $\partial\mathcal{B}$. Governing equations (3.5) hold in this domain. Now one can multiply (3.5a) by \mathbf{v} and integrate over Ω ,

$$\int_{\Omega} \rho ([\nabla \mathbf{v}] \mathbf{v}) \cdot \mathbf{v} \, dv = \int_{\Omega} (\operatorname{div} \mathbb{T}) \cdot \mathbf{v} \, dv. \quad (3.6)$$

Application of standard identities yields

$$\int_{\Omega} \frac{1}{2} \rho \mathbf{v} \cdot (\nabla |\mathbf{v}|^2) \, dv = \int_{\Omega} \operatorname{div} (\mathbb{T}^{\top} \mathbf{v}) \, dv - \int_{\Omega} \mathbb{T} : \mathbb{D} \, dv. \quad (3.7)$$

The first term on the right hand side can be in virtue of the Stokes theorem rewritten as a sum of integrals over the boundary of the ball and the boundary of the body

$$\int_{\Omega} \operatorname{div} (\mathbb{T}^{\top} \mathbf{v}) \, dv = \int_{\{\mathbf{x} \in \mathbb{R}^3, |\mathbf{x}|=R\}} (\mathbb{T}^{\top} \mathbf{v}) \cdot \mathbf{n} \, ds - \int_{\partial \mathcal{B}} (\mathbb{T}^{\top} \mathbf{v}) \cdot \mathbf{n} \, ds = \int_{\{\mathbf{x} \in \mathbb{R}^3, |\mathbf{x}|=R\}} (\mathbb{T}^{\top} \mathbf{v}) \cdot \mathbf{n} \, ds - \mathbf{U} \cdot \int_{\partial \mathcal{B}} \mathbb{T} \mathbf{n} \, ds, \quad (3.8)$$

where the boundary condition (3.5c) has been used. (Note that the last integral is taken over the surface of *the body*, hence one needs to add the minus sign in order to compensate the opposite orientation of the surface of the body and the surface of Ω .)

Concerning the left hand side of (3.7) integration by parts implies

$$\int_{\Omega} \frac{1}{2} \rho \mathbf{v} \cdot (\nabla |\mathbf{v}|^2) \, dv = \int_{\partial \Omega} \frac{1}{2} \rho |\mathbf{v}|^2 \mathbf{v} \cdot \mathbf{n} \, ds - \int_{\Omega} \frac{1}{2} \rho |\mathbf{v}|^2 \operatorname{div} \mathbf{v} \, dv = \int_{\{\mathbf{x} \in \mathbb{R}^3, |\mathbf{x}|=R\}} \frac{1}{2} \rho |\mathbf{v}|^2 \mathbf{v} \cdot \mathbf{n} \, ds, \quad (3.9)$$

where the boundary condition (3.5c) and the incompressibility, $\operatorname{div} \mathbf{v} = 0$, have been used.

Summing up all partial results, it follows that (3.7) reduces to

$$\int_{\{\mathbf{x} \in \mathbb{R}^3, |\mathbf{x}|=R\}} \frac{1}{2} \rho |\mathbf{v}|^2 \mathbf{v} \cdot \mathbf{n} \, ds = \int_{\{\mathbf{x} \in \mathbb{R}^3, |\mathbf{x}|=R\}} (\mathbb{T}^{\top} \mathbf{v}) \cdot \mathbf{n} \, ds - \mathbf{U} \cdot \int_{\partial \mathcal{B}} \mathbb{T} \mathbf{n} \, ds - \int_{\Omega} \mathbb{T} : \mathbb{D} \, dv. \quad (3.10)$$

Now one can take the limit $R \rightarrow +\infty$, and use the fact that the velocity vanishes sufficiently fast for $R \rightarrow +\infty$. This means that the surface integrals in (3.10) vanish for $R \rightarrow +\infty$, and that (3.10) reduces to

$$\mathbf{U} \cdot \int_{\partial \mathcal{B}} \mathbb{T} \mathbf{n} \, ds = - \int_{\Omega} \mathbb{T} : \mathbb{D} \, dv, \quad (3.11)$$

which yields the proposition.

The implication of formula (3.4) is, that if the stress power $\mathbb{T} : \mathbb{D}$ is pointwise nonnegative, then the drag direction is opposite to the direction of the motion. (The drag force is acting against the motion of the body.) This is definitely a desirable outcome from the point of everyday experience, and, as it has been shown, this outcome is closely related to the second law of thermodynamics.

3.2. Stability of the rest state. Let Ω denote a vessel occupied at time t_0 by a homogeneous incompressible viscous fluid, and let no external body force acts on the fluid. The Cauchy stress tensor is again assumed to be symmetric. Further, it is assumed that the fluid adheres to the surface of the vessel,

$$\mathbf{v}|_{\partial \Omega} = \mathbf{0}. \quad (3.12)$$

The everyday experience is that whatever has been the initial state of the fluid, the fluid comes, after some time, to the state of rest, that is $\mathbf{v} = \mathbf{0}$ in Ω . The question is whether it is possible to recover this fact for a general homogeneous incompressible viscous fluid.

A good measure of the deviation from the rest state is the net kinetic energy of the fluid

$$E_{\text{kin}} =_{\text{def}} \frac{1}{2} \int_{\Omega} \rho(\mathbf{x}, t) |\mathbf{v}(\mathbf{x}, t)|^2 \, dv. \quad (3.13)$$

In order to assess the stability of the rest state, one needs to find an evolution equation for a measure of the deviation from the rest state. This is an easy task if the measure of the deviation from the rest state is the net kinetic energy introduced in (3.13).

The evolution equations for the motion of the fluid are

$$\rho \frac{d\mathbf{v}}{dt} = \operatorname{div} \mathbb{T}, \quad (3.14a)$$

$$\operatorname{div} \mathbf{v} = 0, \quad (3.14b)$$

and the multiplication of (3.14a) with \mathbf{v} followed by integration over the domain Ω yields

$$\int_{\Omega} \frac{d}{dt} \left(\rho \frac{1}{2} \mathbf{v} \cdot \mathbf{v} \right) \, dv = \int_{\Omega} (\operatorname{div} \mathbb{T}) \cdot \mathbf{v} \, dv. \quad (3.15)$$

(See identity (2.5).) The left hand side is equal to the time derivative of the net kinetic energy (3.13). Concerning the right hand side, one can use the identity $\operatorname{div} (\mathbb{A}^{\top} \mathbf{a}) = (\operatorname{div} \mathbb{A}) \cdot \mathbf{a} + \mathbb{A} : \nabla \mathbf{a}$, the Stokes theorem, and the fact that \mathbf{v} vanishes on the boundary to get

$$\int_{\Omega} (\operatorname{div} \mathbb{T}) \cdot \mathbf{v} \, dv = - \int_{\Omega} \mathbb{T} : \mathbb{D} \, dv. \quad (3.16)$$

This implies that the evolution equation for the net kinetic energy reads

$$\frac{dE_{\text{kin}}}{dt} = - \int_{\Omega} \mathbb{T} : \mathbb{D} \, dv. \quad (3.17)$$

It follows that if the stress power $\mathbb{T} : \mathbb{D}$ is pointwise positive, then the right hand side of (3.17) is negative, and the net kinetic energy decays in time. If one was interested in the rate of decay, and in the proof that the net kinetic energy decays to zero, then one would need further information on the relation between the Cauchy stress tensor and the symmetric part of the velocity gradient. (The details are not elaborated here, interested reader is referred to Serrin [86] for the detailed

treatment of the Navier–Stokes fluid, $\mathbb{T} = -p\mathbb{I} + 2\mu\mathbb{D}$. Note that the net kinetic energy does not completely vanish in finite time.) The decay of the kinetic energy of the fluid contained in a closed vessel is definitely a desirable outcome from the point of view of everyday experience, and, as it has been shown, the decay is closely related to the second law of thermodynamics.

4. CONSTITUTIVE RELATIONS

The motion of a single continuous medium is governed by the following system of partial differential equations

$$\frac{d\rho(\mathbf{x}, t)}{dt} + \rho(\mathbf{x}, t) \operatorname{div} \mathbf{v}(\mathbf{x}, t) = 0, \quad (4.1a)$$

$$\rho(\mathbf{x}, t) \frac{d\mathbf{v}(\mathbf{x}, t)}{dt} = \operatorname{div} \mathbb{T}(\mathbf{x}, t) + \rho(\mathbf{x}, t) \mathbf{b}(\mathbf{x}, t), \quad (4.1b)$$

$$\mathbb{T}(\mathbf{x}, t) = \mathbb{T}^\top(\mathbf{x}, t), \quad (4.1c)$$

$$\rho(\mathbf{x}, t) \frac{de(\mathbf{x}, t)}{dt} = \mathbb{T}(\mathbf{x}, t) : \mathbb{D}(\mathbf{x}, t) - \operatorname{div} \mathbf{j}_q(\mathbf{x}, t) \quad (4.1d)$$

that are mathematical expressions of the balance law for the mass, linear momentum, angular momentum and the total energy. (See equations (2.4), (2.13), (2.14) and (2.22).) The unknown quantities are the density ρ , the velocity field \mathbf{v} and the specific internal energy e . (For the first reading the internal energy can be thought of as a proxy for the temperature field $\theta(\mathbf{x}, t)$.)

These equations are insufficient for the description of the evolution of the quantities of interest. The reason is that the Cauchy stress tensor \mathbb{T} and the heat flux \mathbf{j}_q act in (4.1) as additional unknowns *a priori* unrelated to the density ρ , the velocity field \mathbf{v} and the specific internal energy e . Therefore, in order to get a closed system of governing equations, system (4.1) must be supplemented by a set of equations relating the stress and the heat flux to the other quantities. These relations are called the *constitutive relations*, and they describe the *response of the material to the considered stimuli*.

It is worth emphasising that the *constitutive relations are specific for the given material*. For example, the Cauchy stress tensor is a quantity that describes how the given volume of the material is affected by its surrounding, see Section 2.1.2. Clearly, the interaction between the given volume of the material and its surrounding depends on the particular type of the material. Similarly, the heat flux describes the thermal energy transfer capabilities of the given material, hence it is material specific. The fact that the constitutive relations are material specific means that they indeed provide an extra piece of information supplementing the balance laws. Consequently, the constitutive relations can be derived only if one appeals to physical concepts that go beyond the balance laws.

Moreover, the constitutive relations are inevitably simplified and reduced descriptions of the physical reality, and as such they are designed to describe only the behaviour of the given *material* in a certain class of *processes*. For example, the same material, say steel, can be processed by hot forging, it can deform as a part of a truss bridge or move as a projectile. The mathematical models for the response of the material in these processes are however different despite the fact that the material remains the same. *The specification of the constitutive relations therefore depends on two things—the material and the considered processes.*

The most *convenient* form of the constitutive relations would be a set of equations of the form

$$\mathbb{T} = \mathbb{T}(\rho, \mathbf{v}, e), \quad (4.2a)$$

$$\mathbf{j}_q = \mathbf{j}_q(\rho, \mathbf{v}, e). \quad (4.2b)$$

This would allow one to substitute for \mathbb{T} and \mathbf{j}_q into (4.1), and get a system of evolution equations for the unknown fields ρ , \mathbf{v} and e . An example of a system of constitutive relations of the type (4.2) are the well known constitutive relations for the compressible viscous heat conducting Navier–Stokes fluid,

$$\mathbb{T} = -p_{\text{th}}(\rho, \theta)\mathbb{I} + \lambda(\operatorname{div} \mathbf{v})\mathbb{I} + 2\nu\mathbb{D}, \quad (4.3a)$$

$$\mathbf{j}_q = -\kappa\nabla\theta, \quad (4.3b)$$

where $p_{\text{th}}(\rho, \theta)$ denotes the thermodynamic pressure determined by an equation of state. (See Section 4.2 for details.) Substituting (4.3) into (4.1) then leads to the well known Navier–Stokes–Fourier system of partial differential equations.

Besides the constitutive relations the system of balance laws must be supplemented with *initial and boundary conditions*. The boundary conditions can be seen as a special case of constitutive relations at the interface between two materials. As such the boundary conditions can be very complex. In fact, the processes at the interface can have, for example, their own dynamics, meaning that they can be governed by an extra set of partial differential equations at the interface. Unfortunately, discussion of complex boundary conditions goes beyond the scope of the present contribution, and the issue is only briefly touched in Section 4.6. Consequently, overall the discussion of boundary conditions is mainly restricted to the claim that the considered boundary conditions are the standard ones such as the no-slip boundary condition for the velocity field. The reader should be however aware of the fact that the specification of the boundary conditions is far from being trivial, and that it again requires additional physical insight into the problem.

The early efforts concerning the theory of constitutive relations for fluids, see for example Rivlin and Ericksen [83], Oldroyd [65] and Noll [64] or the historical essay by Tanner and Walters [90], were mainly focused on the specification of the Cauchy stress tensor in terms of the kinematical variables. These early approaches were based almost exclusively on mechanical considerations, such as the symmetry of the material and the requirement of the invariance of the constitutive relations with respect to the change of the observer. Thermodynamic consideration were rarely the leading theme, and were mainly reduced to the *a posteriori* verification of the nonnegativity of the stress power.

Since then thermodynamics started to play an increasingly important role in the theory of constitutive relations, see for example Coleman [19] and Truesdell and Noll [91]. This paradigm shift went hand in hand with the development of the field of nonequilibrium thermodynamics, see for example de Groot and Mazur [34], Glansdorff and Prigogine [32], Ziegler [97] and Müller [62]. In what follows a modern thermodynamics based approach to the phenomenological theory of constitutive relations is presented. The presented approach is essentially based on the work of Rajagopal and Srinivasa [78], see also Rajagopal and Srinivasa [80], who partially took inspiration from various earlier achievements in the field, most notably from the work of Ziegler [97] and Ziegler and Wehrli [98]. The reader who is interested into some comments concerning the precursors of the current approach is referred to Rajagopal and Srinivasa [78].

The advantage of the presented approach is that the second law of thermodynamics plays a key role in the theory of constitutive relations. Unlike in some other approaches, the second law is not used *a posteriori* in checking whether the derived constitutive relations conform to the second law. In fact, the opposite is true, the second law is the starting point of the presented approach. The constitutive relations for the Cauchy stress tensor, the heat flux and the other quantities of interest are in the presented approach *derived as consequences of the choice of the specific form for the internal energy e and the entropy production ξ* .

If the entropy production ξ is chosen to be nonnegative, then the second law is satisfied. Since the relations of the type (4.2) are in the presented approach the consequences of the choice of e and ξ , then it is clear that the arising constitutive equations can not violate the second law. The second law is automatically built in the arising constitutive relations of the type (4.2). Further, the specification of two *scalar* quantities e and ξ is apparently much easier than the direct specification of the constitutive relations between the *vectorial* and *tensorial* quantities as in (4.2). This brings simplicity into the theory of constitutive relations. Two scalar quantities determine everything.

Finally, the advocated approach is *robust* enough to handle complex materials. Nonlinear constitutive relations, constitutive relations for constrained materials as well as constitutive relations for materials reacting to the stimuli of various origin (thermal, mechanical, electromagnetic, chemical) are relatively easy to work with in the presented approach.

A general outline of the advocated approach is given in Section 4.1, and then it is shown how the general approach can be used in various settings. First, the approach is applied in a very simple setting, namely the well known constitutive relations for the standard compressible Navier–Stokes–Fourier fluid are derived in Section 4.2. This example should allow the reader to get familiar with the basic concepts. Then the discussion proceeds to more complex settings, namely that of Korteweg fluid, see Section 4.3. Finally, see Section 4.4, the discussion of the approach is concluded by the derivation of constitutive equations for viscoelastic fluids.

4.1. General framework. The main idea behind the presented approach is that the behaviour of the material in the processes of interest is determined by two factors, namely its ability to *store energy* and *produce entropy*. The energy storage mechanisms are specified by the choice of the energetic equation of state, that is by expressing the internal energy e as a function of the state variables. (Other thermodynamic potentials such as the Helmholtz free energy, Gibbs potential or the enthalpy can be used as well. The discussion below is however focused exclusively on the internal energy.) The entropy production mechanisms are specified by the choice of the formula for the entropy production ξ .

The derivation of the constitutive relations (4.2) from the knowledge of e and ξ then proceeds in the following steps.

STEP 1: Specify the energy storage mechanisms by fixing the constitutive relation for the specific internal energy e in the form of the energetic equation of state

$$e = e(\eta, y_1, \dots, y_m) \quad (4.4)$$

or in the form of the entropic equation of state (2.26). At this level it is sufficient to determine the state variables y_i that enter (4.4).

STEP 2: Find an expression for the material time derivative of the specific entropy η . This can be achieved by the application of the material time derivative to (4.4), and by the multiplication of the result by $\rho(\mathbf{x}, t)$, which yields

$$\rho(\mathbf{x}, t) \frac{de(\mathbf{x}, t)}{dt} = \rho(\mathbf{x}, t) \frac{\partial e(\eta, y_1, \dots, y_m)}{\partial \eta} \bigg|_{\eta=\eta(\mathbf{x}, t), y_1=y_1(\mathbf{x}, t), \dots, y_m=y_m(\mathbf{x}, t)} \frac{d\eta(\mathbf{x}, t)}{dt} + \sum_{i=1}^m \rho(\mathbf{x}, t) \frac{\partial e(\eta, y_1, \dots, y_m)}{\partial y_i} \bigg|_{\eta=\eta(\mathbf{x}, t), y_1=y_1(\mathbf{x}, t), \dots, y_m=y_m(\mathbf{x}, t)} \frac{dy_i(\mathbf{x}, t)}{dt}. \quad (4.5)$$

The definition of the thermodynamic temperature, see (2.29), and (4.5) then yield

$$\rho(\mathbf{x}, t) \theta(\mathbf{x}, t) \frac{d\eta(\mathbf{x}, t)}{dt} = \rho(\mathbf{x}, t) \frac{de(\mathbf{x}, t)}{dt} - \sum_{i=1}^m \rho(\mathbf{x}, t) \frac{\partial e(\eta, y_1, \dots, y_m)}{\partial y_i} \bigg|_{y_j=y_j(\mathbf{x}, t), \eta=\eta(\mathbf{x}, t)} \frac{dy_i(\mathbf{x}, t)}{dt}, \quad (4.6)$$

which is the sought formula for $\frac{d\eta}{dt}$.

STEP 3: Identify the entropy production. Use the balance equations and kinematics to write down (derive) the formulae for the material time derivative of the state variables $\frac{dy_i(\mathbf{x}, t)}{dt}$, $i = 1, \dots, m$, and substitute these formulae into (4.6). Rewrite the equation for $\rho(\mathbf{x}, t) \frac{d\eta(\mathbf{x}, t)}{dt}$ in the form

$$\rho(\mathbf{x}, t) \frac{d\eta(\mathbf{x}, t)}{dt} + \operatorname{div} \mathbf{j}_\eta(\mathbf{x}, t) = \frac{1}{\theta(\mathbf{x}, t)} \sum_{\alpha=1}^m \mathbf{j}_\alpha(\mathbf{x}, t) \cdot \mathbf{a}_\alpha(\mathbf{x}, t), \quad (4.7)$$

where $\mathbf{j}_\alpha(\mathbf{x}, t) \cdot \mathbf{a}_\alpha(\mathbf{x}, t)$ denotes the scalar product of vector or tensor quantities respectively. The right hand side of (4.7) is the entropy production, where each summand is supposed to represent an independent entropy producing mechanism.

The quantities $\mathbf{j}_\alpha(\mathbf{x}, t)$ are called the *thermodynamic fluxes*, and the quantities $\mathbf{a}_\alpha(\mathbf{x}, t)$ are called the *thermodynamic affinities*. The affinities are usually the spatial gradients of the involved quantities, for example $\nabla\theta$ or \mathbb{D} , while the fluxes are for example the heat flux \mathbf{j}_q or the Cauchy stress tensor \mathbb{T} . (As a rule of thumb, the fluxes are the quantities that appear under the divergence operator in the balance laws (4.1), see also Rajagopal and Srinivasa [78] for further comments.) The quantity $\mathbf{j}_\eta(\mathbf{x}, t)$ is called the entropy flux and in standard cases it is tantamount to $\frac{\mathbf{j}_q(\mathbf{x}, t)}{\theta(\mathbf{x}, t)}$.

STEP 4* (Linear non-equilibrium thermodynamics): The second law of thermodynamics states that the entropy production $\xi(\mathbf{x}, t) =_{\text{def}} \rho(\mathbf{x}, t) \frac{d\eta(\mathbf{x}, t)}{dt} + \text{div } \mathbf{j}_\eta(\mathbf{x}, t)$ is nonnegative, see Section 2.3.3. Referring to (4.7), it follows that

$$\xi(\mathbf{x}, t) = \frac{1}{\theta(\mathbf{x}, t)} \sum_{\alpha=1}^m \mathbf{j}_\alpha(\mathbf{x}, t) \cdot \mathbf{a}_\alpha(\mathbf{x}, t) \quad (4.8)$$

must be nonnegative. A simple way to fulfil this requirement is to consider linear relations between each pair of $\mathbf{j}_\alpha(\mathbf{x}, t)$ and $\mathbf{a}_\alpha(\mathbf{x}, t)$, that is

$$\mathbf{j}_\alpha(\mathbf{x}, t) = \gamma_\alpha \mathbf{a}_\alpha(\mathbf{x}, t), \quad (4.9)$$

where γ_α , $\alpha = 1, \dots, m$, are nonnegative constants. Alternatively, one can consider cross-effects by assuming that the relations between $\mathbf{j}_\alpha(\mathbf{x}, t)$ and $\mathbf{a}_\alpha(\mathbf{x}, t)$ take the form

$$\mathbf{j}_\alpha(\mathbf{x}, t) = \sum_{\beta=1}^m \Gamma_{\alpha\beta} \mathbf{a}_\beta(\mathbf{x}, t), \quad (4.10)$$

where $\Gamma_{\alpha\beta}$ is a symmetric positive definite matrix. This is essentially the approach of linear non-equilibrium thermodynamics, see de Groot and Mazur [34] for details.

STEP 4 (Nonlinear non-equilibrium thermodynamics): Since the linear relationships between the fluxes $\mathbf{j}_\alpha(\mathbf{x}, t)$ and affinities $\mathbf{a}_\alpha(\mathbf{x}, t)$ can be insufficient for a proper description of the behaviour of complex materials, an alternative procedure is needed. In particular, the procedure should allow one to derive nonlinear constitutive relations of the type $\mathbf{j}_i = \mathbf{j}_i(\mathbf{a}_1, \dots, \mathbf{a}_m)$ or *vice versa*.

Here it comes to the core of the approach suggested by Rajagopal and Srinivasa [78]. As argued by Rajagopal and Srinivasa [78] one first specifies function ζ in one of the following forms

$$\zeta = \zeta_{\mathbf{a}_1, \dots, \mathbf{a}_m}(\mathbf{j}_1, \dots, \mathbf{j}_m), \quad (4.11a)$$

or

$$\zeta = \zeta_{\mathbf{j}_1, \dots, \mathbf{j}_m}(\mathbf{a}_1, \dots, \mathbf{a}_m). \quad (4.11b)$$

Note that the state variables can enter the constitutive relations (4.11) as well, but they are not, for the sake of compactness of the notation, written explicitly in (4.11).

Formula (4.11a) or (4.11b) is a *constitutive relation that determines the entropy production* ξ , $\xi =_{\text{def}} \frac{\zeta}{\theta}$. Since the constitutive function ζ is—up to the positive factor θ —tantamount to the entropy production, it must be *nonnegative*, which guarantees the fulfilment of the second law of thermodynamics. Further, ζ should vanish if the fluxes vanish. Other restrictions concerning the formula for the entropy production can come from classical requirements such as the symmetry and the invariance with respect to the change of the observer.

Moreover, the assumed form of the entropy production must be compatible with the already derived form of the entropy production (4.8). Consequently, the following equation must hold

$$\xi_{\mathbf{j}_1, \dots, \mathbf{j}_m}(\mathbf{a}_1, \dots, \mathbf{a}_m) - \frac{1}{\theta(\mathbf{x}, t)} \sum_{\alpha=1}^m \mathbf{j}_\alpha(\mathbf{x}, t) \cdot \mathbf{a}_\alpha(\mathbf{x}, t) = 0, \quad (4.12)$$

and similarly for $\xi_{\mathbf{a}}(\mathbf{j}_1, \dots, \mathbf{j}_m)$. In terms of the constitutive function ζ this reduces to the requirement

$$\zeta_{\mathbf{a}_1, \dots, \mathbf{a}_m}(\mathbf{j}_1, \dots, \mathbf{j}_m) - \sum_{\alpha=1}^m \mathbf{j}_\alpha(\mathbf{x}, t) \cdot \mathbf{a}_\alpha(\mathbf{x}, t) = 0, \quad (4.13a)$$

or to

$$\zeta_{\mathbf{j}_1, \dots, \mathbf{j}_m}(\mathbf{a}_1, \dots, \mathbf{a}_m) - \sum_{\alpha=1}^m \mathbf{j}_\alpha(\mathbf{x}, t) \cdot \mathbf{a}_\alpha(\mathbf{x}, t) = 0, \quad (4.13b)$$

respectively, depending whether one starts with (4.11a) or (4.11b).

Relations (4.13) can be rewritten in the form

$$\zeta_{\mathbf{A}}(\mathbf{J}) - \mathbf{J} \cdot \mathbf{A} = 0, \quad (4.14a)$$

$$\zeta_{\mathbf{J}}(\mathbf{A}) - \mathbf{J} \cdot \mathbf{A} = 0, \quad (4.14b)$$

where $\mathbf{A} =_{\text{def}} [\mathbf{a}_1 \ \dots \ \mathbf{a}_m]^\top$ and $\mathbf{J} = [\mathbf{j}_1 \ \dots \ \mathbf{j}_m]^\top$ are vectors in $\mathbb{R}^{M'}$, $M' > m$, that contain all the affinities and fluxes respectively. Here the tensorial quantities such as the Cauchy stress tensor \mathbb{T} are understood as column vectors $[\mathbb{T}_{11} \ \mathbb{T}_{12} \ \dots \ \mathbb{T}_{33}]^\top$.

Having fixed a formula for the constitutive function ζ via (4.11a) or (4.11b) respectively, the task is to determine the fluxes $\mathbf{j}_1, \dots, \mathbf{j}_m$ or affinities $\mathbf{a}_1, \dots, \mathbf{a}_m$ that are compatible with the single constraint (4.14a) or (4.14b)

respectively. If the fluxes/affinities are vectorial or tensorial quantities, then the single constraint is not sufficient to fully determine the sought relation between the fluxes and the affinities. (Meaning that in general there exist many constitutive relations of the type $\mathbf{j}_i = \mathbf{j}_i(\mathbf{a}_1, \dots, \mathbf{a}_m)$ or *vice versa* such that (4.14a) or (4.14b) holds.)

Rajagopal and Srinivasa [78] argued that the choice between the multiple constitutive relations that fulfil the constraint (4.14a) or (4.14b) can be based on the assumption of *maximisation of the entropy production*. The assumption simply requires that the sought constitutive relation is the constitutive relation that leads to the maximal entropy production in the material, and that is compatible with other available information concerning the behaviour of the material.

In more operational terms, the maximisation of the entropy production leads to the following problem. Given the function $\zeta_{\mathbf{A}}(\mathbf{J})$ and the values of the state variables and the values of the affinities \mathbf{A} , the corresponding values of the fluxes \mathbf{J} are those which maximise $\zeta_{\mathbf{A}}(\mathbf{J})$ subject to the constraint (4.14a), and alternatively to other possible constraints. (Note that since θ is a positive quantity, then the task to maximise ζ with respect to the fluxes is indeed tantamount to the task of maximising the entropy production ξ with respect to the fluxes.) A similar reformulation can be made for $\zeta_{\mathbf{J}}(\mathbf{A})$; it suffices to switch the role of the fluxes and affinities.

The constrained maximisation problems arising from the assumption on the maximisation of the entropy production read

$$\max_{\mathbf{J} \in \mathcal{J}} \zeta_{\mathbf{A}}(\mathbf{J}) \quad (4.15)$$

where $\mathcal{J} =_{\text{def}} \left\{ \mathbf{J} \in \mathbb{R}^{M'}, \zeta_{\mathbf{A}}(\mathbf{J}) - \mathbf{J} \cdot \mathbf{A} = 0 \right\}$, and

$$\max_{\mathbf{A} \in \mathcal{A}} \zeta_{\mathbf{J}}(\mathbf{A}) \quad (4.16)$$

where $\mathcal{A} =_{\text{def}} \left\{ \mathbf{A} \in \mathbb{R}^{M'}, \zeta_{\mathbf{J}}(\mathbf{A}) - \mathbf{J} \cdot \mathbf{A} = 0 \right\}$. Assuming that $\zeta_{\mathbf{A}}$ or $\zeta_{\mathbf{J}}$ are smooth and strictly convex with respect to their variables, then the corresponding values of \mathbf{J} and \mathbf{A} respectively are uniquely determined, and can be found easily by employing the Lagrange multipliers, see Rajagopal and Srinivasa [78].

For example, if the starting point is the constitutive function $\zeta_{\mathbf{A}}(\mathbf{J})$, then the auxiliary function for the constrained maximisation reads $\Phi(\mathbf{J}) =_{\text{def}} \zeta_{\mathbf{A}}(\mathbf{J}) + \ell [\zeta_{\mathbf{A}}(\mathbf{J}) - \mathbf{J} \cdot \mathbf{A}]$, where ℓ is a Lagrange multiplier. The condition for the value of the flux \mathbf{J} that corresponds to maximal entropy production is $\frac{\partial \Phi(\mathbf{J})}{\partial \mathbf{J}} = \mathbf{0}$ which leads to equation

$$\mathbf{A} = \frac{1 + \ell}{\ell} \frac{\partial \zeta_{\mathbf{A}}(\mathbf{J})}{\partial \mathbf{J}}, \quad (4.17)$$

where

$$\frac{1 + \ell}{\ell} = \frac{\zeta_{\mathbf{A}}(\mathbf{J})}{\frac{\partial \zeta_{\mathbf{A}}(\mathbf{J})}{\partial \mathbf{J}} \cdot \mathbf{J}}. \quad (4.18)$$

Relation (4.17) is the sought relation between \mathbf{J} and \mathbf{A} .

Consequently, if one accepts the assumption on the *maximisation of the entropy production*, then the relations between the fluxes and affinities are due to the strict convexity of $\zeta_{\mathbf{A}}(\mathbf{J})$ indeed *uniquely determined* by the choice of the constitutive function $\zeta_{\mathbf{A}}(\mathbf{J})$. Moreover, if the constitutive function $\zeta_{\mathbf{A}}(\mathbf{J})$ is quadratic in \mathbf{J} , then one recovers the result known from linear non-equilibrium thermodynamics, namely that the fluxes are linear functions of the affinities, see (4.10). Apparently, a similar procedure can be followed if the starting point is $\zeta_{\mathbf{J}}(\mathbf{A})$ instead of $\zeta_{\mathbf{A}}(\mathbf{J})$.

STEP 5: Relations (4.9) or (4.10) or (4.17) are the sought constitutive relations.

The rest of the present contribution is focused mainly on linear relations between the fluxes and affinities, hence a quadratic *ansatz* for the constitutive function ζ is predominantly used in the rest of the text. This means that STEP 4 is rarely referred to in its full complexity, and that one basically stays in the framework of STEP 4*.

The reason is that the following text is mainly focused on the most difficult step of the advocated approach which is the correct specification of the functions e and ζ . This is a nontrivial task in the development of the mathematical model, since the correct specification of these functions requires physical insight into the problem. However, the key physical arguments concerning the choice of the functions e and ζ can be easily documented in the simplest possible case of a quadratic *ansatz*; generalisation of the quadratic *ansatz* to a more complex one is then a relatively straightforward procedure. Also note that once the functions e and ζ are specified, the derivation of the constitutive relations is only a technical problem not worth of lengthy discussion.

4.2. Compressible and incompressible viscous heat conducting fluids. The application of the outlined procedure is first documented in a very simple case of the derivation of constitutive relations for the compressible Navier–Stokes–Fourier fluid, see Section 4.2.1, which is a simple model for a compressible viscous heat conducting fluid. The next section, see Section 4.2.2, is devoted to reduced models that are variants of the compressible Navier–Stokes–Fourier fluid model. Finally, the *incompressible* counterparts of the former models are discussed in Section 4.2.3.

4.2.1. Compressible Navier–Stokes–Fourier fluid.

STEP 1: The specific internal energy e is assumed to be a function of the specific entropy η and the density ρ ,

$$e = e(\eta, \rho). \quad (4.19)$$

This is a straightforward generalisation of the classical energetic equation of state $E = E(S, V)$ known for the equilibrium thermodynamics, see for example Callen [15]. (For the sake of clarity of the notation the spatial and

temporal variable is omitted in (4.19). If written in full, the energetic equation of state should read $e(\mathbf{x}, t) = e(\eta(\mathbf{x}, t), \rho(\mathbf{x}, t))$. The same approach is applied in the rest of this section.)

STEP 2: Taking the material derivative of (4.19) yields

$$\rho \frac{\partial e}{\partial \eta} \frac{d\eta}{dt} = \rho \frac{de}{dt} - \rho \frac{\partial e}{\partial \rho} \frac{d\rho}{dt}. \quad (4.20)$$

Recalling the definition of the temperature, see (2.29), and introducing the thermodynamic pressure p_{th} through

$$\theta =_{\text{def}} \frac{\partial e}{\partial \eta}, \quad (4.21a)$$

$$p_{\text{th}} =_{\text{def}} \rho^2 \frac{\partial e}{\partial \rho}, \quad (4.21b)$$

which are again the counterparts of the classical relations known from equilibrium thermodynamics, one can rewrite (4.20) as

$$\rho \theta \frac{d\eta}{dt} = \rho \frac{de}{dt} - \frac{p_{\text{th}}}{\rho} \frac{d\rho}{dt}. \quad (4.22)$$

STEP 3: Using the evolution equation for the internal energy (4.1d) and the balance of mass (4.1a) one can in (4.22) substitute for $\frac{de}{dt}$ and $\frac{d\rho}{dt}$ which yields

$$\rho \theta \frac{d\eta}{dt} = \mathbb{T} : \mathbb{D} - \text{div } \mathbf{j}_q + p_{\text{th}} \text{div } \mathbf{v}. \quad (4.23)$$

The right hand side can be further rewritten as

$$\mathbb{T} : \mathbb{D} - \text{div } \mathbf{j}_q + p_{\text{th}} \text{div } \mathbf{v} = \mathbb{T}_\delta : \mathbb{D}_\delta + (m + p_{\text{th}}) \text{div } \mathbf{v} - \text{div } \mathbf{j}_q, \quad (4.24)$$

where

$$m =_{\text{def}} \frac{1}{3} \text{Tr } \mathbb{T} \quad (4.25)$$

denotes the mean normal stress, and

$$\mathbb{T}_\delta =_{\text{def}} \mathbb{T} - \frac{1}{3} (\text{Tr } \mathbb{T}) \mathbb{I}, \quad (4.26)$$

$$\mathbb{D}_\delta =_{\text{def}} \mathbb{D} - \frac{1}{3} (\text{Tr } \mathbb{D}) \mathbb{I} \quad (4.27)$$

denote the traceless part of \mathbb{T} and \mathbb{D} respectively. Since the thermodynamic temperature is positive one can, after some manipulation, rewrite (4.23) as

$$\rho \frac{d\eta}{dt} + \text{div} \left(\frac{\mathbf{j}_q}{\theta} \right) = \frac{1}{\theta} \left[\mathbb{T}_\delta : \mathbb{D}_\delta + (m + p_{\text{th}}) \text{div } \mathbf{v} - \mathbf{j}_q \cdot \frac{\nabla \theta}{\theta} \right] \quad (4.28)$$

which is the evolution equation for η in the desired form (4.7).

The rationale for using the traceless parts of \mathbb{T} and \mathbb{D} in (4.28) is the following. The quantities \mathbb{D} and $\text{div } \mathbf{v}$ that appear in the first and the last term on the right hand side of (4.23) are not independent quantities. (Recall that $\text{Tr } \mathbb{D} = \text{div } \mathbf{v}$.) However, the fluxes one would like to identify when writing (4.23) in the form (4.7) should be independent quantities. Therefore, it is necessary to split \mathbb{D} to mutually independent quantities \mathbb{D}_δ and $\text{div } \mathbf{v}$, which requires one to split the Cauchy stress tensor in a similar manner.

A closer inspection of (4.28) indicates that there exist three “independent” entropy producing mechanisms in the material. The first one, $-\mathbf{j}_q \cdot \frac{\nabla \theta}{\theta}$, is entropy production due to heat transfer, the second one, $(m + p_{\text{th}}) \text{div } \mathbf{v}$, is entropy production due to volume changes, and the last entropy production mechanism, $\mathbb{T}_\delta : \mathbb{D}_\delta$, is due to isochoric processes such as shearing.

STEP 4: The entropy production ξ —that is the right hand side of (4.28)—takes the form

$$\xi = \frac{1}{\theta} \sum_{\alpha=1}^3 \mathbf{j}_\alpha \cdot \mathbf{a}_\alpha = \frac{1}{\theta} \left[\mathbb{T}_\delta : \mathbb{D}_\delta + (m + p_{\text{th}}) \text{div } \mathbf{v} - \mathbf{j}_q \cdot \frac{\nabla \theta}{\theta} \right]. \quad (4.29)$$

Using the flux/affinity nomenclature, the fluxes are the traceless part of the Cauchy stress tensor \mathbb{T}_δ , the mean normal stress plus the thermodynamic pressure $m + p_{\text{th}}$ and the heat flux \mathbf{j}_q . The affinities are \mathbb{D}_δ , $\text{div } \mathbf{v}$ and $-\nabla \theta$. (Strictly speaking the last affinity is not $-\nabla \theta$ but $-\frac{\nabla \theta}{\theta}$. However, the positive factor $\frac{1}{\theta}$ is of no importance.) The entropy production is a positive quantity if the constitutive relations are chosen as follows,

$$\mathbb{T}_\delta = 2\nu \mathbb{D}_\delta, \quad (4.30a)$$

$$m + p_{\text{th}} = \tilde{\lambda} \text{div } \mathbf{v}, \quad (4.30b)$$

$$\mathbf{j}_q = -\kappa \nabla \theta, \quad (4.30c)$$

where $\nu > 0$, $\tilde{\lambda} > 0$ and $\kappa > 0$ are given positive functions of the state variables ρ and η . This choice of constitutive relations follows the template specified in (4.9). (Note that since \mathbb{D}_δ is a symmetric tensor, then \mathbb{T}_δ is also symmetric,

hence the balance of angular momentum (4.1c) is satisfied.) The coefficients ν , $\tilde{\lambda}$ and κ are called the shear viscosity, the bulk viscosity and the heat conductivity. Traditionally, the bulk viscosity is written in the form

$$\tilde{\lambda} = \frac{3\lambda + 2\nu}{3}, \quad (4.31)$$

where λ is a function of the state variables such that $\tilde{\lambda}$ remains positive.

STEP 5: It follows from (4.30) that the constitutive relation for the full Cauchy stress tensor $\mathbb{T} = \mathbb{T}_\delta + m\mathbb{1}$ is

$$\mathbb{T} = 2\nu\mathbb{D}_\delta + \tilde{\lambda}(\operatorname{div} \mathbf{v})\mathbb{1} - p_{\text{th}}\mathbb{1} \quad (4.32)$$

which can be in virtue of (4.31) rewritten as

$$\mathbb{T} = -p_{\text{th}}\mathbb{1} + 2\nu\mathbb{D} + \lambda(\operatorname{div} \mathbf{v})\mathbb{1}. \quad (4.33a)$$

This is the standard formula for the Cauchy stress tensor in the so-called compressible Navier–Stokes fluid. The constitutive relation for the heat flux reads

$$\mathbf{j}_q = -\kappa\nabla\theta, \quad (4.33b)$$

which is the standard Fourier law of thermal conduction.

The coefficients in the constitutive relations can be functions of the state variables η and ρ . This choice of variables is however inconvenient in practice. Solving the equation (4.21a) for the entropy one can see that the entropy could be written as a function of the temperature and the density

$$\eta = f(\theta, \rho). \quad (4.34)$$

If this is possible, then the coefficients can be rewritten as functions of the temperature and the density,

$$p_{\text{th}}^*(\theta, \rho) = p_{\text{th}}(f(\theta, \rho), \rho), \quad (4.35a)$$

$$\nu^*(\theta, \rho) = \nu(f(\theta, \rho), \rho), \quad (4.35b)$$

$$\lambda^*(\theta, \rho) = \lambda(f(\theta, \rho), \rho), \quad (4.35c)$$

$$\kappa^*(\theta, \rho) = \kappa(f(\theta, \rho), \rho), \quad (4.35d)$$

$$e^*(\theta, \rho) = e(f(\theta, \rho), \rho). \quad (4.35e)$$

Consequently, the final set of the governing differential equations arising from the balance laws (4.1) and the constitutive relations (4.33) reads

$$\frac{d\rho}{dt} = -\rho \operatorname{div} \mathbf{v}, \quad (4.36a)$$

$$\rho \frac{d\mathbf{v}}{dt} = \operatorname{div} \mathbb{T} + \rho \mathbf{b}, \quad (4.36b)$$

$$\rho \frac{de^*(\theta, \rho)}{dt} = \mathbb{T} : \mathbb{D} - \operatorname{div} \mathbf{j}_q, \quad (4.36c)$$

$$\mathbb{T} = -p_{\text{th}}^*(\theta, \rho)\mathbb{1} + 2\nu^*(\theta, \rho)\mathbb{D} + \lambda^*(\theta, \rho)(\operatorname{div} \mathbf{v})\mathbb{1}, \quad (4.36d)$$

$$\mathbf{j}_q = -\kappa^*(\theta, \rho)\nabla\theta. \quad (4.36e)$$

These are the standard governing equations for the so-called compressible Navier–Stokes–Fourier fluids. If necessary, the evolution equation for the internal energy (4.36c) can be reformulated as a balance of energy, that is

$$\rho \frac{d}{dt} \left(e^*(\theta, \rho) + \frac{1}{2} |\mathbf{v}|^2 \right) = \rho \mathbf{b} \cdot \mathbf{v} + \operatorname{div} (\mathbb{T} \mathbf{v}) - \operatorname{div} \mathbf{j}_q. \quad (4.37)$$

Note that if the internal energy *as a function of the temperature and the density* takes the simple form $e^* = c_V \theta$, where c_V is a constant referred to as the specific heat capacity, then the evolution equation for the internal energy (4.36c) takes the well-known form

$$\rho c_V \frac{d\theta}{dt} = \mathbb{T} : \mathbb{D} - \operatorname{div} \mathbf{j}_q. \quad (4.38)$$

4.2.2. Other linear models for compressible fluids. Referring to (4.29) one can notice that the entropy production ξ can be written in the form

$$\theta \xi = [\mathbb{T}_\delta, m + p_{\text{th}}, -\mathbf{j}_q] \cdot \left[\mathbb{D}_\delta, \operatorname{div} \mathbf{v}, \frac{\nabla\theta}{\theta} \right] = \mathbf{J} \cdot \mathbf{A}. \quad (4.39)$$

If the constitutive relation for any of the quantities \mathbb{T}_δ , $m + p_{\text{th}}$, \mathbf{j}_q is trivial, that is if $\mathbb{T}_\delta = \mathbb{0}$, $m + p_{\text{th}} = 0$ or $\mathbf{j}_q = \mathbf{0}$, then the corresponding term in the entropy production vanishes. Such models are referred to as the reduced models. For example $\mathbb{T}_\delta = \mathbb{0}$ corresponds to an inviscid compressible heat conducting fluid (Euler–Fourier fluid).

On the other hand, if any of the quantities \mathbb{D}_δ , $\operatorname{div} \mathbf{v}$, $\nabla\theta$ vanishes, then the corresponding entropy production also vanishes *regardless of the particular constitutive equation* for \mathbb{T}_δ , $m + p_{\text{th}}$ or \mathbf{j}_q , respectively. The processes in which \mathbb{D}_δ , $\operatorname{div} \mathbf{v}$ or $\nabla\theta$ vanish are the motion with a velocity field in the form $\mathbf{v}(\mathbf{x}, t) =_{\text{def}} \mathbf{a}(t) \times \mathbf{x} + \mathbf{b}(t)$, where \mathbf{a} and \mathbf{b} are arbitrary time dependent vectors, the *isochoric motion*, that is volume preserving motion, and *isothermal process*, that is a process with no temperature variations, respectively.

Going back to the constitutive relations, the entropy production completely vanishes if the constitutive relations take the form

$$\mathbb{T}_\delta = \mathbb{0}, \quad m = -p_{\text{th}}, \quad \text{and} \quad \mathbf{j}_q = \mathbf{0}. \quad (4.40)$$

This means that

$$\mathbb{T} = -p_{\text{th}}^*(\theta, \rho)\mathbb{1}, \quad \text{and} \quad \mathbf{j}_q = \mathbf{0}, \quad (4.41)$$

which are the constitutive equations for a *compressible Euler fluid*. The corresponding system of partial differential equations reads

$$\frac{d\rho}{dt} = -\rho \operatorname{div} \mathbf{v}, \quad (4.42a)$$

$$\rho \frac{d\mathbf{v}}{dt} = -\nabla p_{\text{th}}^*(\theta, \rho) + \rho \mathbf{b}, \quad (4.42b)$$

$$\rho \frac{d}{dt} \left(e^*(\theta, \rho) + \frac{1}{2} |\mathbf{v}|^2 \right) = -\operatorname{div} (p_{\text{th}}^*(\theta, \rho) \mathbf{v}) + \rho \mathbf{b} \cdot \mathbf{v}. \quad (4.42c)$$

There is a hierarchy of models between the compressible Euler fluid (4.42) with no entropy production and the compressible Navier–Stokes–Fourier fluid (4.36) in which all entropy production mechanisms are active. These models are for example the Euler–Fourier fluid where the constitutive relations read

$$\mathbb{T}_\delta = \mathbf{0}, \quad m = -p_{\text{th}}, \quad \text{and} \quad \mathbf{j}_q = -\kappa^*(\theta, \rho) \nabla \theta, \quad (4.43)$$

the fluid where thermodynamic pressure coincides (up to the sign) with the mean normal stress, that is the fluid with constitutive relations

$$m = -p_{\text{th}}, \quad \mathbf{j}_q = -\kappa^*(\theta, \rho) \nabla \theta, \quad \mathbb{T}_\delta = 2\nu^*(\theta, \rho) \mathbb{D}_\delta, \quad (4.44)$$

which leads to $\mathbb{T} = -p_{\text{th}}^*(\theta, \rho)\mathbb{1} + 2\nu^*(\theta, \rho)\mathbb{D}_\delta$, or the fluid dissipating due to volume changes but not due to shearing, that is the fluid with constitutive relations

$$\mathbb{T}_\delta = \mathbf{0}, \quad m = -p_{\text{th}}^*(\theta, \rho) + \lambda^*(\theta, \rho) \operatorname{div} \mathbf{v}, \quad \mathbf{j}_q = -\kappa^*(\theta, \rho) \nabla \theta. \quad (4.45)$$

Finally, one can observe that if one deals with the ideal gas, that is with the fluid given by constitutive relations (4.36) and $e^*(\theta, \rho) = c_V \theta$, where c_V is a constant, then one can in some cases consider *isothermal processes*. (The temperature is a constant $\theta(\mathbf{x}, t) = \theta^*$.) Indeed, if the initial temperature distribution is uniform, and if the fluid undergoes only small volume changes, and if the entropy production mechanisms in the fluid are weak, then the terms

$$\mathbb{T} : \mathbb{D} = -p_{\text{th}} \operatorname{div} \mathbf{v} + \tilde{\lambda} (\operatorname{div} \mathbf{v})^2 + 2\nu \mathbb{D}_\delta : \mathbb{D}_\delta, \quad (4.46)$$

and $\operatorname{div} \mathbf{j}_q$ do not significantly contribute to the right hand side of (4.38). In such a case, and under favorable boundary conditions for the temperature, the evolution equation (4.38) for the internal energy/temperature is of no interest, and one can focus only on the mechanical part of the system, which leads to the *compressible Navier–Stokes equations*

$$\frac{d\rho}{dt} = -\rho \operatorname{div} \mathbf{v}, \quad (4.47a)$$

$$\rho \frac{d\mathbf{v}}{dt} = -\nabla \tilde{p}_{\text{th}}(\rho) + \operatorname{div} (2\tilde{\nu}(\rho) \mathbb{D}) + \nabla (\tilde{\lambda}(\rho) \operatorname{div} \mathbf{v}) + \rho \mathbf{b}, \quad (4.47b)$$

with $\tilde{\nu}(\rho) > 0$ and $2\tilde{\nu}(\rho) + 3\tilde{\lambda}(\rho) > 0$. Here $\tilde{p}_{\text{th}}(\rho) =_{\text{def}} p_{\text{th}}^*(\theta^*, \rho)$, $\tilde{\nu}(\rho) =_{\text{def}} \nu^*(\theta^*, \rho)$ and $\tilde{\lambda}(\rho) =_{\text{def}} \lambda^*(\theta^*, \rho)$. Note that genuine isothermal processes are in fact impossible in a fluid with nonvanishing entropy production due to mechanical effects. Once there is entropy production due to $\mathbb{T} : \mathbb{D}$, kinetic energy is lost in favour of thermal energy and the temperature *must* change, see (4.36c) or (4.38). The isothermal process is in this case only an approximation.

Other simplified systems that arise from (4.47) are the *compressible Euler equations*

$$\frac{d\rho}{dt} = -\rho \operatorname{div} \mathbf{v}, \quad (4.48a)$$

$$\rho \frac{d\mathbf{v}}{dt} = -\nabla \tilde{p}_{\text{th}}(\rho) + \rho \mathbf{b}, \quad (4.48b)$$

the *compressible “bulk viscosity” equations*

$$\frac{d\rho}{dt} = -\rho \operatorname{div} \mathbf{v}, \quad (4.49a)$$

$$\rho \frac{d\mathbf{v}}{dt} = -\nabla \left(\tilde{p}_{\text{th}}(\rho) + \frac{2\tilde{\nu}(\rho) + 3\tilde{\lambda}(\rho)}{3} \operatorname{div} \mathbf{v} \right) + \rho \mathbf{b}. \quad (4.49b)$$

and the *compressible “shear viscosity” equations*

$$\frac{d\rho}{dt} = -\rho \operatorname{div} \mathbf{v}, \quad (4.50a)$$

$$\rho \frac{d\mathbf{v}}{dt} = -\nabla \tilde{p}_{\text{th}}(\rho) - \operatorname{div} (2\tilde{\nu}(\rho) \mathbb{D}) + \rho \mathbf{b}. \quad (4.50b)$$

4.2.3. *Incompressible Navier–Stokes–Fourier fluid.* Incompressibility means that the density of any given material point \mathbf{X} is constant in time. In terms of the Eulerian density field $\rho(\mathbf{x}, t)$ this requirement translates into the requirement of vanishing material time derivative of $\rho(\mathbf{x}, t)$,

$$\frac{d\rho}{dt} = 0. \quad (4.51)$$

(Note that the density can still vary in space, that is the density assigned to different material points can be different. In such a case the material is referred to as *inhomogeneous* material.) Using the balance of mass (4.1a), it follows from (4.51) that

$$\operatorname{div} \mathbf{v} = 0, \quad (4.52)$$

which means that the material can undergo only *isochoric*—that is volume preserving—motions. In this sense the incompressible material can be understood as a *constrained* material, meaning that the class of motions possible in the given material is constrained by the requirement $\operatorname{div} \mathbf{v} = 0$.

If one takes into account the constraint $\operatorname{div} \mathbf{v} = 0$, then the term

$$\mathbb{T} : \mathbb{D} = \mathbb{T}_\delta : \mathbb{D}_\delta + m \operatorname{div} \mathbf{v} \quad (4.53)$$

in the evolution equation for the internal energy (4.1d) reduces to $\mathbb{T}_\delta : \mathbb{D}_\delta$. (Recall that m denotes the mean normal stress, $m \stackrel{\text{def}}{=} \frac{1}{3} \operatorname{Tr} \mathbb{T}$, and that $\operatorname{Tr} \mathbb{D} = \operatorname{div} \mathbf{v}$.) This implies that the mean normal stress can not be directly present in the entropy production in the form of a flux/affinity pair, because the corresponding flux $\operatorname{div} \mathbf{v}$ identically vanishes. This observation is easy to document by inspecting the entropy production formula (4.29) for compressible heat conducting fluids, where the constraint $\operatorname{div} \mathbf{v} = 0$ would imply that $(m + p_{\text{th}}) \operatorname{div} \mathbf{v} = 0$.

However, the specification of the constitutive relations is based on the presence of the quantities of interest in the formula for the entropy production in the form of a flux/affinity product. In this context one could say that the mean normal stress *can not be specified constitutively*. (Meaning that the mean normal stress m is not—in contrast to the traceless part \mathbb{T}_δ of the Cauchy stress tensor—given by a constitutive relation in terms of other variables such as the kinematical quantities.)

If thought of carefully, this is a natural consequence of the concept of incompressibility. The mean normal stress in an incompressible fluid must incorporate the force mechanism that prevents the fluid from changing its volume. (In mathematical terms this means that it must depend on the Lagrange multiplier enforcing the incompressibility constraint (4.52).) As such it can not be specified without the knowledge of boundary conditions. Think for example of a vessel completely filled with an incompressible fluid at rest. The value of the mean normal stress in the vessel can not be determined without the knowledge of the forces acting on the vessel walls.

This makes the normal stress in an incompressible fluid a totally different quantity than the mean normal stress in a compressible fluid. In a compressible fluid, see for example (4.30b), the mean normal stress is a function of the thermodynamic pressure p_{th} and the velocity field, and the thermodynamic pressure is a function of the density and the temperature. Therefore, the mean normal stress in a compressible fluid is fully specified in terms of the local values of the state variables and the velocity field. On the other hand, *the mean normal stress in an incompressible fluid is not a function of the local values of the state variables and the velocity field, it constitutes another unknown in the governing equations.*

Unfortunately, the simplest model for an incompressible viscous fluid is the Navier–Stokes fluid where the Cauchy stress tensor is given by the formula

$$\mathbb{T} = -p\mathbb{1} + 2\nu\mathbb{D}, \quad (4.54)$$

where p is called the “pressure”. This could be misleading since the quantity called “pressure” also appears in the compressible Navier–Stokes fluid, albeit the pressure in the compressible Navier–Stokes fluid is the *thermodynamic pressure*, which is a totally different quantity than the pressure p in (4.54). Further, the mean normal stress m in the incompressible Navier–Stokes fluid model (4.54) is $m = -p$, hence it differs from the “pressure” p by a mere sign. Consequently, the notions of the mean normal stress and the “pressure” are often used interchangeably, which is a bad practice since these notions do not coincide if one deals with incompressible fluid models that go beyond (4.54).

Concerning the compressible Navier–Stokes fluid model (4.36d) the mean normal stress is given by the formula $m = -p_{\text{th}} + \frac{3\lambda+2\nu}{3} \operatorname{div} \mathbf{v}$, hence the mean normal stress differs from the thermodynamic pressure by more than a sign. On the other hand, the mean normal stress coincides with the thermodynamic pressure if one adopts so-called Stokes assumption $3\lambda + 2\nu = 0$. In such a case one is allowed to use interchangeably terms thermodynamic pressure and mean normal stress, which is otherwise not correct.

The subtleties concerning the notion of the pressure, Lagrange multiplier enforcing the incompressibility constraint, thermodynamic pressure and the mean normal stress can be of importance if one for example wants to talk about viscoelastic materials with “pressure” dependent coefficients. The different contexts in which the term pressure is used are discussed in detail by Rajagopal [76], see also comments by Huilgol [43] and Dealy [22], and this issue is not further commented in the present treatise. The reader should be however aware of the fact that the notion of “pressure” becomes complicated in particular if one deals with non-Newtonian fluids.

Concerning the possible approaches to the derivation of constitutive relations for incompressible materials, one can either opt for the strategy outlined in Section 4.1, and enforce the incompressibility constraint via an additional Lagrange multiplier. Examples of such approaches can be found in Málek and Rajagopal [54] (incompressible Navier–Stokes fluid) and Málek et al [58] (incompressible viscoelastic fluids). This approach allows one to find a relation between the Lagrange multiplier enforcing the incompressibility constraint and the mean normal stress. However, this relation is usually of no interest in the final constitutive relations. Therefore, a different and more pragmatic approach is adopted in the rest of the text.

The constitutive relations are derived in a standard manner with the constraint (4.52) in mind, which leads to a constitutive relation for the traceless part of the Cauchy stress tensor \mathbb{T}_δ . As shown above, the incompressibility constraint makes the search for a constitutive relation for the mean normal stress pointless, hence one can leave the final formula for the full Cauchy stress tensor in the form

$$\mathbb{T} = m\mathbb{1} + \mathbb{T}_\delta, \quad (4.55)$$

where m is understood as a new unknown quantity to be solved for. (In (4.55) one can further exploit the fact that the incompressibility constraint (4.52) allows one to write $\mathbb{D} = \mathbb{D}_\delta$.)

In particular, if the outlined approach is applied in the case of the constitutive relations derived in Section 4.2.1, one gets $\mathbb{T} = m\mathbb{1} + \mathbb{T}_\delta = m\mathbb{1} + 2\nu^*(\theta, \rho)\mathbb{D}_\delta$, hence

$$\mathbb{T} = m\mathbb{1} + 2\nu^*(\theta, \rho)\mathbb{D}, \quad (4.56a)$$

where the relation $\mathbb{D} = \mathbb{D}_\delta$ has been exploited. The constitutive relation for the heat flux remains formally the same,

$$\mathbf{j}_q = -\kappa^*(\theta, \rho)\nabla\theta. \quad (4.56b)$$

These are the constitutive relations for the *incompressible Navier–Stokes–Fourier fluid*. Note that unlike in the majority of the literature the constitutive relation for the Cauchy stress tensor is written as (4.56a) and not as

$$\mathbb{T} = -p\mathbb{1} + 2\nu^*(\theta, \rho)\mathbb{D}. \quad (4.57)$$

This notation emphasises the different nature the thermodynamic pressure p_{th} in compressible fluids, which is frequently denoted as p , and the “pressure” $p =_{\text{def}} -m$ in incompressible fluids.

The governing equations for the *incompressible Navier–Stokes–Fourier fluid* then take the form

$$\frac{d\rho}{dt} = 0, \quad (4.58a)$$

$$\text{div } \mathbf{v} = 0, \quad (4.58b)$$

$$\rho \frac{d\mathbf{v}}{dt} = \nabla m + \text{div} (2\nu^*(\theta, \rho)\mathbb{D}) + \rho\mathbf{b}, \quad (4.58c)$$

$$\rho \frac{d}{dt} \left(e^*(\theta, \rho) + \frac{1}{2} |\mathbf{v}|^2 \right) = \text{div} (m\mathbf{v} + 2\nu^*(\theta, \rho)\mathbb{D}\mathbf{v} + \kappa^*(\theta, \rho)\nabla\theta) + \rho\mathbf{b} \cdot \mathbf{v}. \quad (4.58d)$$

The first equation in (4.58), $\frac{\partial\rho}{\partial t} + \mathbf{v} \cdot \nabla\rho = 0$, implies that ρ is transported along the characteristics,

$$\rho(\mathbf{x}, t) = \rho_0(\mathbf{X}) = \rho_0(\chi^{-1}(\mathbf{x}, t)), \quad (4.59)$$

where ρ_0 is the density in the initial (reference) configuration. Consequently the density $\rho(\mathbf{x}, t)$ is constant in space and time if the initial (reference) density ρ_0 is uniform, that is if

$$\rho_0(\mathbf{X}_1) = \rho_0(\mathbf{X}_2) \quad (4.60)$$

holds for all $\mathbf{X}_1, \mathbf{X}_2 \in \mathcal{B}$. If (4.60) does not hold, then the fluid at its initial (reference) state is inhomogeneous. This is why the system (4.58) is sometimes called *inhomogeneous incompressible Navier–Stokes–Fourier equations*.

Obviously the incompressible Navier–Stokes–Fourier fluid model can be further simplified. Setting $\mathbb{T}_\delta = \mathbb{0}$ one gets a model for a fluid without shear viscosity. Such a model can be referred to as *inhomogeneous incompressible Euler–Fourier fluid model*, and the governing equations reduce to

$$\frac{d\rho}{dt} = 0, \quad (4.61a)$$

$$\text{div } \mathbf{v} = 0, \quad (4.61b)$$

$$\rho \frac{d\mathbf{v}}{dt} = \nabla m + \rho\mathbf{b}, \quad (4.61c)$$

$$\rho \frac{d}{dt} \left(e^*(\theta, \rho) + \frac{1}{2} |\mathbf{v}|^2 \right) = \text{div} (m\mathbf{v} + \kappa^*(\theta, \rho)\nabla\theta) + \rho\mathbf{b} \cdot \mathbf{v}. \quad (4.61d)$$

Note that equations (4.61a)–(4.61c) are not coupled with the temperature and can provide a solution for ρ and \mathbf{v} independently of the energy equation. The fluid described by (4.61a)–(4.61c) is called the *inhomogeneous incompressible Euler fluid*.

If the viscosity in (4.58) does not depend on the temperature, $\nu^*(\theta, \rho) = \tilde{\nu}(\rho)$, then energy equation again decouples from the system and one can solve only the mechanical part of (4.58). This leads to *inhomogeneous incompressible Navier–Stokes equations*

$$\frac{d\rho}{dt} = 0, \quad (4.62a)$$

$$\text{div } \mathbf{v} = 0, \quad (4.62b)$$

$$\rho \frac{d\mathbf{v}}{dt} = \nabla m + \text{div} (2\tilde{\nu}(\rho)\mathbb{D}) + \rho\mathbf{b}. \quad (4.62c)$$

If the density at initial (reference) configuration is uniform, then as a consequence of (4.60) and (4.59) one finds that

$$\rho(\mathbf{x}, t) =_{\text{def}} \rho_\star \in (0, +\infty) \quad (4.63)$$

for all $t > 0$, $\mathbf{x} \in \mathcal{B}$. System (4.58) then simplifies to the so-called *homogeneous incompressible Navier–Stokes–Fourier equations*

$$\operatorname{div} \mathbf{v} = 0, \quad (4.64a)$$

$$\rho \frac{d\mathbf{v}}{dt} = \nabla m + \operatorname{div} (2\hat{\nu}(\theta)\mathbb{D}) + \rho \mathbf{b}, \quad (4.64b)$$

$$\rho \frac{d}{dt} \left(\hat{e}(\theta) + \frac{1}{2} |\mathbf{v}|^2 \right) = \operatorname{div} (m\mathbf{v} + 2\hat{\nu}(\theta)\mathbb{D}\mathbf{v} + \hat{\kappa}(\theta)\nabla\theta) + \rho \mathbf{b} \cdot \mathbf{v}, \quad (4.64c)$$

where $\hat{\nu}(\theta) =_{\text{def}} \nu^*(\theta, \rho_*)$, $\hat{e}(\theta) =_{\text{def}} e^*(\theta, \rho_*)$ and $\hat{\kappa}(\theta) =_{\text{def}} \kappa^*(\theta, \rho_*)$. Following the same template as above, one can introduce *homogeneous incompressible Euler–Fourier fluids*.

If the viscosity does not depend on the temperature, $\nu_* =_{\text{def}} \hat{\nu}(\theta_*) = \nu^*(\theta_*, \rho_*)$, then (4.64c) decouples from the rest of the system (4.64), and one can solve only the mechanical part of (4.64) for the mechanical variables m and \mathbf{v} . This leads to the classical *incompressible Navier–Stokes equations*

$$\operatorname{div} \mathbf{v} = 0, \quad (4.65a)$$

$$\rho \frac{d\mathbf{v}}{dt} = \nabla m + \operatorname{div} (2\nu_*\mathbb{D}) + \rho \mathbf{b}, \quad (4.65b)$$

where the right hand side of (4.65b) can be rewritten as $\nabla m + \operatorname{div} (2\nu_*\mathbb{D}) + \rho \mathbf{b} = \nabla m + \nu_* \Delta \mathbf{v} + \rho \mathbf{b}$. Finally, if $\mathbb{T}_\delta = 0$, then one ends up with the *incompressible Euler equations*

$$\operatorname{div} \mathbf{v} = 0, \quad (4.66a)$$

$$\rho \frac{d\mathbf{v}}{dt} = \nabla m + \rho \mathbf{b}. \quad (4.66b)$$

4.3. Compressible Korteweg fluids. Another popular model describing the behaviour of fluids is the model introduced by Korteweg [51]. The model has been developed with the aim to describe phase transition phenomena, but it is also used for the modelling of the behaviour of some granular materials. The key feature of the model is that the Cauchy stress tensor includes terms of the type $\nabla\rho \otimes \nabla\rho$, which is natural given the fact that the model is designed to take into account steep density changes that can occur, for example, at a fluid/vapour interface. In what follows it is shown how to derive the model using the thermodynamical procedure outlined in Section 4.1. (The reader interested in various applications of the model and the details concerning the derivation of the model is referred to Málek and Rajagopal [55] and Heida and Málek [38].)

Since the density gradient is the main object of interest, for later use it is convenient to observe that the balance of mass (4.1a) implies

$$\frac{d}{dt} (\nabla\rho) = -\nabla (\rho \operatorname{div} \mathbf{v}) - [\nabla\mathbf{v}]^\top \nabla\rho. \quad (4.67)$$

STEP 1: Consider the constitutive equation for the specific internal energy—or the specific entropy η —in the form

$$\eta = \tilde{\eta}(e, \rho, \nabla\rho) \quad \text{or} \quad e = \tilde{e}(\eta, \rho, \nabla\rho). \quad (4.68)$$

The presence of the density gradient $\nabla\rho$ in the formula for the internal energy/entropy means that in this specific example one goes, for the first time in this text, beyond classical equilibrium thermodynamics. Moreover, the energetic equation of the state is considered in a special form

$$e =_{\text{def}} \tilde{e}(\eta, \rho, \nabla\rho) = \bar{e}(\eta, \rho) + \frac{\sigma}{2\rho} |\nabla\rho|^2, \quad (4.69)$$

where σ is a positive constant. This choice is motivated by the fact that one expects the density gradient $\nabla\rho$ to contribute to the energy storage mechanisms, and the fact that the norm of the gradient $\nabla\rho$ is the simplest possible choice if one wants the internal energy to be a scalar isotropic function of $\nabla\rho$.

STEP 2 and 3: Applying the material time derivative to (4.69), multiplying the result by ρ and using the evolution equation for the internal energy (2.22), the balance of mass (2.4) and identity (4.67) yield

$$\rho \frac{\partial e}{\partial \eta} \frac{d\eta}{dt} = \mathbb{T} : \mathbb{D} - \operatorname{div} \mathbf{j}_q + \rho^2 \frac{\partial \tilde{e}}{\partial \rho} \operatorname{div} \mathbf{v} + \sigma (\nabla\rho) \cdot \nabla (\rho \operatorname{div} \mathbf{v}) + \sigma (\nabla\mathbf{v}) : (\nabla\rho \otimes \nabla\rho). \quad (4.70)$$

Introducing the thermodynamic pressure and temperature via

$$\theta =_{\text{def}} \frac{\partial \tilde{e}}{\partial \eta}, \quad (4.71a)$$

$$p_{\text{th}}^{\text{K}} =_{\text{def}} \rho^2 \frac{\partial \tilde{e}}{\partial \rho}, \quad (4.71b)$$

one ends up with a formula for the material time derivative of the entropy

$$\rho \theta \frac{d\eta}{dt} = (\mathbb{T}_\delta + \sigma (\nabla\rho \otimes \nabla\rho)_\delta) : \mathbb{D}_\delta + \left(m + p_{\text{th}}^{\text{K}} + \frac{\sigma}{3} |\nabla\rho|^2 \right) \operatorname{div} \mathbf{v} - \operatorname{div} \mathbf{j}_q + \operatorname{div} (\sigma \rho (\operatorname{div} \mathbf{v}) \nabla\rho) - \sigma \rho \Delta \rho \operatorname{div} \mathbf{v}, \quad (4.72)$$

where the relevant tensors have been split to their traceless part and the rest, see Section 4.2 for the rationale of this step. Notice however that this thermodynamic pressure p_{th}^{K} is different from the thermodynamic pressure $p_{\text{th}}^{\text{NSE}} =_{\text{def}} \rho^2 \frac{\partial \bar{e}}{\partial \rho}$ for the Navier–Stokes fluid as they are related through

$$p_{\text{th}}^{\text{K}} = p_{\text{th}}^{\text{NSE}} - \frac{\sigma}{2} |\nabla\rho|^2. \quad (4.73)$$

Equation (4.72) can be further rewritten as

$$\rho\theta\frac{d\eta}{dt} = (\mathbb{T}_\delta + \sigma(\nabla\rho \otimes \nabla\rho)_\delta) : \mathbb{D}_\delta + \left(m + p_{\text{th}}^{\text{K}} + \frac{\sigma}{3}|\nabla\rho|^2 - \sigma\rho\Delta\rho\right) \operatorname{div} \mathbf{v} - \operatorname{div}(\mathbf{j}_q - \sigma\rho(\nabla\rho) \operatorname{div} \mathbf{v}), \quad (4.74)$$

and using the notation

$$\mathbf{j}_\eta =_{\text{def}} \mathbf{j}_q - \sigma\rho\nabla\rho, \quad (4.75)$$

and applying the standard manipulation finally yields

$$\rho\frac{d\eta}{dt} + \operatorname{div}\left(\frac{\mathbf{j}_\eta}{\theta}\right) = \frac{1}{\theta} \left[(\mathbb{T}_\delta + \sigma(\nabla\rho \otimes \nabla\rho)_\delta) : \mathbb{D}_\delta + \left(m + p_{\text{th}}^{\text{K}} + \frac{\sigma}{3}|\nabla\rho|^2 - \sigma\rho\Delta\rho\right) \operatorname{div} \mathbf{v} - \mathbf{j}_q \cdot \frac{\nabla\theta}{\theta} + \sigma\rho(\operatorname{div} \mathbf{v})(\nabla\rho) \cdot \frac{\nabla\theta}{\theta} \right]. \quad (4.76)$$

The affinities are in the present case \mathbb{D}_δ , $\operatorname{div} \mathbf{v}$ and $\nabla\theta$. Apparently, the last term on the right hand side of (4.76) can be interpreted either as

$$\left[\sigma\rho(\nabla\rho) \cdot \frac{\nabla\theta}{\theta} \right] \operatorname{div} \mathbf{v} \quad (4.77)$$

and grouped with the second term $\left(m + p_{\text{th}} + \frac{\sigma}{3}|\nabla\rho|^2 - \sigma\rho\Delta\rho\right) \operatorname{div} \mathbf{v}$, or it can be read as

$$[\sigma\rho(\operatorname{div} \mathbf{v})(\nabla\rho)] \cdot \frac{\nabla\theta}{\theta} \quad (4.78)$$

and grouped with the third term $\mathbf{j}_q \cdot \frac{\nabla\theta}{\theta}$. The question is left unresolved, and a parameter $\delta \in [0, 1]$ that splits the last term as

$$\sigma\rho(\operatorname{div} \mathbf{v})(\nabla\rho) \cdot \frac{\nabla\theta}{\theta} = (1-\delta) \left[\sigma\rho(\nabla\rho) \cdot \frac{\nabla\theta}{\theta} \right] \operatorname{div} \mathbf{v} + \delta [\sigma\rho(\operatorname{div} \mathbf{v})(\nabla\rho)] \cdot \frac{\nabla\theta}{\theta}, \quad (4.79)$$

is introduced. The arising terms are then grouped with the corresponding terms in (4.76). This yields

$$\begin{aligned} & \rho\frac{d\eta}{dt} + \operatorname{div}\left(\frac{\mathbf{j}_\eta}{\theta}\right) \\ &= \frac{1}{\theta} \left[(\mathbb{T}_\delta + \sigma(\nabla\rho \otimes \nabla\rho)_\delta) : \mathbb{D}_\delta + \left(m + p_{\text{th}}^{\text{K}} + \frac{\sigma}{3}|\nabla\rho|^2 - \sigma\rho\Delta\rho + (1-\delta)\sigma\rho(\nabla\rho) \cdot \frac{\nabla\theta}{\theta}\right) \operatorname{div} \mathbf{v} - (\mathbf{j}_q - \delta\sigma\rho(\operatorname{div} \mathbf{v})\nabla\rho) \cdot \frac{\nabla\theta}{\theta} \right]. \end{aligned} \quad (4.80)$$

STEP 4: The entropy production ξ —that is the right hand side of (4.80)—takes the form

$$\xi = \frac{1}{\theta} \sum_{\alpha=1}^3 \mathbf{j}_\alpha \cdot \mathbf{a}_\alpha, \quad (4.81)$$

where the affinities are \mathbb{D}_δ , $\operatorname{div} \mathbf{v}$ and $\nabla\theta$. Requiring the linear relations between the fluxes and affinities in each term contributing to the rate of entropy production leads to

$$\mathbb{T}_\delta + \sigma(\nabla\rho \otimes \nabla\rho)_\delta = 2\nu\mathbb{D}_\delta, \quad (4.82a)$$

$$m + p_{\text{th}}^{\text{K}} + \frac{\sigma}{3}|\nabla\rho|^2 - \sigma\rho\Delta\rho + (1-\delta)\sigma\rho(\nabla\rho) \cdot \frac{\nabla\theta}{\theta} = \frac{2\nu + 3\lambda}{3} \operatorname{div} \mathbf{v}, \quad (4.82b)$$

$$\mathbf{j}_q - \delta\sigma\rho(\operatorname{div} \mathbf{v})\nabla\rho = -\kappa\nabla\theta \quad (4.82c)$$

where $\nu > 0$, $\frac{2\nu+3\lambda}{3} > 0$ and $\kappa > 0$ are positive constants. This choice of constitutive relations follows the template specified in (4.9).

STEP 5: It follows from (4.82) that the constitutive relation for the full Cauchy stress tensor $\mathbb{T} = \mathbb{T}_\delta + m\mathbb{I}$ is

$$\mathbb{T} = -p_{\text{th}}^{\text{K}}\mathbb{I} + 2\nu\mathbb{D} + \lambda(\operatorname{div} \mathbf{v})\mathbb{I} - \sigma(\nabla\rho \otimes \nabla\rho) + \sigma\rho(\Delta\rho)\mathbb{I} - (1-\delta)\sigma\rho(\nabla\rho) \cdot \frac{\nabla\theta}{\theta}\mathbb{I} \quad (4.83)$$

that can be upon introducing the notation

$$\phi =_{\text{def}} p_{\text{th}}^{\text{NSE}} - \frac{\sigma}{2}|\nabla\rho|^2 - \sigma\rho\Delta\rho + (1-\delta)\sigma\rho(\nabla\rho) \cdot \frac{\nabla\theta}{\theta} \quad (4.84a)$$

rewritten as

$$\mathbb{T} = -\phi\mathbb{I} + 2\nu\mathbb{D} + \lambda(\operatorname{div} \mathbf{v})\mathbb{I} - \sigma(\nabla\rho \otimes \nabla\rho). \quad (4.84b)$$

Concerning the heat/energy flux one gets

$$\mathbf{j}_q = -\kappa\nabla\theta + \delta\sigma\rho(\operatorname{div} \mathbf{v})\nabla\rho. \quad (4.84c)$$

Note that if only *isothermal* processes are considered, then (4.83) reduces to

$$\mathbb{T} = -p_{\text{th}}^{\text{NSE}}\mathbb{I} + 2\nu\mathbb{D} + \lambda(\operatorname{div} \mathbf{v})\mathbb{I} + \sigma(\nabla\rho \otimes \nabla\rho) + \sigma\left(\frac{|\nabla\rho|^2}{2} + \rho(\Delta\rho)\right)\mathbb{I}, \quad (4.85)$$

which is the constitutive relation obtained by Korteweg [51].

4.4. Compressible and incompressible viscoelastic heat conducting fluids. Viscoelastic materials are materials that exhibit simultaneously two fundamental modes of behaviour. They can store the energy in the form of strain energy, hence they deserve to be called elastic, and they dissipate the energy, hence they deserve to be called viscous. Since the two modes are coupled, the nomenclature viscoelastic is obvious.

A *rough visual representation* of materials that exhibit viscoelastic behaviour is provided by systems composed of springs and dashpots. The springs represent the elastic behaviour, while the dashpots represent the dissipation. Such a visual representation is frequently used in the discussion of viscoelastic properties of materials, see for example Burgers [14] or more recently Wineman and Rajagopal [95]. The use of the visual representation as a motivation for the subsequent study of the constitutive relations for viscoelastic fluids is also followed in the subsequent discussion.

A simple example of a spring-dashpot system is the Maxwell element consisting of a viscous dashpot and an elastic spring connected in series, see Figure 3a. The response of the element to step loading is the following. (The step loading is a loading that is constant and is applied only over time interval $[t_0, t_1]$, otherwise the loading is zero.) Initially, the element is unloaded, it is in an initial state, see Figure 3a. Once the loading is applied at time t_0 the spring extends and the dashpot starts to move as well, see Figure 3b. When the loading is suddenly removed at some time t_1 , see Figure 3c, the spring, that is the elastic element, instantaneously shrinks to its initial equilibrium length. On the other hand, the sudden unloading does not change the length of the dashpot at all. (The term “length of the dashpot” denotes the distance between the piston and the dashpot left wall.)

This means that the instantaneous response to the sudden load removal is purely elastic, while the configuration (length) to which the material relaxes after the sudden load removal is determined by the length of the dashpot. Therefore, the unloaded configuration is determined by the behaviour of the purely dissipative element.

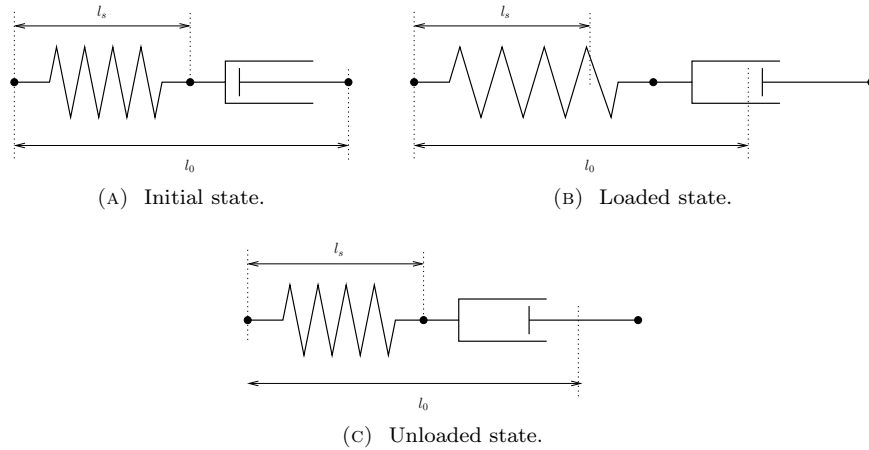


FIGURE 3. Maxwell element.

4.4.1. Concept of natural configuration and associated kinematics. Now the question is whether one can use this observation in the development of the constitutive relations for viscoelastic materials. It turns out that this is possible. One can associate these three states (initial/loaded/unloaded) of the Maxwell element with the three states of a continuous body:

- (1) the *initial (reference) configuration* $\kappa_0(\mathcal{B})$,
- (2) the *current configuration* $\kappa_t(\mathcal{B})$ that the body takes at time $t > 0$ during the deformation process due to the external load,
- (3) the *natural configuration* $\kappa_{p(t)}(\mathcal{B})$ that would be taken by the considered body at time $t > 0$ upon *sudden load removal*.

The evolution from the initial configuration to the current configuration is then *virtually* decomposed to the evolution of the natural configuration (dissipative process) and instantaneous elastic response (non-dissipative process) from the natural configuration to the current configuration. Figure 4 depicts the situation. Referring back to the spring-dashpot analogue, the evolution of the natural configuration plays the role of the dashpot, while the instantaneous elastic response from the current configuration to the natural configuration plays the role of the spring.

Derivation of constitutive relations for viscoelastic materials by appealing to the procedure outlined in Section 4.1 can then proceed as follows. Since the energy storage mechanisms in a viscoelastic fluid are determined by the elastic part—the spring—the plan is to enrich the constitutive relation for the internal energy, see (4.4), by a state variable that measures the deformation of the elastic part. (Deformation from the natural to the current configuration.)

The next step of the thermodynamic procedure requires one to take material time derivative of the internal energy, hence a formula for the material time derivative of the chosen measure of the deformation of the elastic part is needed. This task requires a careful analysis of the kinematics of continuous media with multiple configurations.

Recall that the key quantities in the kinematics of continuous media are the deformation gradient

$$\mathbb{F}(\mathbf{X}, t) =_{\text{def}} \frac{\partial \chi_{\kappa_0}(\mathbf{X}, t)}{\partial \mathbf{X}}, \quad (4.86)$$

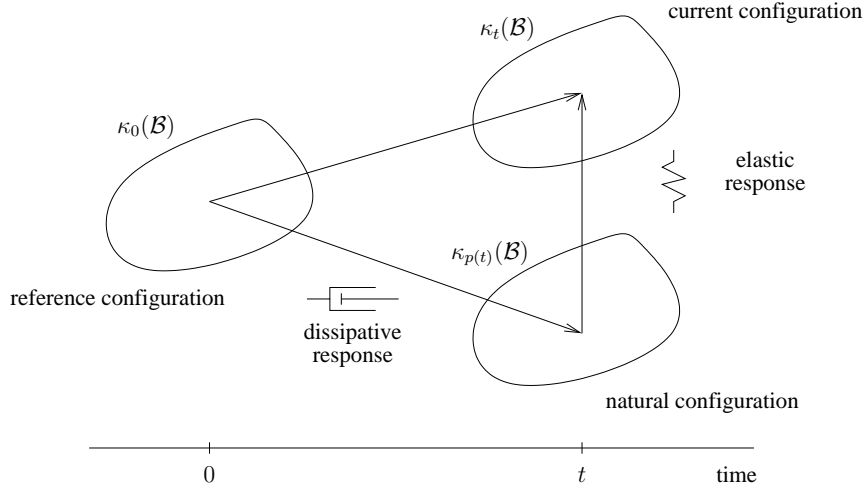


FIGURE 4. Initial (reference), current and natural configurations associated with a material body.

and the spatial velocity field

$$\mathbf{v}(\mathbf{x}, t) =_{\text{def}} \left. \frac{\partial \chi_{\kappa_0}(\mathbf{X}, t)}{\partial t} \right|_{\mathbf{X}=\chi_{\kappa_0}^{-1}(\mathbf{x}, t)}. \quad (4.87)$$

(The subscript κ_0 recalls that the deformation gradient is taken with respect to the initial configuration.) Other quantities of interest are the left Cauchy–Green tensor and the right Cauchy–Green tensor $\mathbb{B} =_{\text{def}} \mathbb{F}\mathbb{F}^\top$, $\mathbb{C} =_{\text{def}} \mathbb{F}^\top\mathbb{F}$, the (spatial) velocity gradient $\mathbb{L} =_{\text{def}} \frac{\partial \mathbf{v}}{\partial \mathbf{x}}$, and its symmetric part \mathbb{D} . The material time derivative of \mathbb{F} is then given by the formula

$$\frac{d\mathbb{F}}{dt} = \mathbb{L}\mathbb{F}. \quad (4.88)$$

Within the framework consisting of three configurations $\kappa_0(\mathcal{B})$, $\kappa_t(\mathcal{B})$ and $\kappa_{p(t)}(\mathcal{B})$, the standard kinematical setup is extended by the deformation gradient $\mathbb{F}_{\kappa_{p(t)}}$ describing the deformation between the natural and the current configuration, and the deformation gradient \mathbb{G} describing the deformation between the initial (reference) configuration and the natural configuration.

Obviously, see Figure 4, the following relation holds

$$\mathbb{F} = \mathbb{F}_{\kappa_{p(t)}}\mathbb{G}. \quad (4.89)$$

For later use, one also introduces notation

$$\mathbb{B}_{\kappa_{p(t)}} =_{\text{def}} \mathbb{F}_{\kappa_{p(t)}}\mathbb{F}_{\kappa_{p(t)}}^\top, \quad (4.90a)$$

$$\mathbb{C}_{\kappa_{p(t)}} =_{\text{def}} \mathbb{F}_{\kappa_{p(t)}}^\top\mathbb{F}_{\kappa_{p(t)}}, \quad (4.90b)$$

for the left and right Cauchy–Green tensors for the deformation from the natural to the current configuration. *The left Cauchy–Green tensor $\mathbb{B}_{\kappa_{p(t)}}$ is the sought measure of the deformation associated with the instantaneous elastic part of the deformation.*

The reason is the following. In the standard finite elasticity theory, one uses the left Cauchy–Green tensor $\mathbb{B} =_{\text{def}} \mathbb{F}\mathbb{F}^\top$ in order to characterise the finite deformation of a body. In the current setting the elastic response is the response from the natural to the current configuration, hence the left Cauchy–Green $\mathbb{B}_{\kappa_{p(t)}}$ tensor built using the relative deformation gradient $\mathbb{F}_{\kappa_{p(t)}}$ instead of the full deformation gradient \mathbb{F} is used.

Now one needs to find an expression for the material time derivative of $\mathbb{B}_{\kappa_{p(t)}}$. (The knowledge of an expression for the time derivative is needed in the STEP 2 of the procedure discussed in Section 4.1.) The aim is to express $\mathbb{B}_{\kappa_{p(t)}}$ as a function of $\mathbb{F}_{\kappa_{p(t)}}$ and a rate quantity associated with the *dissipative* part of the response and a rate quantity associated with the total response.

Noticing that (4.88) implies that $\mathbb{L} = \frac{d\mathbb{F}}{dt}\mathbb{F}^{-1}$ a new tensorial quantity $\mathbb{L}_{\kappa_{p(t)}}$ is introduced through

$$\mathbb{L}_{\kappa_{p(t)}} =_{\text{def}} \frac{d\mathbb{G}}{dt}\mathbb{G}^{-1}, \quad (4.91)$$

and its symmetric part is denoted as $\mathbb{D}_{\kappa_{p(t)}}$,

$$\mathbb{D}_{\kappa_{p(t)}} =_{\text{def}} \frac{1}{2} \left(\mathbb{L}_{\kappa_{p(t)}} + \mathbb{L}_{\kappa_{p(t)}}^\top \right). \quad (4.92)$$

Relations (4.89), (4.88) and (4.91) together with the formula

$$\frac{d}{dt}(\mathbb{G}^{-1}) = -\mathbb{G}^{-1}\frac{d\mathbb{G}}{dt}\mathbb{G}^{-1} \quad (4.93)$$

then yield

$$\frac{d\mathbb{F}_{\kappa_{p(t)}}}{dt} = \frac{d\mathbb{F}}{dt}\mathbb{G}^{-1} + \mathbb{F}\frac{d\mathbb{G}^{-1}}{dt} = \mathbb{L}\mathbb{F}\mathbb{G}^{-1} - \mathbb{F}\mathbb{G}^{-1}\frac{d\mathbb{G}}{dt}\mathbb{G}^{-1} = \mathbb{L}\mathbb{F}_{\kappa_{p(t)}} - \mathbb{F}_{\kappa_{p(t)}}\mathbb{L}_{\kappa_{p(t)}}, \quad (4.94)$$

which implies

$$\frac{d\mathbb{B}_{\kappa_p(t)}}{dt} = \mathbb{L}\mathbb{B}_{\kappa_p(t)} + \mathbb{B}_{\kappa_p(t)}\mathbb{L}^\top - 2\mathbb{F}_{\kappa_p(t)}\mathbb{D}_{\kappa_p(t)}\mathbb{F}_{\kappa_p(t)}^\top. \quad (4.95)$$

This is the sought expression for the time derivative of the chosen measure of the deformation. As required, the time derivative is a function of $\mathbb{F}_{\kappa_p(t)}$ and the rate quantities $\mathbb{D}_{\kappa_p(t)}$ and \mathbb{L} that are associated to the dissipative part of the response and the total response respectively.

Introducing the so-called *upper convected time derivative* through the formula

$$\overset{\nabla}{\mathbb{A}} =_{\text{def}} \frac{d\mathbb{A}}{dt} - \mathbb{L}\mathbb{A} - \mathbb{A}\mathbb{L}^\top, \quad (4.96)$$

where \mathbb{A} is a second order tensor, it follows from (4.95) that

$$\overset{\nabla}{\mathbb{B}_{\kappa_p(t)}} = -2\mathbb{F}_{\kappa_p(t)}\mathbb{D}_{\kappa_p(t)}\mathbb{F}_{\kappa_p(t)}^\top. \quad (4.97)$$

For later reference it is worth noticing that (4.96) implies

$$\overset{\nabla}{\mathbb{I}} = -2\mathbb{D}, \quad (4.98)$$

and that (4.95) implies

$$\frac{d}{dt} \text{Tr} \mathbb{B}_{\kappa_p(t)} = 2\mathbb{B}_{\kappa_p(t)} : \mathbb{D} - 2\mathbb{C}_{\kappa_p(t)} : \mathbb{D}_{\kappa_p(t)}. \quad (4.99)$$

Since $\frac{d}{dt} \det \mathbb{A} = (\det \mathbb{A}) \text{Tr} \left(\frac{d\mathbb{A}}{dt} \mathbb{A}^{-1} \right)$ one can also observe that

$$\frac{d}{dt} (\ln [\det \mathbb{B}_{\kappa_p(t)}]) = \text{Tr} \left(\frac{d\mathbb{B}_{\kappa_p(t)}}{dt} \mathbb{B}_{\kappa_p(t)}^{-1} \right) = 2\mathbb{I} : \mathbb{D} - 2\mathbb{I} : \mathbb{D}_{\kappa_p(t)}. \quad (4.100)$$

Finally, the upper convected derivative of the traceless part of $\mathbb{B}_{\kappa_p(t)}$ reads

$$\begin{aligned} \left(\overset{\nabla}{\mathbb{B}_{\kappa_p(t)}} \right)_\delta &= \frac{d(\mathbb{B}_{\kappa_p(t)})_\delta}{dt} - \mathbb{L}(\mathbb{B}_{\kappa_p(t)})_\delta - (\mathbb{B}_{\kappa_p(t)})_\delta \mathbb{L}^\top = \frac{d\mathbb{B}_{\kappa_p(t)}}{dt} - \frac{1}{3} \frac{d \text{Tr} \mathbb{B}_{\kappa_p(t)}}{dt} \mathbb{I} - \mathbb{L}\mathbb{B}_{\kappa_p(t)} - \mathbb{B}_{\kappa_p(t)}\mathbb{L}^\top + \frac{2}{3} (\text{Tr} \mathbb{B}_{\kappa_p(t)}) \mathbb{D} \\ &= \overset{\nabla}{\mathbb{B}_{\kappa_p(t)}} - \frac{2}{3} (\mathbb{B}_{\kappa_p(t)} : \mathbb{D}) \mathbb{I} + \frac{2}{3} (\mathbb{C}_{\kappa_p(t)} : \mathbb{D}_{\kappa_p(t)}) \mathbb{I} + \frac{2}{3} (\text{Tr} \mathbb{B}_{\kappa_p(t)}) \mathbb{D} \\ &= -2\mathbb{F}_{\kappa_p(t)}\mathbb{D}_{\kappa_p(t)}\mathbb{F}_{\kappa_p(t)}^\top - \frac{2}{3} (\mathbb{B}_{\kappa_p(t)} : \mathbb{D}) \mathbb{I} + \frac{2}{3} (\mathbb{C}_{\kappa_p(t)} : \mathbb{D}_{\kappa_p(t)}) \mathbb{I} + \frac{2}{3} (\text{Tr} \mathbb{B}_{\kappa_p(t)}) \mathbb{D}. \end{aligned} \quad (4.101)$$

4.4.2. Application of the thermodynamic procedure in the context of natural configuration. The application of the thermodynamic procedure discussed in Section 4.1 in the setting of a material with an evolving natural configuration goes as follows.

STEP 1: The fact that the energy storage mechanisms are required to be related to the elastic part of the deformation, see Figure 4, suggests that the internal energy e should be enriched by a term measuring the elastic part of the deformation. As it has been already noted, a suitable measure of the deformation is the left Cauchy–Green tensor $\mathbb{B}_{\kappa_p(t)}$, hence the entropic/energetic equation of state is assumed to take the form

$$\eta = \tilde{\eta}(e, \rho, \mathbb{B}_{\kappa_p(t)}) \quad \text{or} \quad e = \tilde{e}(\eta, \rho, \mathbb{B}_{\kappa_p(t)}). \quad (4.102)$$

For the sake of simplicity of the presentation the energetic equation of state is further assumed to take the form

$$e = \hat{e}(\eta, \rho, \text{Tr} \mathbb{B}_{\kappa_p(t)}, \det \mathbb{B}_{\kappa_p(t)}) =_{\text{def}} \bar{e}(\eta, \rho) + \frac{\mu}{2\rho} (\text{Tr} \mathbb{B}_{\kappa_p(t)} - 3 - \ln \det \mathbb{B}_{\kappa_p(t)}), \quad (4.103)$$

where μ is a constant. The *motivation* for this particular choice comes from the theory of constitutive relations for isotropic compressible elastic materials, see for example Horgan and Saccomandi [41] and Horgan and Murphy [40] for a list of some frequently used constitutive relations in the theory of compressible elastic materials.

STEP 2: Applying the material time derivative to (4.103), multiplying the result by ρ and using the balance of mass (4.1a) and the evolution equation for the internal energy (4.1d) together with the identities (4.99) and (4.100) one gets

$$\rho\theta \frac{d\eta}{dt} = \mathbb{T} : \mathbb{D} - \text{div} \mathbf{j}_q + p_{\text{th}}^{\text{M}} \text{div} \mathbf{v} - \mu \mathbb{B}_{\kappa_p(t)} : \mathbb{D} + \mu \mathbb{C}_{\kappa_p(t)} : \mathbb{D}_{\kappa_p(t)} + \mu \mathbb{D} : \mathbb{I} - \mu \mathbb{D}_{\kappa_p(t)} : \mathbb{I} \quad (4.104)$$

where

$$p_{\text{th}}^{\text{M}} =_{\text{def}} \rho^2 \frac{\partial \hat{e}}{\partial \rho} = \rho^2 \frac{\partial \bar{e}}{\partial \rho} - \frac{\mu}{2} (\text{Tr} \mathbb{B}_{\kappa_p(t)} - 3 - \ln \det \mathbb{B}_{\kappa_p(t)}) = p_{\text{th}}^{\text{NSE}} - \frac{\mu}{2} (\text{Tr} \mathbb{B}_{\kappa_p(t)} - 3 - \ln \det \mathbb{B}_{\kappa_p(t)}) \quad (4.105)$$

denotes the “pressure”, and $p_{\text{th}}^{\text{NSE}} =_{\text{def}} \rho^2 \frac{\partial \bar{e}}{\partial \rho}$.

STEP 3: Splitting the tensors on the right-hand side of (4.104) into the traceless part and the rest yields

$$\begin{aligned} \rho\theta \frac{d\eta}{dt} &= (\mathbb{T}_\delta - \mu (\mathbb{B}_{\kappa_p(t)})_\delta) : \mathbb{D}_\delta + \left(m + p_{\text{th}}^{\text{M}} - \frac{\mu}{3} \text{Tr} \mathbb{B}_{\kappa_p(t)} + \mu \right) \text{div} \mathbf{v} + \mu (\mathbb{C}_{\kappa_p(t)})_\delta : (\mathbb{D}_{\kappa_p(t)})_\delta \\ &\quad + \mu \left(\frac{\text{Tr} \mathbb{B}_{\kappa_p(t)}}{3} - 1 \right) \text{Tr} \mathbb{D}_{\kappa_p(t)} - \text{div} \mathbf{j}_q, \end{aligned} \quad (4.106)$$

where the notation $m =_{\text{def}} \frac{1}{3} \text{Tr } \mathbb{T}$ for the mean normal stress has been used. (See Section 4.2.1 for the rationale of the splitting.) The standard manipulation finally leads to

$$\begin{aligned} & \rho \frac{d\eta}{dt} + \text{div} \left(\frac{\mathbf{j}_q}{\theta} \right) \\ &= \frac{1}{\theta} \left[\left(\mathbb{T}_\delta - \mu (\mathbb{B}_{\kappa_p(t)})_\delta \right) : \mathbb{D}_\delta + \left(m + p_{\text{th}}^M - \frac{\mu}{3} \text{Tr } \mathbb{B}_{\kappa_p(t)} + \mu \right) \text{div } \mathbf{v} + \mu (\mathbb{C}_{\kappa_p(t)})_\delta : (\mathbb{D}_{\kappa_p(t)})_\delta + \mu \left(\frac{\text{Tr } \mathbb{B}_{\kappa_p(t)}}{3} - 1 \right) \text{Tr } \mathbb{D}_{\kappa_p(t)} - \mathbf{j}_q \cdot \frac{\nabla \theta}{\theta} \right] \end{aligned} \quad (4.107)$$

which is the sought formula that allows one to identify the entropy production. The flux-affinity pairs are $\mathbb{T}_\delta - \mu (\mathbb{B}_{\kappa_p(t)})_\delta$ versus \mathbb{D}_δ and so on.

STEP 4: The entropy production—the right hand side of (4.107)—is positive provided that the linear relations between the fluxes and affinities are

$$\mathbb{T}_\delta - \mu (\mathbb{B}_{\kappa_p(t)})_\delta = 2\nu \mathbb{D}_\delta, \quad (4.108a)$$

$$m + p_{\text{th}}^M - \frac{\mu}{3} \text{Tr } \mathbb{B}_{\kappa_p(t)} + \mu = \frac{2\nu + 3\lambda}{3} \text{div } \mathbf{v}, \quad (4.108b)$$

$$\mu (\mathbb{C}_{\kappa_p(t)})_\delta = 2\nu_1 (\mathbb{D}_{\kappa_p(t)})_\delta, \quad (4.108c)$$

$$\mu \left(\frac{\text{Tr } \mathbb{B}_{\kappa_p(t)}}{3} - 1 \right) = \frac{2\nu_1 + 3\lambda_1}{3} \text{Tr } \mathbb{D}_{\kappa_p(t)}, \quad (4.108d)$$

$$\mathbf{j}_q = -\kappa \nabla \theta, \quad (4.108e)$$

where $\nu > 0$, $\frac{2\nu+3\lambda}{3} > 0$, $\nu_1 > 0$, $\frac{2\nu_1+3\lambda_1}{3} > 0$ and $\kappa > 0$ are constants. This choice of constitutive relations follows the template specified in (4.9).

STEP 5: The first two equations in (4.108) allow one to identify the constitutive relation for the full Cauchy stress tensor $\mathbb{T} = m\mathbb{1} + \mathbb{T}_\delta$,

$$\mathbb{T} = 2\nu \mathbb{D}_\delta + \mu (\mathbb{B}_{\kappa_p(t)})_\delta + \frac{2\nu + 3\lambda}{3} (\text{div } \mathbf{v}) \mathbb{1} - p_{\text{th}}^M \mathbb{1} + \frac{\mu}{3} (\text{Tr } \mathbb{B}_{\kappa_p(t)}) \mathbb{1} - \mu \mathbb{1}, \quad (4.109)$$

which can be further rewritten as

$$\mathbb{T} = -p_{\text{th}}^M \mathbb{1} + 2\nu \mathbb{D} + \lambda (\text{div } \mathbf{v}) \mathbb{1} + \mu (\mathbb{B}_{\kappa_p(t)} - \mathbb{1}), \quad (4.110)$$

or, in virtue of (4.105), as

$$\mathbb{T} = -p_{\text{th}}^{\text{NSE}} \mathbb{1} + \frac{\mu}{2} (\text{Tr } \mathbb{B}_{\kappa_p(t)} - 3 - \ln \det \mathbb{B}_{\kappa_p(t)}) \mathbb{1} + 2\nu \mathbb{D} + \lambda (\text{div } \mathbf{v}) \mathbb{1} + \mu (\mathbb{B}_{\kappa_p(t)} - \mathbb{1}). \quad (4.111)$$

The last step leading to the complete description of the material behaviour is the elimination of $\mathbb{D}_{\kappa_p(t)}$ from the constitutive relations. Note that the Cauchy stress is given in terms of \mathbb{D} , that is the velocity field \mathbf{v} , and the left Cauchy–Green tensor $\mathbb{B}_{\kappa_p(t)}$. The evolution equation for $\mathbb{B}_{\kappa_p(t)}$ is (4.97), that is

$$\frac{\overset{\nabla}{\mathbb{B}}}{\mathbb{B}_{\kappa_p(t)}} = -2 \mathbb{F}_{\kappa_p(t)} \mathbb{D}_{\kappa_p(t)} \mathbb{F}_{\kappa_p(t)}^\top. \quad (4.112)$$

The equation expresses the time derivative of $\mathbb{B}_{\kappa_p(t)}$ as a function of \mathbb{L} , $\mathbb{F}_{\kappa_p(t)}$ and $\mathbb{D}_{\kappa_p(t)}$. If the right hand side of (4.97) can be rewritten as a function of $\mathbb{B}_{\kappa_p(t)}$ and \mathbb{L} , then the time evolution of $\mathbb{B}_{\kappa_p(t)}$ would be given in terms of the other quantities directly present in the governing equations, and the process of specification of the constitutive relation would be finished. This can be achieved as follows.

Summing (4.108c) and (4.108d) multiplied by the identity tensor yields

$$\mu (\mathbb{C}_{\kappa_p(t)} - \mathbb{1}) = 2\nu_1 \mathbb{D}_{\kappa_p(t)} + \lambda_1 (\text{Tr } \mathbb{D}_{\kappa_p(t)}) \mathbb{1} \quad (4.113)$$

and

$$\text{Tr } \mathbb{D}_{\kappa_p(t)} = \frac{3\mu}{2\nu_1 + 3\lambda_1} \left(\frac{\text{Tr } \mathbb{C}_{\kappa_p(t)}}{3} - 1 \right), \quad (4.114)$$

which leads to

$$\mu (\mathbb{C}_{\kappa_p(t)} - \mathbb{1}) = 2\nu_1 \mathbb{D}_{\kappa_p(t)} + \frac{3\mu\lambda_1}{2\nu_1 + 3\lambda_1} \left(\frac{\text{Tr } \mathbb{C}_{\kappa_p(t)}}{3} - 1 \right) \mathbb{1}. \quad (4.115)$$

This is an explicit relation between $\mathbb{D}_{\kappa_p(t)}$ and $\mathbb{C}_{\kappa_p(t)}$. Recalling the definition of $\mathbb{C}_{\kappa_p(t)}$ and $\mathbb{B}_{\kappa_p(t)}$, see (4.90), and noticing that $\text{Tr } \mathbb{C}_{\kappa_p(t)} = \text{Tr } \mathbb{B}_{\kappa_p(t)}$, it follows that the multiplication of (4.115) from the left by $\mathbb{F}_{\kappa_p(t)}$ and from the right by $\mathbb{F}_{\kappa_p(t)}^\top$ yields

$$\mu \left(\mathbb{B}_{\kappa_p(t)}^2 - \mathbb{B}_{\kappa_p(t)} \right) = 2\nu_1 \mathbb{F}_{\kappa_p(t)} \mathbb{D}_{\kappa_p(t)} \mathbb{F}_{\kappa_p(t)}^\top + \frac{3\mu\lambda_1}{2\nu_1 + 3\lambda_1} \left(\frac{\text{Tr } \mathbb{C}_{\kappa_p(t)}}{3} - 1 \right) \mathbb{B}_{\kappa_p(t)}. \quad (4.116)$$

Substituting the formula just derived for $\mathbb{F}_{\kappa_p(t)} \mathbb{D}_{\kappa_p(t)} \mathbb{F}_{\kappa_p(t)}^\top$ into (4.112) then gives

$$\nu_1 \frac{\overset{\nabla}{\mathbb{B}}}{\mathbb{B}_{\kappa_p(t)}} + \mu \left(\mathbb{B}_{\kappa_p(t)}^2 - \mathbb{B}_{\kappa_p(t)} \right) = \frac{3\mu\lambda_1}{2\nu_1 + 3\lambda_1} \left(\frac{\text{Tr } \mathbb{B}_{\kappa_p(t)}}{3} - 1 \right) \mathbb{B}_{\kappa_p(t)}, \quad (4.117)$$

which is the sought evolution equation for $\mathbb{B}_{\kappa_p(t)}$ that contains only $\mathbb{B}_{\kappa_p(t)}$ and \mathbb{L} .

The set of equations (4.1) supplemented with the constitutive equations for the heat flux, see (4.108e), the Cauchy stress tensor, see (4.111), and the evolution equation for the left Cauchy–Green tensor $\mathbb{B}_{\kappa_p(t)}$, see (4.117), forms a closed system of equations for the density ρ , the velocity field \mathbf{v} , the specific internal energy e (or the temperature θ), and the left Cauchy–Green tensor $\mathbb{B}_{\kappa_p(t)}$.

The constitutive relation for the Cauchy stress tensor, see (4.111), can be further manipulated as follows. Introducing the notation

$$\phi =_{\text{def}} -p_{\text{th}}^{\text{NSE}} + \frac{\mu}{2} \left(\text{Tr} \mathbb{B}_{\kappa_p(t)} - 3 - \ln \det \mathbb{B}_{\kappa_p(t)} \right), \quad (4.118a)$$

and

$$\mathbb{S} =_{\text{def}} \mu \left(\mathbb{B}_{\kappa_p(t)} - \mathbb{1} \right), \quad (4.118b)$$

the equations (4.111) and (4.117) take the form

$$\mathbb{T} = \phi \mathbb{1} + 2\nu \mathbb{D} + \lambda (\text{div} \mathbf{v}) \mathbb{1} + \mathbb{S}, \quad (4.119)$$

and

$$\nu_1 \overset{\nabla}{\mathbb{S}} + \mathbb{S}^2 + \mu \mathbb{S} = 2\nu_1 \mu \mathbb{D} + \frac{\lambda_1}{2\nu_1 + 3\lambda_1} (\text{Tr} \mathbb{S}) (\mathbb{S} + \mu \mathbb{1}). \quad (4.120)$$

Note that if $\lambda_1 = 0$, then (4.120) simplifies to

$$\nu_1 \overset{\nabla}{\mathbb{S}} + \mathbb{S}^2 + \mu \mathbb{S} = 2\nu_1 \mu \mathbb{D}, \quad (4.121)$$

hence the derived model could be seen as a compressible variant of the classical model for a viscoelastic incompressible fluid developed by Giesekus [31].

If the material is constrained in such a way that

$$\text{Tr} \mathbb{D} = \text{Tr} \mathbb{D}_{\kappa_p(t)} = 0, \quad (4.122)$$

which means that the material is assumed to be an incompressible material and that the response from the initial to the natural configuration is assumed to be isochoric, it is clear that neither $\text{Tr} \mathbb{B}_{\kappa_p(t)}$ nor m can be specified constitutively. (These quantities correspond to the forces that make the material resistant to the volumetric changes, see Section 4.2 for a discussion.) However, formula (4.108a) still holds, the only difference is that $\mathbb{D} = \mathbb{D}_\delta$, hence

$$\mathbb{T} = m \mathbb{1} + \mathbb{T}_\delta = m \mathbb{1} + 2\nu \mathbb{D} + \mu \left(\mathbb{B}_{\kappa_p(t)} \right)_\delta. \quad (4.123)$$

Similarly, (4.108c) is also valid, hence

$$\mu \left(\mathbb{C}_{\kappa_p(t)} - \frac{1}{3} (\text{Tr} \mathbb{C}_{\kappa_p(t)}) \mathbb{1} \right) = 2\nu_1 \left(\mathbb{D}_{\kappa_p(t)} \right)_\delta, \quad (4.124)$$

where, in virtue of (4.122), $\mathbb{D}_{\kappa_p(t)} = \left(\mathbb{D}_{\kappa_p(t)} \right)_\delta$. Multiplication of (4.124) by $\mathbb{F}_{\kappa_p(t)}^\top$ from the right and $\mathbb{F}_{\kappa_p(t)}$ from the left and the evolution equation for the left Cauchy–Green tensor (4.97) then yield

$$\nu_1 \overset{\nabla}{\mathbb{B}_{\kappa_p(t)}} + \mu \left(\mathbb{B}_{\kappa_p(t)}^2 - \frac{1}{3} (\text{Tr} \mathbb{B}_{\kappa_p(t)}) \mathbb{B}_{\kappa_p(t)} \right) = 0 \quad (4.125)$$

as the evolution equation for $\mathbb{B}_{\kappa_p(t)}$.

4.4.3. Application of the maximisation of the entropy production—constitutive relations for Oldroyd-B and Maxwell viscoelastic fluids. The last example is devoted to discussion of the derivation of incompressible Oldroyd-B and Maxwell models for viscoelastic fluids and their compressible counterparts. Unlike in the previous example the full thermodynamic procedure based on the assumption of the maximisation of the entropy production is now applied.

The starting point is the formula for the entropy production derived in the previous section, see (4.107), that can be rewritten in the form

$$\xi = \frac{1}{\theta} \left[\left(\mathbb{T}_\delta - \mu \left(\mathbb{B}_{\kappa_p(t)} \right)_\delta \right) : \mathbb{D}_\delta + \left(m + p_{\text{th}}^{\text{M}} - \frac{\mu}{3} \text{Tr} \mathbb{B}_{\kappa_p(t)} + \mu \right) \text{div} \mathbf{v} + \mu \left(\mathbb{C}_{\kappa_p(t)} - \mathbb{1} \right) : \mathbb{D}_{\kappa_p(t)} - \mathbf{j}_q \cdot \frac{\nabla \theta}{\theta} \right]. \quad (4.126)$$

Using this formula one can continue with STEP 4 of the full thermodynamic procedure discussed in Section 4.1.

STEP 4: At this point the constitutive function ζ , $\zeta = \theta \xi$, is chosen as

$$\zeta =_{\text{def}} \tilde{\zeta} \left(\mathbb{D}_\delta, \text{div} \mathbf{v}, \mathbb{D}_{\kappa_p(t)}, \nabla \theta \right) = 2\nu |\mathbb{D}_\delta|^2 + \frac{2\nu + 3\lambda}{3} (\text{div} \mathbf{v})^2 + 2\nu_1 \mathbb{D}_{\kappa_p(t)} : \mathbb{C}_{\kappa_p(t)} \mathbb{D}_{\kappa_p(t)} + \kappa \frac{|\nabla \theta|^2}{\theta}, \quad (4.127)$$

where the right Cauchy–Green tensor $\mathbb{C}_{\kappa_p(t)}$ is understood as a state variable and ν , $\frac{2\nu+3\lambda}{3}$, ν_1 and κ are positive constants. Using the definition of the right Cauchy–Green tensor, see (4.90b), and the properties of the trace, it is easy to see that $\mathbb{D}_{\kappa_p(t)} : \mathbb{C}_{\kappa_p(t)} \mathbb{D}_{\kappa_p(t)} = \left| \mathbb{F}_{\kappa_p(t)} \mathbb{D}_{\kappa_p(t)} \right|^2 \geq 0$, hence the chosen constitutive function is nonnegative as required by the second law of thermodynamics. Further it is a strictly convex smooth function.

Introducing the auxiliary function Φ for constrained maximisation problem

$$\max_{\mathbb{D}_\delta, \text{div} \mathbf{v}, \mathbb{D}_{\kappa_p(t)}, \nabla \theta} \tilde{\zeta} \left(\mathbb{D}_\delta, \text{div} \mathbf{v}, \mathbb{D}_{\kappa_p(t)}, \nabla \theta \right) \quad (4.128)$$

subject to the constraint (4.126) as

$$\begin{aligned} \Phi =_{\text{def}} & \tilde{\zeta} \left(\mathbb{D}_\delta, \operatorname{div} \mathbf{v}, \mathbb{D}_{\kappa_{p(t)}}, \nabla \theta \right) \\ & + \ell \left[\tilde{\zeta} \left(\mathbb{D}_\delta, \operatorname{div} \mathbf{v}, \mathbb{D}_{\kappa_{p(t)}}, \nabla \theta \right) - \left(\mathbb{T}_\delta - \mu \left(\mathbb{B}_{\kappa_{p(t)}} \right)_\delta \right) : \mathbb{D}_\delta - \left(m + p_{\text{th}}^{\text{M}} - \frac{\mu}{3} \operatorname{Tr} \mathbb{B}_{\kappa_{p(t)}} + \mu \right) \operatorname{div} \mathbf{v} - \mu \left(\mathbb{C}_{\kappa_{p(t)}} - \mathbb{I} \right) : \mathbb{D}_{\kappa_{p(t)}} + \mathbf{j}_q \cdot \frac{\nabla \theta}{\theta} \right], \end{aligned} \quad (4.129)$$

where ℓ is the Lagrange multiplier, the conditions for the extrema are

$$\frac{1 + \ell}{\ell} \frac{\partial \tilde{\zeta}}{\partial \mathbb{D}_\delta} = \mathbb{T}_\delta - \mu \left(\mathbb{B}_{\kappa_{p(t)}} \right)_\delta, \quad (4.130a)$$

$$\frac{1 + \ell}{\ell} \frac{\partial \tilde{\zeta}}{\partial \operatorname{div} \mathbf{v}} = m + p_{\text{th}}^{\text{M}} - \frac{\mu}{3} \operatorname{Tr} \mathbb{B}_{\kappa_{p(t)}} + \mu, \quad (4.130b)$$

$$\frac{1 + \ell}{\ell} \frac{\partial \tilde{\zeta}}{\partial \mathbb{D}_{\kappa_{p(t)}}} = \mu \left(\mathbb{C}_{\kappa_{p(t)}} - \mathbb{I} \right), \quad (4.130c)$$

$$\frac{1 + \ell}{\ell} \frac{\partial \tilde{\zeta}}{\partial \nabla \theta} = -\frac{\mathbf{j}_q}{\theta}. \quad (4.130d)$$

On the other hand, direct differentiation of (4.127) yields

$$\frac{\partial \tilde{\zeta}}{\partial \mathbb{D}_\delta} = 4\nu \mathbb{D}_\delta, \quad (4.131a)$$

$$\frac{\partial \tilde{\zeta}}{\partial \operatorname{div} \mathbf{v}} = \frac{2}{3} (2\nu + 3\lambda) \operatorname{div} \mathbf{v}, \quad (4.131b)$$

$$\frac{\partial \tilde{\zeta}}{\partial \mathbb{D}_{\kappa_{p(t)}}} = 2\nu_1 \left(\mathbb{C}_{\kappa_{p(t)}} \mathbb{D}_{\kappa_{p(t)}} + \mathbb{D}_{\kappa_{p(t)}} \mathbb{C}_{\kappa_{p(t)}} \right), \quad (4.131c)$$

$$\frac{\partial \tilde{\zeta}}{\partial \nabla \theta} = 2\kappa \frac{\nabla \theta}{\theta}. \quad (4.131d)$$

Now it is necessary to find a formula for the Lagrange multiplier ℓ . This can be done as follows. First, each equation in (4.130) is multiplied by the corresponding affinity that is by \mathbb{D}_δ , $\operatorname{div} \mathbf{v}$, $\mathbb{D}_{\kappa_{p(t)}}$ and $\nabla \theta$ respectively, and then the sum of all equations is taken. This manipulation yields

$$\begin{aligned} \frac{1 + \ell}{\ell} \left[\frac{\partial \tilde{\zeta}}{\partial \mathbb{D}_\delta} : \mathbb{D}_\delta + \frac{\partial \tilde{\zeta}}{\partial \operatorname{div} \mathbf{v}} \operatorname{div} \mathbf{v} + \frac{\partial \tilde{\zeta}}{\partial \mathbb{D}_{\kappa_{p(t)}}} : \mathbb{D}_{\kappa_{p(t)}} + \frac{\partial \tilde{\zeta}}{\partial \nabla \theta} \cdot \nabla \theta \right] \\ = \left(\mathbb{T}_\delta - \mu \left(\mathbb{B}_{\kappa_{p(t)}} \right)_\delta \right) : \mathbb{D}_\delta + \left(m + p_{\text{th}}^{\text{M}} - \frac{\mu}{3} \operatorname{Tr} \mathbb{B}_{\kappa_{p(t)}} + \mu \right) \operatorname{div} \mathbf{v} + \mu \left(\mathbb{C}_{\kappa_{p(t)}} - \mathbb{I} \right) : \mathbb{D}_{\kappa_{p(t)}} - \mathbf{j}_q \cdot \frac{\nabla \theta}{\theta}. \end{aligned} \quad (4.132)$$

The right hand side is identical to $\tilde{\zeta} = \theta \xi$, see (4.126), while the term on the left hand side reduces, in virtue of (4.127) and (4.131), to $2\tilde{\zeta}$. Consequently $\frac{1 + \ell}{\ell} = \frac{\tilde{\zeta}}{2\tilde{\zeta}}$, which fixes the value of the Lagrange multiplier

$$\frac{1 + \ell}{\ell} = \frac{1}{2}. \quad (4.133)$$

Inserting (4.131) and (4.133) into (4.130) one finally concludes that

$$\mathbb{T}_\delta - \mu \left(\mathbb{B}_{\kappa_{p(t)}} \right)_\delta = 2\nu \mathbb{D}_\delta, \quad (4.134a)$$

$$m + p_{\text{th}}^{\text{M}} - \frac{\mu}{3} \operatorname{Tr} \mathbb{B}_{\kappa_{p(t)}} + \mu = \frac{2\nu + 3\lambda}{3} \operatorname{div} \mathbf{v}, \quad (4.134b)$$

$$\mu \left(\mathbb{C}_{\kappa_{p(t)}} - \mathbb{I} \right) = \nu_1 \left(\mathbb{C}_{\kappa_{p(t)}} \mathbb{D}_{\kappa_{p(t)}} + \mathbb{D}_{\kappa_{p(t)}} \mathbb{C}_{\kappa_{p(t)}} \right), \quad (4.134c)$$

$$\mathbf{j}_q = -\kappa \nabla \theta. \quad (4.134d)$$

Further, if (4.134c) holds, then it can be shown that the symmetric positive definite matrix $\mathbb{C}_{\kappa_{p(t)}}$ and the symmetric matrix $\mathbb{D}_{\kappa_{p(t)}}$ commute. (In order to prove that $\mathbb{C}_{\kappa_{p(t)}}$ and $\mathbb{D}_{\kappa_{p(t)}}$ commute it suffices to show that the eigenvectors of $\mathbb{C}_{\kappa_{p(t)}}$ and $\mathbb{D}_{\kappa_{p(t)}}$ coincide, which is in virtue of (4.134c) an easy task. See the Appendix in Rajagopal and Srinivasa [77] for details.) If the matrices commute, then (4.134c) in fact reads

$$\mu \left(\mathbb{C}_{\kappa_{p(t)}} - \mathbb{I} \right) = 2\nu_1 \mathbb{C}_{\kappa_{p(t)}} \mathbb{D}_{\kappa_{p(t)}}. \quad (4.135)$$

STEP 5: The first two equations in (4.134) allow one to identify the constitutive relation for the full Cauchy stress tensor $\mathbb{T} = m\mathbb{I} + \mathbb{T}_\delta$,

$$\mathbb{T} = -p_{\text{th}}^{\text{M}} + 2\nu \mathbb{D} + \mu \left(\mathbb{B}_{\kappa_{p(t)}} - \mathbb{I} \right) + \lambda \left(\operatorname{div} \mathbf{v} \right) \mathbb{I}. \quad (4.136)$$

Further, (4.135) can be rewritten as

$$\mu \left(\mathbb{C}_{\kappa_{p(t)}} - \mathbb{I} \right) = 2\nu_1 \mathbb{F}_{\kappa_{p(t)}}^\top \mathbb{F}_{\kappa_{p(t)}} \mathbb{D}_{\kappa_{p(t)}}. \quad (4.137)$$

which upon multiplication by $\mathbb{F}_{\kappa_p(t)}^\top$ from the right and by $\mathbb{F}_{\kappa_p(t)}^{-\top}$ from the left yields a formula for $\mathbb{F}_{\kappa_p(t)} \mathbb{D}_{\kappa_p(t)} \mathbb{F}_{\kappa_p(t)}^\top$. This formula can be substituted into (4.97) that yields the evolution equation for the left Cauchy–Green tensor,

$$\nu_1 \overline{\mathbb{B}_{\kappa_p(t)}} + \mu (\mathbb{B}_{\kappa_p(t)} - \mathbb{1}) = 0. \quad (4.138)$$

The set of equations (4.1) supplemented with the constitutive equations for the heat flux, see (4.134d), the Cauchy stress tensor, see (4.136), and the evolution equation for the left Cauchy–Green tensor $\mathbb{B}_{\kappa_p(t)}$, see (4.138), forms a closed system of equations for the density ρ , the velocity field \mathbf{v} , the specific internal energy e (or the temperature θ), and the left Cauchy–Green tensor $\mathbb{B}_{\kappa_p(t)}$.

Introducing the extra stress tensor \mathbb{S} by $\mathbb{S} =_{\text{def}} \mu (\mathbb{B}_{\kappa_p(t)} - \mathbb{1})$ equations (4.136) and (4.138) can be rewritten as

$$\mathbb{T} = -p_{\text{th}}^{\text{M}} + 2\nu \mathbb{D} + \mathbb{S} + \lambda (\text{div } \mathbf{v}) \mathbb{1}, \quad (4.139a)$$

$$\frac{\nu_1}{\mu} \overline{\mathbb{S}} + \mathbb{S} = 2\nu_1 \mathbb{D}. \quad (4.139b)$$

Further manipulation based on the redefinition of the extra stress tensor $\tilde{\mathbb{S}} =_{\text{def}} \mathbb{S} + 2\nu \mathbb{D}$ allows one to rewrite system (4.139) as

$$\mathbb{T} = -p_{\text{th}}^{\text{M}} + \tilde{\mathbb{S}} + \lambda (\text{div } \mathbf{v}) \mathbb{1}, \quad (4.140a)$$

$$\frac{\nu_1}{\mu} \tilde{\mathbb{S}} + \tilde{\mathbb{S}} = 2(\nu_1 + \nu) \mathbb{D} + \frac{2\nu_1 \nu}{\mu} \overline{\mathbb{D}}. \quad (4.140b)$$

The expressions (4.140) suggest that the derived model can be seen as a *compressible variant of the classical Oldroyd-B model* for viscoelastic incompressible fluids developed by Oldroyd [65].

On the other hand, if the constitutive relation for the traceless part of the Cauchy stress tensor reads

$$\mathbb{T}_\delta - \mu (\mathbb{B}_{\kappa_p(t)})_\delta = 0, \quad (4.141)$$

which corresponds to $\nu = 0$ in (4.134a), and the constitutive relation for the mean normal stress is

$$m + p_{\text{th}}^{\text{M}} - \frac{\mu}{3} \text{Tr } \mathbb{B}_{\kappa_p(t)} + \mu = 0, \quad (4.142)$$

which corresponds to the choice $\frac{2\nu+3\lambda}{3} = 0$ in (4.134b), then the formula for the full Cauchy stress tensor reads

$$\mathbb{T} = -p_{\text{th}}^{\text{M}} \mathbb{1} + \mu (\mathbb{B}_{\kappa_p(t)} - \mathbb{1}). \quad (4.143)$$

Introducing the extra stress tensor $\mathbb{S} =_{\text{def}} \mu (\mathbb{B}_{\kappa_p(t)} - \mathbb{1})$, it follows that the system (4.139) reduces to

$$\mathbb{T} = -p_{\text{th}}^{\text{M}} \mathbb{1} + \mathbb{S}, \quad (4.144a)$$

$$\frac{\nu_1}{\mu} \overline{\mathbb{S}} + \mathbb{S} = 2\nu_1 \mathbb{D}. \quad (4.144b)$$

This model can be denoted as a *compressible variant of the classical Maxwell model* for viscoelastic incompressible fluids, see for example Tanner and Walters [90].

Finally, if the fluid is assumed to be *incompressible*, then it is subject to constraint

$$\text{Tr } \mathbb{D} = 0. \quad (4.145)$$

However, then the same procedure as above can be still applied. One starts from (4.127)–(4.128) with the only modification that the terms with $\text{div } \mathbf{v}$ disappear, and one ends up with the same system of equations as those given in (4.134). (With the only exception that the second equation in (4.134b) is missing.) The derived constitutive relations read

$$\mathbb{T}_\delta = 2\nu \mathbb{D}_\delta + \mu (\mathbb{B}_{\kappa_p(t)})_\delta, \quad (4.146a)$$

$$\mu (\mathbb{C}_{\kappa_p(t)} - \mathbb{1}) = 2\nu_1 \mathbb{C}_{\kappa_p(t)} \mathbb{D}_{\kappa_p(t)}, \quad (4.146b)$$

$$\mathbf{j}_q = -\kappa \nabla \theta, \quad (4.146c)$$

which translates to

$$\mathbb{T} = m \mathbb{1} + 2\nu \mathbb{D}_\delta + \mu (\mathbb{B}_{\kappa_p(t)})_\delta \quad (4.147)$$

where the mean normal stress m is a quantity that can not be specified via a constitutive relation. (See Section 4.2 for discussion.) Concerning the alternative approach based on the enforcement of the incompressibility constraint by an addition of an extra Lagrange multiplier to the maximisation procedure the interested reader is referred to Málek et al [58].

Introducing the notation

$$\phi =_{\text{def}} m - \frac{\mu}{3} \text{Tr } \mathbb{B}_{\kappa_p(t)} + \mu, \quad (4.148)$$

it follows that (4.147) can be rewritten as

$$\mathbb{T} = \phi \mathbb{1} + 2\nu \mathbb{D} + \mu (\mathbb{B}_{\kappa_p(t)} - \mathbb{1}). \quad (4.149a)$$

(Recall that in virtue of (4.145) one has $\mathbb{D} = \mathbb{D}_\delta$.) Further, the evolution equation for the left Cauchy–Green tensor $\mathbb{B}_{\kappa_p(t)}$ reads

$$\nu_1 \overline{\mathbb{B}_{\kappa_p(t)}} + \mu (\mathbb{B}_{\kappa_p(t)} - \mathbb{1}) = 0. \quad (4.149b)$$

Defining the extra stress tensor as $\mathbb{S} =_{\text{def}} \mu (\mathbb{B}_{\kappa_p(t)} - \mathbb{1})$ or as $\tilde{\mathbb{S}} =_{\text{def}} 2\nu\mathbb{D} + \mathbb{S}$ it follows that (4.149) can be converted into the equivalent form

$$\mathbb{T} = \phi\mathbb{1} + 2\nu\mathbb{D} + \mathbb{S}, \quad (4.150a)$$

$$\frac{\nu_1}{\mu} \overset{\nabla}{\mathbb{S}} + \mathbb{S} = 2\nu_1\mathbb{D}, \quad (4.150b)$$

or into the following equivalent form

$$\mathbb{T} = \phi\mathbb{1} + \tilde{\mathbb{S}}, \quad (4.151a)$$

$$\frac{\nu_1}{\mu} \overset{\nabla}{\tilde{\mathbb{S}}} + \tilde{\mathbb{S}} = 2(\nu_1 + \nu)\mathbb{D} + \frac{2\nu_1\nu}{\mu} \overset{\nabla}{\mathbb{D}}, \quad (4.151b)$$

which are the frequently used forms of constitutive relations for the *Oldroyd-B fluid*, which is a popular model for viscoelastic fluids derived by Oldroyd [65]. (Oldroyd [65] has used formulae (4.151).) Further, if one formally sets $\nu = 0$, then one gets the standard incompressible *Maxwell fluid*.

Note however that the classical derivation by Oldroyd [65] is based only on mechanical considerations, and that the compatibility of the model with the second law of thermodynamics is not discussed at all. Second, the present approach naturally gives one an evolution equation for the internal energy that automatically takes into account the storage mechanisms related to the “elastic” part of the deformation. If the internal energy is expressed as a function of the temperature and other variables, then the evolution equation for the internal energy leads, upon the application of the chain rule, *directly to the evolution equation for the temperature*. (See Section 4.2.1 for the same in the context of a compressible Navier–Stokes–Fourier fluid.) Moreover, the inclusion of the storage mechanisms in the internal energy is compatible with the specification of the constitutive relation for the Cauchy stress tensor. Again, such issues have not been discussed in the seminal contribution by Oldroyd [65], or for that matter by many following works on viscoelasticity.

Obviously, more complex viscoelastic models can be designed by appealing to the analogy with more involved spring-dashpot systems, see for example Karra and Rajagopal [49, 50], Hron et al [42], Průša and Rajagopal [72] or Málek et al [59].

4.5. Beyond linear constitutive theory. In the previous parts the development of the constitutive equations has been based either on linear relationships between the affinities and fluxes or on postulating *quadratic* constitutive equations for the entropy production. In general, this limitation to linear constitutive relations or to a quadratic *ansatz* for the entropy production is not necessary. In fact a plethora of nonlinear models can be developed in a straightforward manner following the method based on the maximisation of entropy production. Their relevance with respect to real material behaviour should be however carefully justified.

A list of some popular simple nonlinear models for incompressible fluids is given below. Clearly, the list is not complete, and other models can be found in the literature as well. *In particular, the list does not include nonlinear viscoelastic models at all.*

The first class of nonlinear models is the class of models where the Cauchy stress tensor is decomposed as

$$\mathbb{T} = m\mathbb{1} + \mathbb{S}, \quad (4.152)$$

where m is the mean normal stress, and the relation between the traceless extra stress tensor \mathbb{S} and the symmetric part of the velocity gradient \mathbb{D} takes the form of an algebraic relation

$$\mathbf{f}(\mathbb{S}, \mathbb{D}) = \mathbb{0}, \quad (4.153)$$

where \mathbf{f} is a tensorial function. This implicit relation is a generalisation of the standard constitutive relation for the incompressible Navier–Stokes fluid, see Section 4.2.3, where

$$\mathbb{S} - 2\nu_*\mathbb{D} = \mathbb{0}. \quad (4.154)$$

Note that the standard way of writing algebraic constitutive relations for a non-Newtonian fluid is $\mathbb{S} = \mathbf{f}(\mathbb{D})$. However, it has been argued by Rajagopal [73, 74] that the standard setting is too restrictive, and that (4.153) should be preferred to $\mathbb{S} = \mathbf{f}(\mathbb{D})$. (See for example Málek et al [57], Průša and Rajagopal [71], Le Roux and Rajagopal [53], Perláková and Průša [69] and Janečka and Průša [45] for further developments of the idea. Mathematical issues concerning some of the models that belong to the class (4.153) have been discussed for example by Bulíček et al [12] and Bulíček et al [13].)

The implicit relation (4.153) opens the possibility of describing—in terms of the same quantities that appear in (4.154)—various non-Newtonian phenomena such as stress thickening or stress thinning, shear thickening or shear thinning, yield stress, and even normal stress differences. None of these important phenomena can be captured by the standard Navier–Stokes model (4.154). (The reader is referred to Málek and Rajagopal [54] or any textbook on non-Newtonian fluid mechanics for the discussion of these phenomena and their importance.) The mechanics of complex fluids is indeed an unfailing source of qualitative phenomena that go beyond the reach of the Navier–Stokes model. For interesting recent observations concerning the behaviour of complex fluids see for example the references in the reviews by Olmsted [66] and Divoux et al [23].

Particular models that fall into class (4.153) are the models in the form

$$\mathbb{S} = 2\nu(\mathbb{D})\mathbb{D}, \quad (4.155)$$

where the generalised viscosity $\nu(\mathbb{D})$ is given by one of the formulae listed below. Model

$$\nu(\mathbb{D}) = \nu_0 |\mathbb{D}|^{n-1}, \quad (4.156)$$

where ν_0 is a positive constant and n is a real constant, is called Ostwald–de Waele power law model, see Ostwald [67] and de Waele [94]. Models

$$\nu(\mathbb{D}) = \nu_\infty + \frac{\nu_0 - \nu_\infty}{(1 + \alpha |\mathbb{D}|^2)^{\frac{n}{2}}}, \quad (4.157)$$

$$\nu(\mathbb{D}) = \nu_\infty + (\nu_0 - \nu_\infty) (1 + \alpha |\mathbb{D}|^a)^{\frac{n-1}{a}}, \quad (4.158)$$

are called Carreau model, see Carreau [16], and Carreau–Yasuda model, see Yasuda [96], respectively. Here ν_0 and ν_∞ are positive real constants and n and a are real constants. Other models with nonconstant viscosity are the Eyring models, see Eyring [26] and Ree et al [82], where the generalised viscosity takes the form

$$\nu(\mathbb{D}) = \nu_\infty + (\nu_0 - \nu_\infty) \frac{\operatorname{arcsinh}(\alpha |\mathbb{D}|)}{\alpha |\mathbb{D}|}, \quad (4.159)$$

$$\nu(\mathbb{D}) = \nu_0 + \nu_1 \frac{\operatorname{arcsinh}(\alpha_1 |\mathbb{D}|)}{\alpha_1 |\mathbb{D}|} + \nu_2 \frac{\operatorname{arcsinh}(\alpha_2 |\mathbb{D}|)}{\alpha_2 |\mathbb{D}|}, \quad (4.160)$$

and $\nu_0, \nu_1, \nu_2, \nu_\infty, \alpha_1$ and α_2 are positive real constants. Finally, the model named after Cross [21], takes the viscosity in the form

$$\nu(\mathbb{D}) = \nu_\infty + \frac{\nu_0 - \nu_\infty}{1 + \alpha |\mathbb{D}|^n} \quad (4.161)$$

and the model named after Sisko [88] reads

$$\nu(\mathbb{D}) = \nu_\infty + \alpha |\mathbb{D}|^{n-1}, \quad (4.162)$$

where ν_0, ν_∞ and α are positive real constants and n is a real constant.

Another subset of general models of the type (4.153) are models where the generalised viscosity depends on the traceless part of the Cauchy stress tensor $\mathbb{T}_\delta = \mathbb{S}$, that is models where

$$\mathbb{S} = \nu(\mathbb{S})\mathbb{D}. \quad (4.163)$$

Examples are the Ellis model, see for example Matsuhisa and Bird [61],

$$\nu(\mathbb{S}) = \frac{\nu_0}{1 + \alpha |\mathbb{S}|^{n-1}}, \quad (4.164)$$

where ν_0 and α are positive real constants and n is a real constant, or the model proposed by Glen [33],

$$\nu(\mathbb{S}) = \alpha |\mathbb{S}|^{n-1}, \quad (4.165)$$

where α is a positive real constant and n is a real constant, the model by Seely [85]

$$\nu(\mathbb{S}) = \nu_\infty + (\nu_0 - \nu_\infty) e^{-\frac{|\mathbb{S}|}{\tau_0}}, \quad (4.166)$$

or the models used for the description of the flow of the ice,

$$\nu(\mathbb{S}) = \frac{A}{(|\mathbb{S}|^2 + \tau_0^2)^{\frac{n-1}{2}}}, \quad (4.167)$$

see for example Pettit and Waddington [70] and Blatter [5]. Here $\nu_0, \nu_\infty, \tau_0$ and A are positive real constants and n is a real constant. Particular parameter values for models (4.156)–(4.162) and (4.164)–(4.167) can be found in the referred works and/or in the follow-up works.

Other popular models are the models with activation criterion introduced by Bingham [3] and Herschel and Bulkley [39]. These models are usually, see for example Duvaut and Lions [25], written down in the form of a dichotomy relation

$$|\mathbb{S}| \leq \tau_* \Leftrightarrow \mathbb{D} = \mathbb{0} \quad \text{and} \quad |\mathbb{S}| > \tau_* \Leftrightarrow \mathbb{S} = \frac{\tau_* \mathbb{D}}{|\mathbb{D}|} + 2\nu(|\mathbb{D}|)\mathbb{D}, \quad (4.168)$$

where ν is a positive function and τ_* is a positive constant. (Constant τ_* is called the yield stress.) It is worth emphasising that these models can be rewritten as

$$\mathbb{D} = \frac{1}{2\nu(|\mathbb{D}|)} \frac{(|\mathbb{S}| - \tau_*)^+}{|\mathbb{S}|} \mathbb{S}, \quad (4.169)$$

where $x^+ = \max\{x, 0\}$, which shows that the yield stress models also fall into the class (4.153). This observation can be exploited in the discussion of the physical and mathematical properties of the models, see Rajagopal and Srinivasa [79] and Bulíček et al [13].

Note that if (4.168) holds, then \mathbb{S} can not be considered as a function of \mathbb{D} , while (4.169) gives a functional (continuous) dependence of \mathbb{D} on \mathbb{S} . Since the function at the right-hand side of (4.169) is tacitly supposed to be zero for $\mathbb{S} = \mathbb{0}$, the alternative viewpoint given by (4.153) with a continuous tensorial function \mathbf{f} defined on the Cartesian product of \mathbb{S} and \mathbb{D} allows one to avoid description of the material via a multi-valued or discontinuous function. See Bulíček et al [13], Bulíček et al [10] for exploiting this possibility as well as the symmetric roles of \mathbb{S} and \mathbb{D} in (4.153) in the analysis of the corresponding initial and boundary value problems. Another advantage of the formulation (4.169) is that it allows one to replace, in a straightforward way, the constant yield stress τ_* by a yield function that can depend on the invariants of both \mathbb{S} and \mathbb{D} , $\tau_* = \tau_*(\mathbb{S}, \mathbb{D})$.

Finally, the class of implicit relations (4.153) can be viewed as a subclass of models where the *full* Cauchy stress tensor \mathbb{T} and the symmetric part of the velocity gradient \mathbb{D} are related implicitly,

$$f(\mathbb{T}, \mathbb{D}) = 0. \quad (4.170)$$

This apparently subtle difference has significant consequences. Constitutive relations in the form (4.170) provide, contrary to (4.153), a solid theoretical background to incompressible fluid models where the viscosity depends on the pressure (mean normal stress), see Rajagopal [74] and Málek and Rajagopal [56] for an in-depth discussion. Such models have been proposed a long time ago by Barus [2], and the practical relevance of such models has been demonstrated by Bridgman [6] and Bridgman [7]. In the simplest settings the model for a fluid with pressure dependent viscosity can take the form

$$\mathbb{T} = -p\mathbb{1} + 2\nu_{\text{ref}}e^{\beta(p-p_{\text{ref}})}\mathbb{D}, \quad (4.171)$$

where p_{ref} —the reference pressure—and ν_{ref} —the reference viscosity—are positive constants. If necessary, this model can be combined with power law type models. This is a popular choice in lubrication theory, see for example Málek and Rajagopal [56].

4.6. Boundary conditions for internal flows of incompressible fluids. As it has been already noted, the specification of the boundary conditions is a nontrivial task. Since the boundary conditions can be seen as a special case of constitutive relations at the interface between two materials, thermodynamical considerations could be of use even in the discussion of the boundary conditions. A simple example concerning the role of thermodynamics in the specification of the boundary conditions for incompressible viscous heat non-conducting fluids is given below.

The problem of internal flow in a fixed vessel represented by the domain Ω has been discussed in Section 3.2 and it is revisited here in a slightly different setting. In Section 3.2 the boundary condition on the vessel wall has been the no-slip boundary condition

$$\mathbf{v}|_{\partial\Omega} = \mathbf{0}. \quad (4.172)$$

In the present case one enforces only the no-penetration boundary condition

$$\mathbf{v} \cdot \mathbf{n}|_{\partial\Omega} = 0, \quad (4.173)$$

where \mathbf{n} denotes the unit outward normal to Ω , and the question concerning the value of the velocity vector in the *tangential* direction to the vessel wall is for the moment left open.

Introducing the notation

$$\mathbf{u}_\tau =_{\text{def}} \mathbf{u} - (\mathbf{u} \cdot \mathbf{n})\mathbf{n} \quad (4.174)$$

for the projection of any vector \mathbf{u} to the tangent plane to the boundary, it follows that the product $(\mathbb{T}\mathbf{v}) \cdot \mathbf{n}$ can be rewritten as

$$(\mathbb{T}\mathbf{v}) \cdot \mathbf{n} = m\mathbf{v} \cdot \mathbf{n} + \mathbb{S} : (\mathbf{v} \otimes \mathbf{n}) = \mathbb{S} : (\mathbf{n} \otimes \mathbf{v}) = (\mathbb{S}\mathbf{n}) \cdot \mathbf{v} = (\mathbb{S}\mathbf{n})_\tau \cdot \mathbf{v}_\tau. \quad (4.175)$$

This observation is a consequence of the symmetry of the Cauchy stress tensor and the decomposition of the Cauchy stress tensor to the mean normal stress and the traceless part, see (4.152).

The multiplication of the balance of momentum (3.14a) by \mathbf{v} followed by integration over the domain Ω yields

$$\int_{\Omega} \frac{d}{dt} \left(\rho \frac{1}{2} \mathbf{v} \cdot \mathbf{v} \right) dv = \int_{\Omega} (\text{div } \mathbb{T}) \cdot \mathbf{v} dv. \quad (4.176)$$

The right hand side can be, following Section 3.2, manipulated as

$$\int_{\Omega} (\text{div } \mathbb{T}) \cdot \mathbf{v} dv = \int_{\Omega} (\text{div } \mathbb{T}\mathbf{v}) dv - \int_{\Omega} \mathbb{T} : \mathbb{D} dv = - \int_{\Omega} \mathbb{T} : \mathbb{D} dv + \int_{\partial\Omega} \mathbb{T}\mathbf{v} \cdot \mathbf{n} ds. \quad (4.177)$$

Consequently, the evolution equation for the net kinetic energy E_{kin} reads

$$\frac{dE_{\text{kin}}}{dt} = - \int_{\Omega} \mathbb{T} : \mathbb{D} dv + \int_{\partial\Omega} \mathbb{T}\mathbf{v} \cdot \mathbf{n} ds, \quad (4.178)$$

which can be in virtue of (4.175) and the incompressibility condition $\text{div } \mathbf{v} = 0$ further rewritten as

$$\frac{dE_{\text{kin}}}{dt} = - \int_{\Omega} \mathbb{S} : \mathbb{D} dv - \int_{\partial\Omega} \mathbf{s} \cdot \mathbf{v}_\tau ds, \quad (4.179)$$

where the notation

$$\mathbf{s} =_{\text{def}} -(\mathbb{S}\mathbf{n})_\tau \quad (4.180)$$

has been used.

Unlike in Section 3.2 one now gets a *boundary term contributing to the evolution equation for the net kinetic energy*. The boundary term is the key to the thermodynamically based discussion of the appropriate boundary conditions. The desired decay of the net kinetic energy is in the considered case guaranteed if one enforces pointwise positivity of the product $\mathbb{T} : \mathbb{D}$ in Ω , and the pointwise positivity of the product $\mathbf{s} \cdot \mathbf{v}_\tau$ at $\partial\Omega$. This restriction can be used to narrow down the class of possible relations between the value of the velocity in the tangential direction \mathbf{v}_τ and the projection of the stress tensor $(\mathbb{S}\mathbf{n})_\tau$, where the relation between \mathbf{v}_τ and $(\mathbb{S}\mathbf{n})_\tau$ is the sought boundary condition.

Note that in the full thermodynamic setting both the volumetric term $\int_{\Omega} \mathbb{T} : \mathbb{D} dv$ and the boundary term $\int_{\partial\Omega} \mathbf{s} \cdot \mathbf{v}_\tau ds$ would appear in the entropy production *for the whole system*. Both the boundary term and the volumetric term have the flux/affinity structure. In linear non-equilibrium thermodynamics the fluxes and affinities in the volumetric term are

connected *linearly* via a positive (non-negative) coefficient of proportionality in order to guarantee the validity of the second law of thermodynamics. Application of the same approach to the boundary term leads to a linear relation between \mathbf{s} and \mathbf{v}_τ

$$\mathbf{s} = \gamma_* \mathbf{v}_\tau, \quad (4.181)$$

where γ_* is a positive constant. This is the *Navier slip boundary condition*, see Navier [63]. Moreover, one can identify two cases where the boundary term vanishes. If $\mathbf{s} = \mathbf{0}$, then one gets the *perfect slip boundary condition*, and if $\mathbf{v}_\tau = \mathbf{0}$ then one gets the standard *no-slip boundary condition*.

Further, a general relation between \mathbf{s} and \mathbf{v}_τ can take, following (4.153), the form of an implicit constitutive relation

$$\mathbf{f}(\mathbf{s}, \mathbf{v}_\tau) = \mathbf{0}, \quad (4.182)$$

which considerably expands the number of possible boundary conditions. In particular, the *threshold-slip* (or stick-slip) boundary condition that is usually described by the dichotomy relation

$$|\mathbf{s}| \leq \sigma_* \Leftrightarrow \mathbf{v}_\tau = \mathbf{0} \quad \text{and} \quad |\mathbf{s}| > \sigma_* \Leftrightarrow \mathbf{s} = \frac{\sigma_* \mathbf{v}_\tau}{|\mathbf{v}_\tau|} + \gamma_* \mathbf{v}_\tau, \quad (4.183)$$

where σ_* and γ_* are positive constants, can be seen as a special case of (4.182). Indeed, (4.183) can be rewritten as

$$\mathbf{v}_\tau = \frac{1}{\gamma_*} \frac{(|\mathbf{s}| - \sigma_*)^+}{|\mathbf{s}|} \mathbf{s}. \quad (4.184)$$

(Note the similarity between the threshold slip boundary condition (4.183) and the Bingham/Herschel–Bulkley model for fluids with the yield stress behaviour (4.169). The formulation of the *threshold-slip* boundary condition in the form (4.184) can be again exploited in the mathematical analysis of the corresponding governing equations, see Bulíček and Málek [11].)

An example of more involved thermodynamical treatment of boundary conditions can be found in the study by Heida [37]. Concerning a recent review of the non-standard boundary conditions used by practitioners in polymer science the reader is referred for example to Hatzikiriakos [36].

5. CONCLUSION

Although the classical (in)compressible Navier–Stokes–Fourier fluid models have been successfully used in the mathematical modelling of the behaviour of various substances, they are worthless from the perspective of modern applications such as polymer processing. Navier–Stokes–Fourier models are simply incapable of capturing many phenomena observed in complex fluids, see for example the list of non-Newtonian phenomena in Málek and Rajagopal [54], the historical essay by Tanner and Walters [90] or the classical experimentally oriented treatises by Coleman et al [20], Barnes et al [1] or Malkin and Isayev [60] to name a few.

The need to develop mathematical models for the behaviour of complex materials lead to the birth of the theory of constitutive relations. In the early days of the theory, constitutive relations have been designed by appealing to purely mechanical principles. This turns out to be insufficient as the complexity of the models increases.

Nowadays, the mathematical models aim at the description of an interplay between various mechanisms such as heat conduction, mechanical stress, chemical reactions, electromagnetic field or the interaction of several continuous media in mixtures, see for example Humphrey and Rajagopal [44], Rajagopal [75], Dorfmann and Ogden [24] and Pekař and Samohýl [68]. In such cases the correct specification of the energy transfers is clearly crucial. Consequently, one can hardly hope that an *ad hoc* specification of the complex nonlinear constitutive relations for the quantities that facilitate the energy transfers is the way to go. A theory of constitutive relations that focuses on energy transfers, and that guarantees the compatibility of the arising constitutive relations with the second law of thermodynamics is needed.

The modern theory of constitutive relations outlined above can handle the challenge. The theory from the very beginning heavily relies on the concepts from non-equilibrium thermodynamics, and the restrictions arising from the laws of thermodynamics are automatically built into the derived constitutive relations. Naturally, the models designed to describe the behaviour of complex materials in far-from-equilibrium processes are rather complicated. In particular, the arising systems of partial differential equations are large and nonlinear.

Fortunately, the available numerical methods for solving nonlinear partial differential equations as well as the available computational power are now at the level that makes the numerical solution of such systems feasible. This is a substantial difference from the early days of the mechanics and thermodynamics of continuous media, see for example Truesdell and Noll [91]. Since the quantitative predictions based on complex models are nowadays within the reach of the scientific and engineering community, they can actually serve as a basis for answering important questions in the applied sciences and technology. This is a favourable situation for a mathematical modeller equipped with a convenient theory of constitutive relations. *The design of suitable mathematical models for complex materials undergoing far-from-equilibrium processes does matter—from the practical point of view—more than ever.*

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