A sketch of continuum thermodynamics

W. Muschik [a,*], C. Papenfuss [b], H. Ehrentraut [c]

[a] *Institut für Theoretische Physik, Technische Universität Berlin, D-10623 Berlin, Germany*
[b] *Institut für Mechanik, Technische Universität Berlin, D-10623 Berlin, Germany*
[c] *Institut für Mechanik, Technische Universität Darmstadt, D-64289 Darmstadt, Germany*

Abstract

Different formulations of non-equilibrium continuum thermodynamics are discussed: Thermodynamics of Irreversible Processes (TIP), Rational Thermodynamics (RAT), Extended Thermodynamics (ET), Mesoscopic Continuum Thermodynamics (MT), and the GENERIC version of thermodynamics. Concepts as constitutive quantity, state space, material frame indifference, exploiting dissipation inequality, mesoscopic variables, and GENERIC balance equations are taken into consideration. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Continuum thermodynamics, or with respect to a more general view, the non-linear field theory of classical physics, is a discipline having different and wide fields of application. So not only in physics and physical chemistry, but also in mechanical and chemical engineering, material science, energy conversion techniques, air conditioning, refrigeration, heat and stream engine engineering thermodynamical methods are applied successfully in different formulations; continuum thermodynamics and thermodynamics of discrete systems. In the last 20 years, progress was made to elucidate the fundamentals of continuum thermodynamics more rigorously than before. By this analysis, continuum thermodynamics became easier to grasp and hence easier to teach.

Thermodynamics is concerned with the general structure of so-called *Schottky systems* [1] which are defined by a domain moving in space and exchanging heat, work and material with its environment. It is useful to distinguish between considering only one Schottky system in an equilibrium environment, a so-called *discrete system*, and between dealing with a set of sufficiently small Schottky systems, each

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* Corresponding author.
E-mail address: muschik@physik.tu-berlin.de (W. Muschik).

denoted by position and time, exchanging heat, work and material with its adjacent Schottky systems. In doing so, we get a so-called *field formulation of thermodynamics*. Here, we will give a sketch of this continuum thermodynamics, a phenomenological deterministic theory which does not include probabilistic elements in general [2].

The aim of continuum thermodynamics is the determination of the *wanted fields*. In classical theories for simple materials, these are the five fields of mass density, internal energy density and velocity. Complex materials need more than these five fields for their description. If the material consists of non-spherical particles, the spin density (density of internal angular momentum) is an additional wanted field. If the orientation of the particles is of interest, the director or alignment tensor fields have to be introduced as additional wanted fields.

Not only the complexity of the material enforces the introduction of additional fields, but also the classical five-field theory can be extended by introducing additional fields: In so-called 'Extended Thermodynamics', heat flux and stress tensor are considered as additional wanted fields (see Section 3.6).

2. Balance equations

The equations of motion for the wanted fields are the balance equations which are valid for arbitrary materials. That is the reason, why they are not a closed system of differential equations. For making them a closed system, we need *constitutive equations*. Inserting them into the balance equations, we obtain differential equations whose order depend on the special chosen constitutive equations. Consequently, we have to distinguish between the general balance equations being valid for arbitrary materials and those balances after having inserted special constitutive equations which are called *balances on the state space*. This is because the domain of the constitutive equations is called a *state space*.

2.1. Global balances

In this chapter, we start out with global balance equations. They represent the mathematical formulation of the fact, that the amount of an extensive quantity in a volume can change by production, by supply, or by a flux through the boundary of the system (in contrast to production, supply can be suppressed by an appropriate partition). From these global balance equations, local equations can be derived by use of *Reynolds transport theorem*. These local balances are the differential equations governing the evolution of the wanted fields. Here, we will discuss only systems consisting of one single chemical component without chemical reactions. The balances of multi-component systems can be found in [2].

A Schottky system $G(t)$ interacts with its environment by heat exchange, power exchange, and material exchange through its surface ∂G. The global balance equation of $G(t)$ for an arbitrary extensive quantity with specific density ψ, flux $\boldsymbol{J}^{\psi}$, production density π^{ψ}, supply density σ^{ψ}, and surface φ^{ψ} density reads

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{G(t)} \varrho(\boldsymbol{x},t)\psi(\boldsymbol{x},t)\,\mathrm{d}V = -\oint_{\partial G(t)} \boldsymbol{J}^{\psi}(\boldsymbol{x},t)\cdot\mathrm{d}\boldsymbol{a} + \int_{G(t)} (\sigma^{\psi} + \pi^{\psi})(\boldsymbol{x},t)\,\mathrm{d}V + \int_{F(t)} \varphi^{\psi}(\boldsymbol{x},t)\,\mathrm{d}a.$$

(1)

Here, $\varrho(\boldsymbol{x},t)$ is the field of the mass density, $\mathrm{d}\boldsymbol{a} = \boldsymbol{f}\,\mathrm{d}a$, and $\boldsymbol{f}$ is the outward unit normal vector of the surface ∂G of G. Here, $\pi^{\psi}(\boldsymbol{x},t)$ and $\sigma^{\psi}(\boldsymbol{x},t)$ are bulk densities, $\varphi^{\psi}(\boldsymbol{x},t)$ is a surface density on the

interface $F(t)$ which is located in $G(t)$. We call an interface *inert*, if the surface density on it vanishes identically. All fields in $G(t)$ and on $F(t)$ are bounded.

As an example, we consider the *balance of mass* in case of an inert interface $F(t)$. Here, we have

$$\psi \equiv 1 \text{ and } \sigma^1 \equiv 0, \qquad \pi^1 \equiv 0, \qquad \varphi^1 \equiv 0, \tag{2}$$

which expresses the conservation of mass

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{G(t)} \varrho(\boldsymbol{x}, t) \, \mathrm{d}V =: \frac{\mathrm{d}}{\mathrm{d}t} M^G(t) = -\oint_{\partial G(t)} \boldsymbol{J}^1(\boldsymbol{x}, t) \cdot \mathrm{d}\boldsymbol{a}. \tag{3}$$

There are different possible choices for G:

1. G is called a *body*, if $G(t)$ consists always of the same particles. Therefore, the total mass M^G within G is conserved, and $G(t)$ moves with the matter. For a body, we have $M^G = \text{const}$ and

$$\frac{\mathrm{d}}{\mathrm{d}t} M^G(t) = 0 = -\oint_{\partial G(t)} \boldsymbol{J}^1(\boldsymbol{x}, t) \cdot \mathrm{d}\boldsymbol{a}. \tag{4}$$

2. G can be an arbitrary region moving with the so-called *mapping velocity* $\boldsymbol{w}(\boldsymbol{x}, t)$ which is independent of the velocity of the particles. Then, we call $G(t)$ a *controlling area*, and we have

$$0 \neq \frac{\mathrm{d}}{\mathrm{d}t} M^G(t) = -\oint_{\partial G(t)} \boldsymbol{J}^1(\boldsymbol{x}, t) \cdot \mathrm{d}\boldsymbol{a}. \tag{5}$$

The mass flux through the boundary $\partial G(t)$ is given by the convective mass flux

$$\boldsymbol{J}^1 = \varrho(\boldsymbol{v} - \boldsymbol{w}). \tag{6}$$

Here, $\boldsymbol{v}(\boldsymbol{x}, t)$ is the *material velocity* of the particles in $G(t)$. If $\boldsymbol{w} \equiv \boldsymbol{v}$, the region $G(t)$ is a body, and the mass flux through ∂G is 0.

The time derivative of global quantities can be performed by use of the following:

Proposition. *Reynolds transport theorem* [3]:

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{G(t)} \Phi(\boldsymbol{x}, t) \, \mathrm{d}V = \int_{G(t)} \left(\frac{\partial}{\partial t} \Phi(\boldsymbol{x}, t) + \nabla \cdot [\boldsymbol{w}(\boldsymbol{x}, t) \Phi(\boldsymbol{x}, t)] \right) \mathrm{d}V$$
$$- \int_{F(t)} |[\Phi(\boldsymbol{x}, t) \{\boldsymbol{u}(\boldsymbol{x}, t) - \boldsymbol{w}(\boldsymbol{x}, t)\}]| \cdot \mathrm{d}\boldsymbol{a}. \tag{7}$$

Here, $\Phi(\boldsymbol{x}, t)$ is a density, $\boldsymbol{w}(\boldsymbol{x}, t)$, the already introduced field of the mapping velocity belonging to $G(t)$, and $\boldsymbol{u}(\boldsymbol{x}, t)$, the velocity of an interface $F(t)$ in $G(t)$ at which discontinuities, production or supply may appear. Outside of $F(t)$, all fields are differentiable. The bracket symbol in (7) is defined as follows:

$$|[\diamond]| = \diamond^2 - \diamond^1. \tag{8}$$

Here, ^{1} and ^{2} mark the values of the quantity in the bracket on both sides of $F(t)$. The surface element $\mathrm{d}\boldsymbol{a}$ of $F(t)$ is directed from the side marked by ^{1} to that marked by ^{2}.

If we now identify $\Phi(\boldsymbol{x}, t) \equiv \varrho(\boldsymbol{x}, t) \psi(\boldsymbol{x}, t)$ in (7), then (1) results in

$$\int_{G(t)} \left(\frac{\partial}{\partial t}[\varrho(\boldsymbol{x}, t)\psi(\boldsymbol{x}, t)] + \nabla \cdot [\boldsymbol{w}(\boldsymbol{x}, t)\varrho(\boldsymbol{x}, t)\psi(\boldsymbol{x}, t)] \right) \mathrm{d}V$$

$$= -\oint_{\partial G(t)} \boldsymbol{J}^{\psi}(\boldsymbol{x}, t) \cdot \mathrm{d}\boldsymbol{a} + \int_{G(t)} (\sigma^{\psi} + \pi^{\psi})(\boldsymbol{x}, t) \, \mathrm{d}V$$

$$+ \int_{F(t)} \{\varphi^{\psi}(\boldsymbol{x}, t) + |[\varrho(\boldsymbol{x}, t)\psi(\boldsymbol{x}, t)\{\boldsymbol{u}(\boldsymbol{x}, t) - \boldsymbol{w}(\boldsymbol{x}, t)\}]| \cdot \boldsymbol{f}\} \mathrm{d}a. \tag{9}$$

Since in this equation, all differentiations are under the integrals by help of Reynolds transport theorem, we can now derive local balance equations.

2.2. Local balances

We start out with the following [4,5]:

Proposition. *If* (9) *is valid for an arbitrary region G(t) and an arbitrary interface F(t), then the following local balances are valid*

$$\frac{\partial}{\partial t}[\varrho\psi] + \nabla \cdot [\boldsymbol{w}\varrho\psi + \boldsymbol{J}^{\psi}] - \sigma^{\psi} - \pi^{\psi} = 0, \tag{10}$$

$$\varphi^{\psi} + |[\varrho\psi(\boldsymbol{u} - \boldsymbol{w}) - \boldsymbol{J}^{\psi}]| \cdot \boldsymbol{f} = 0. \tag{11}$$

These are the balances and the jump conditions at interfaces of a one component system which we will now discuss in more detail. The flux $\boldsymbol{J}^{\psi}$ can be split into a non-convective part $\boldsymbol{J}^{\psi, \mathrm{nonc}}$ and the convective part $\varrho(\boldsymbol{v} - \boldsymbol{w})\psi$

$$\boldsymbol{J}^{\psi} = \boldsymbol{J}^{\psi, \mathrm{nonc}} + \varrho(\boldsymbol{v} - \boldsymbol{w})\psi = \boldsymbol{J}^{\psi, \mathrm{nonc}} + \boldsymbol{J}^{1}\psi. \tag{12}$$

The convective part vanishes according to (6), if $G(t)$ is a body ($\boldsymbol{v} \equiv \boldsymbol{w}$).

2.2.1. Mass
According to (2) and (6), we obtain for (10) and (11), the local balance of mass and its jump condition

$$\frac{\partial}{\partial t}\varrho + \nabla \cdot (\boldsymbol{v}\varrho) = 0, \tag{13a}$$

$$|[\varrho(\boldsymbol{u} - \boldsymbol{v})]| \cdot \boldsymbol{f} = 0. \tag{13b}$$

2.2.2. Momentum
Because the momentum density is defined by $\varrho(\boldsymbol{x}, t)\boldsymbol{v}(\boldsymbol{x}, t)$, we have

$$\psi \equiv \boldsymbol{v}, \qquad \boldsymbol{J}^{\boldsymbol{v}} \equiv -\boldsymbol{T}^{\mathrm{T}} + \boldsymbol{J}^{1}\boldsymbol{v}, \qquad \sigma^{\boldsymbol{v}} \equiv \varrho\boldsymbol{k}, \qquad \pi^{\boldsymbol{v}} \equiv 0, \qquad \varphi^{\boldsymbol{v}} \equiv 0. \tag{14}$$

According to (12), the non-convective part of the flux of momentum is the negative transposed Cauchy stress tensor $\boldsymbol{T}$. The supply of momentum is the external force density $\varrho(\boldsymbol{x}, t)\boldsymbol{\kappa}(\boldsymbol{x}, t)$, and no production

of momentum appears. Consequently, (10) and (11) result by (14) in

$$\frac{\partial}{\partial t}(\varrho\boldsymbol{v}) + \nabla \cdot (\boldsymbol{v}\varrho\boldsymbol{v} - \boldsymbol{T}^{\mathrm{T}}) - \varrho\boldsymbol{k} = 0, \tag{15}$$

$$|[\varrho\boldsymbol{v}(\boldsymbol{u} - \boldsymbol{v}) + \boldsymbol{T}^{\mathrm{T}})| \cdot \boldsymbol{f} = 0. \tag{16}$$

2.2.3. Angular momentum

Because the specific angular momentum is

$$\boldsymbol{S}(\boldsymbol{x}, t) = \boldsymbol{x} \times \boldsymbol{v}(\boldsymbol{x}, t) + \boldsymbol{s}(\boldsymbol{x}, t), \tag{17}$$

with the specific spin $\boldsymbol{s}(\boldsymbol{x}, t)$ (internal angular momentum), we have

$$\psi \equiv \boldsymbol{S}, \quad \boldsymbol{J}^{\boldsymbol{S}} \equiv -[\boldsymbol{x} \times \boldsymbol{T}]^{\mathrm{T}} - \boldsymbol{W}^{\mathrm{T}} + \boldsymbol{J}^{1}\boldsymbol{v}, \quad \sigma^{\boldsymbol{S}} \equiv \varrho[\boldsymbol{x} \times \boldsymbol{k} \times \boldsymbol{g}], \quad \pi^{\boldsymbol{S}} \equiv 0, \quad \varphi^{\boldsymbol{S}} \equiv 0. \tag{18}$$

Additional to the angular momentum caused by the stress tensor $[\boldsymbol{x} \times \boldsymbol{T}]^{\mathrm{T}}(\boldsymbol{x}, t)$, we have a torque tensor field $\boldsymbol{W}(\boldsymbol{x}, t)$ (couple stress) acting on the specific spin $\boldsymbol{s}(\boldsymbol{x}, t)$. The supply of angular momentum is caused by the moment of the external force density and by an additional external $\boldsymbol{g}(\boldsymbol{x}, t)$, called couple force density. The production terms of angular momentum are zero. Consequently, (10) and (11) result by (18) in

$$\frac{\partial}{\partial t}(\varrho\boldsymbol{S}) + \nabla \cdot (\boldsymbol{v}\varrho\boldsymbol{S} - [\boldsymbol{x} \times \boldsymbol{T}]^{\mathrm{T}} - \boldsymbol{W}^{\mathrm{T}}) - \varrho[\boldsymbol{x} \times \boldsymbol{k} + \boldsymbol{g}] = 0, \tag{19}$$

$$|[\varrho\boldsymbol{S}(\boldsymbol{u} - \boldsymbol{v}) + [\boldsymbol{x} \times \boldsymbol{T}]^{\mathrm{T}} + \boldsymbol{W}^{\mathrm{T}}]| \cdot \boldsymbol{f} = 0. \tag{20}$$

2.2.4. Spin

If we multiply $\boldsymbol{x}$ in (15) and subtract this from (19), we obtain the spin balance from which its jump condition follows:

$$\frac{\partial}{\partial t}(\varrho\boldsymbol{s}) + \nabla \cdot (\boldsymbol{v}\varrho\boldsymbol{s} - \boldsymbol{W}^{\mathrm{T}}) - \boldsymbol{\epsilon} : \boldsymbol{T} - \varrho\boldsymbol{g} = 0, \tag{21}$$

$$|[\varrho\boldsymbol{s}(\boldsymbol{u} - \boldsymbol{v}) + \boldsymbol{W}^{\mathrm{T}}]| \cdot \boldsymbol{f} = 0. \tag{22}$$

Here, $\boldsymbol{\epsilon}$ is the Levi–Civita tensor by which the antisymmetric part of the stress tensor is introduced into the spin balance (21). The field $\boldsymbol{\epsilon}:\boldsymbol{T}(\boldsymbol{x}, t)$ is the spin production, and $\varrho(\boldsymbol{x}, t)\boldsymbol{g}(\boldsymbol{x}, t)$ the field of the spin supply.

2.2.5. Total energy

The total energy is defined by

$$e(\boldsymbol{x}, t) := \tfrac{1}{2}\boldsymbol{v}^2(\boldsymbol{x}, t) + \tfrac{1}{2}\boldsymbol{s}(\boldsymbol{x}, t) \cdot \boldsymbol{\Theta}^{-1}(\boldsymbol{x}, t) \cdot \boldsymbol{s}(\boldsymbol{x}, t) + \varepsilon(\boldsymbol{x}, t). \tag{23}$$

Here, $\boldsymbol{\Theta}(\boldsymbol{x}, t)$ is a moment of inertia tensor field which describes the connection between spin and rotational energy, and $\varepsilon(\boldsymbol{x}, t)$ is the field of internal energy density. For writing down the balance of total energy, we identify

$$\psi = e, \quad \boldsymbol{J}^e \equiv -\boldsymbol{T}^{\mathrm{T}} \cdot \boldsymbol{v} - \boldsymbol{W}^{\mathrm{T}} \cdot \boldsymbol{\Theta}^{-1} \cdot \boldsymbol{s} + \boldsymbol{q} + \boldsymbol{J}^{1}e, \tag{24}$$

$$\sigma^e \equiv \varrho(\boldsymbol{k} \cdot \boldsymbol{v} + \boldsymbol{g} \cdot \boldsymbol{\Theta}^{-1} \cdot \boldsymbol{s} + r), \tag{25}$$

$$\pi^e \equiv 0, \quad \varphi^e \equiv 0. \tag{26}$$

Here, $\boldsymbol{q}(\boldsymbol{x}, t)$ is the field of the heat flux density, and $r(\boldsymbol{x}, t)$ is the supply by energy absorption. Consequently, the balance of total energy writes

$$\frac{\partial}{\partial t}(\varrho e) + \nabla \cdot [\boldsymbol{v}\varrho e - \boldsymbol{T}^{\mathrm{T}} \cdot \boldsymbol{v} - \boldsymbol{W}^{\mathrm{T}} \cdot \boldsymbol{\Theta}^{-1} \cdot \boldsymbol{s} + \boldsymbol{q}] - \varrho\boldsymbol{\kappa} \cdot \boldsymbol{v} - \varrho\boldsymbol{g} \cdot \boldsymbol{\Theta}^{-1} \cdot \boldsymbol{s} - \varrho r = 0, \tag{27}$$

and the jump condition of the total energy is

$$|[\varrho e(\boldsymbol{u} - \boldsymbol{v}) + \boldsymbol{T}^{\mathrm{T}} \cdot \boldsymbol{v} + \boldsymbol{W}^{\mathrm{T}} \cdot \boldsymbol{\Theta}^{-1} \cdot \boldsymbol{s} - \boldsymbol{q}]| \cdot \boldsymbol{f} = 0. \tag{28}$$

2.2.6. Internal energy

Subtracting $\boldsymbol{v}\cdot$(15) and (21)$\cdot\boldsymbol{\Theta}^{-1}\cdot\boldsymbol{s}$ we obtain from (27), the balance of internal energy

$$\frac{\partial}{\partial t}(\varrho\varepsilon) + \nabla \cdot [\boldsymbol{v}\varrho\varepsilon + \boldsymbol{q}) - \nabla\boldsymbol{v} : \boldsymbol{T} - \nabla(\boldsymbol{\Theta}^{-1} \cdot \boldsymbol{s}) - \boldsymbol{W} - \varrho r - (\boldsymbol{\Theta}^{-1} \cdot \boldsymbol{s}) - \boldsymbol{\epsilon} : \boldsymbol{T} = 0. \tag{29}$$

The jump condition of the internal energy follows by (11) from comparison of (29) with (10).

$$\varphi^{\varepsilon} + |[\varrho\varepsilon(\boldsymbol{u} - \boldsymbol{v}) - \boldsymbol{q}]| \cdot \boldsymbol{f} = 0. \tag{30}$$

2.2.7. Entropy

For the specific entropy $s(\boldsymbol{x}, t)$, we have

$$\psi \equiv s, \qquad \boldsymbol{J}^s \equiv \boldsymbol{\Phi} + \boldsymbol{J}^1 s, \qquad \sigma^s \equiv \frac{r}{\Theta}, \qquad \pi^s \geq 0, \qquad \varphi^s \geq 0. \tag{31}$$

Here, $\boldsymbol{\Phi}(\boldsymbol{x}, t)$ is the entropy flux density and $\Theta(\boldsymbol{x}, t)$ the contact temperature field [6,7]. The fact, that the production terms of the entropy $\pi^s(\boldsymbol{x}, t)$ and $\varphi^s(\boldsymbol{x}, t)$ are non-negative for all $(\boldsymbol{x}, t)$, is due to an extended formulation of the *second law* [8]. Consequently, the entropy balance and the jump condition are

$$\frac{\partial}{\partial t}(\varrho s) + \nabla \cdot (\boldsymbol{v}\varrho s + \boldsymbol{\Phi}) - \frac{r}{\Theta} - \pi^s = 0, \tag{32}$$

$$\varphi^s + |[\varrho s(\boldsymbol{u} - \boldsymbol{v}) - \boldsymbol{\Phi}]| \cdot \boldsymbol{f} = 0. \tag{33}$$

3. State spaces classifying thermodynamics

For describing different materials we need constitutive equations, or in a more general formulation, we have to know the constitutive mappings for inserting them into the balance equations which then result in the closed system of balances on the state space. The domain of the constitutive mappings is called a *state space*. In general, the wanted fields are not sufficient to form the state space, because the constitutive equations may also depend on derivatives of the wanted fields. A prominent example for this fact is heat conduction. Here, the heat flux density depends on the gradient of temperature (see (54)).

In Section 2.2, we derived the local balance equations. In classical formulation, that is a five-field theory with additional spin, the wanted fields are

$$\text{mass density}: \ \varrho(\boldsymbol{x}, t), \tag{34}$$

$$\text{material velocity}: \ \boldsymbol{v}(\boldsymbol{x}, t), \tag{35}$$

specific internal energy : $\varepsilon(\boldsymbol{x}, t)$,   (36)

specific spin : $\boldsymbol{s}(\boldsymbol{x}, t)$.   (37)

External given quantities are

specific external force : $\boldsymbol{k}(\boldsymbol{x}, t)$,   (38)

specific couple force : $\boldsymbol{g}(\boldsymbol{x}, t)$.   (39)

All remaining quantities are constitutive equations depending on the special material in consideration

Cauchy stress tensor : $\boldsymbol{T}(\boldsymbol{x}, t)$.   (40)

couple stress tensor : $\boldsymbol{W}(\boldsymbol{x}, t)$,   (41)

moment of inertia tensor : $\boldsymbol{\Theta}(\boldsymbol{x}, t)$,   (42)

heat flux density : $\boldsymbol{q}(\boldsymbol{x}, t)$,   (43)

specific energy supply : $r(\boldsymbol{x}, t)$,   (44)

specific entropy density : $s(\boldsymbol{x}, t)$,   (45)

entropy flux density : $\boldsymbol{\Phi}(\boldsymbol{x}, t)$,   (46)

entropy production density : $\pi^{s}(\boldsymbol{x}, t)$,   (47)

temperature : $\Theta(\boldsymbol{x}, t)$,   (48)

internal surface energy production : $\varphi^{\varepsilon}(\boldsymbol{x}, t)$,   (49)

internal surface entropy production : $\varphi^{s}(\boldsymbol{x}, t)$.   (50)

To perform derivatives of constitutive quantities, such as $\nabla \cdot \boldsymbol{T}$ or $(\partial/\partial t)s$, we need the domain of the constitutive mappings (40)–(50). This domain, the state space, is different from the wanted fields in general and depends on the material in consideration. Consequently, the choice of the state space determines a *class of materials*. Beyond the wanted fields and their derivatives the state space may include additional variables, often called *internal variables* $\boldsymbol{\alpha}(\boldsymbol{x}, t)$, for which also additional equations of motion, the rate equations, are necessary.

An example of a state space is

$$\hat{z}(\boldsymbol{x}, t) = (\varrho, \boldsymbol{v}, \varepsilon, \boldsymbol{\alpha}, \nabla \varrho, \nabla \boldsymbol{v}, \nabla \varepsilon, \nabla \boldsymbol{\alpha}, \dot{\varrho}, \dot{\boldsymbol{v}}, \dot{\varepsilon}, \dot{\boldsymbol{\alpha}})(\boldsymbol{x}, t). \qquad (51)$$

Remarks.

- The state space includes *independent* variables. At one point the values of the fields and the corresponding gradients are independent variables. This independence of the values of the fields and their gradients is only locally true. The mass densities ϱ_1 and ϱ_2 (see Fig. 1) cannot coincide at all points, if their gradients differ.
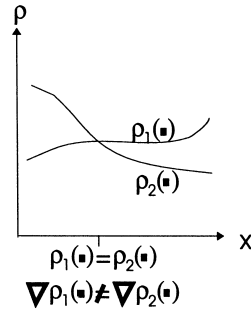
Fig. 1. For different fields of mass density, the values coincide at one point, but the gradients are different at that point.

- The variables spanning the state space do not only depend on the material, but different thermodynamical theories use special state spaces. Therefore, the choice of the state space allows for a classification of different thermodynamical descriptions.

After having chosen the state space, the differentiations of constitutive quantities in the balance equations have to be carried out by use of the chain rule. For example, we obtain for the divergence of the heat flux density from (51)

$$
\begin{aligned}
\nabla \cdot \boldsymbol{q}(\varrho, \boldsymbol{v}, \varepsilon, \boldsymbol{\alpha}, \nabla\varrho, \nabla\boldsymbol{v}, \nabla\varepsilon, \nabla\boldsymbol{\alpha}, \dot{\varrho}, \dot{\boldsymbol{\alpha}}) \\
= \frac{\partial \boldsymbol{q}}{\partial \varrho} \cdot \nabla\varrho + \frac{\partial \boldsymbol{q}}{\partial \boldsymbol{v}} : \nabla\boldsymbol{v} + \frac{\partial \boldsymbol{q}}{\partial \varepsilon} \cdot \nabla\varepsilon + \frac{\partial \boldsymbol{q}}{\partial \boldsymbol{\alpha}} : \nabla\boldsymbol{\alpha} + \frac{\partial \boldsymbol{q}}{\partial \nabla\varrho} : \nabla\nabla\varrho + \frac{\partial \boldsymbol{q}}{\partial \nabla\boldsymbol{v}} : \nabla\nabla\boldsymbol{v} + \frac{\partial \boldsymbol{q}}{\partial \nabla\varepsilon} : \nabla\nabla\varepsilon \\
+ \frac{\partial \boldsymbol{q}}{\partial \nabla\boldsymbol{\alpha}} : \nabla\nabla\boldsymbol{\alpha} + \frac{\partial \boldsymbol{q}}{\partial \dot{\varrho}} \cdot \nabla\dot{\varrho} + \frac{\partial \boldsymbol{q}}{\partial \dot{\boldsymbol{\alpha}}} : \partial\dot{\boldsymbol{\alpha}}.
\end{aligned}
\tag{52}
$$

3.1. Examples

A suitable state space to describe heat conduction includes mass density, temperature, and the gradient of temperature

$$
Z = \{\varrho, \Theta, \nabla\Theta\}.
\tag{53}
$$

A very simple constitutive equation for the heat flux is given by Fourier's law which is linear in the gradient of temperature

$$
\boldsymbol{q} = -\kappa(\Theta, \varrho)\nabla\Theta,
\tag{54}
$$

with the heat conductivity κ.

For a viscous fluid, constitutive quantities depend on the velocity gradient, and a suitable state space is

$$
Z = \{\varrho, \Theta, \nabla\boldsymbol{v}\}.
\tag{55}
$$

A constitutive equation for the stress tensor under the assumption of a linear dependence on the velocity gradient reads

$$
\boldsymbol{T} = -\eta_1(\varrho\Theta)\overline{\nabla\boldsymbol{v}} - \eta_2(\varrho, \Theta)(\nabla \cdot \boldsymbol{v})\mathbf{1} - p(\varrho, \Theta)\mathbf{1},
\tag{56}
$$

where $\overline{}$ denotes the symmetric traceless part of a tensor ($\overline{A} = \frac{1}{2}(A + A^{\mathrm{T}}) - \frac{1}{3}\operatorname{tr}(A)\mathbf{1}$), η_1 and η_2 are viscosity coefficients, and p is the pressure.

For dielectric materials, we choose the state space

$$Z = \{\varrho, \Theta, \mathbf{E}\}. \tag{57}$$

For linear anisotropic materials, the dielectric displacement D is a linear function of the electric field E, and the constitutive mapping is a tensor, the permeability ϵ

$$\mathbf{D} = \epsilon(\varrho, \Theta) \cdot \mathbf{E}. \tag{58}$$

For a given state space, constitutive functions can be written down in a systematic way by using representation theorems [9] which are discussed in Section 4 in more detail.

3.2. Small and large state spaces

Material properties at $(\mathbf{x}, t)$ do not only depend on the state space variables of the same event $(\mathbf{x}, t)$ in general. They are non-local in time and position [10]. The non-locality in position can be approximately taken into account by including gradients into the state space. The non-locality in time depends on the choice of the state space. If the state space is large enough, then an in time local description of the material may be possible. If the chosen state space is too small, we have to describe the material by a constitutive mapping which is non-local in time, because in this state space, the material shows after-effects. Therefore, we give the definition as follows.

Definition. A *state space* is called *large*, if material properties $\mathcal{M}$ are defined by maps being local in time

$$\mathcal{M} : z(t) \mapsto M(t), \quad \forall t. \tag{59}$$

For constitutive mappings which are non-local in time, we need two more definitions:

Definition. For a fixed time t and real $s \geq 0$

$$z^t(s) = z(t - s), \quad s \in [0, \tau] \tag{60}$$

is called the *history of the process* $z(\cdot)$ between t–τ and t.

Definition. A *state space* is called *small*, if material properties $\mathcal{M}$ are defined by maps defined on process histories

$$\mathcal{M} : z^t(\cdot) \mapsto M(t), \quad \forall t. \tag{61}$$

Now, we will consider one example of a constitutive map defined on a small state space. If the dependence of the constitutive functional on the process history $z(\cdot)$ is linear, it can be written as

$$M(t) = \int_0^\tau m(t - \vartheta) z(t - \vartheta) \, \mathrm{d}\vartheta, \tag{62}$$

with an integral kernel m describing after-effects of the material, e.g. fading memory. Especially in ferroelectric materials the dependence of the polarization $\boldsymbol{P}$ on the electric field $\boldsymbol{E}$ is non-local in time, because it depends on the electric field at earlier times

$$\boldsymbol{P}(t) = \int_0^\tau \boldsymbol{\chi}(t - \vartheta) \cdot \boldsymbol{E}(t - \vartheta)\, \mathrm{d}\vartheta, \tag{63}$$

with the susceptibility tensor $\boldsymbol{\chi}$. Measuring polarization and electric field, one observes a hysteresis. The same effect is observed for the dependence of the magnetization on the magnetic field in case of ferromagnets.

3.3. Internal variables

For practical purposes *constitutive functionals* as (61) are not very convenient, and one would like to deal with large state spaces and *constitutive functions*. This can be achieved by including additional *internal variables* $\boldsymbol{\alpha}$ in (51) into the state space [11]. These variables are independent of each other in non-equilibrium. In equilibrium, they depend on the equilibrium variables according to Zeroth law [12].

Internal variables need rate equations. The relaxation of the internal variables cannot be influenced by the environment. This is the reason for calling them 'internal variables'. Always a model is needed to give the internal variables a physical meaning. Thus, the mole fraction of the different crystal modifications, the alignment tensor of orientable molecules [13], or the damage in failure theory [14] are internal variables.

3.4. Thermodynamics of irreversible processes (TIP)

Irreversible thermodynamics is a non-equilibrium theory in field formulation. The following assumptions are made:

- The state space of irreversible thermodynamics is the equilibrium subspace

$$Z(\boldsymbol{x}, t) = \{\varrho, T, \boldsymbol{v}\}(\boldsymbol{x}, t), \tag{64}$$

consisting of the fields of mass density, thermostatic temperature, and material velocity. This presupposition, that the equilibrium subspace is sufficient for describing constitutive properties in non-equilibrium, is called the hypothesis of *local equilibrium*. The values of these fields differ from volume element to volume element, thus, describing a non-equilibrium situation. Gradients or time derivatives are not included in the state space.

- For one-component systems is presupposed, that the entropy transport is only caused by heat transport, that means the entropy flux density is given by

$$\boldsymbol{\Phi} = \frac{1}{T}\boldsymbol{q}. \tag{65}$$

- Also in non-equilibrium, the time derivative of the entropy density satisfies the equilibrium Gibb's equation

$$\frac{\mathrm{d}s}{\mathrm{d}t} = \frac{1}{T}\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} - \frac{p}{\varrho^2 T}\frac{\mathrm{d}\varrho}{\mathrm{d}t}, \tag{66a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t} := \frac{\partial}{\partial t} + \boldsymbol{v} \cdot \nabla. \tag{66b}$$

Gibbs' equation together with the balance equations for mass and internal energy allows to derive an expression for the entropy production, which has the form of a sum of products of 'fluxes and forces', J_i and X_i,

$$\sigma = \sum_i J_i X_i \geq 0. \tag{67}$$

- It is assumed that the fluxes and the forces are connected by linear constitutive laws

$$J_i = \sum_k L_{ik} X_k. \tag{68}$$

Eq. (68) shows that in general, a thermodynamic flux is caused not only by the corresponding force of the same index, but also by all other forces due to cross coupling effects.
- Onsager–Casimir reciprocal relations hold

$$L_{ik}(\boldsymbol{B}, \boldsymbol{\omega} \dots) = \epsilon_i \epsilon_k L_{ki}(-\boldsymbol{B}, -\boldsymbol{\omega} \dots). \tag{69}$$

Here, the quantities $(\boldsymbol{B}, \boldsymbol{\omega} \dots)$ have to transform in such a way that the force density is even under reversal of motion ($\boldsymbol{B}$ is the magnetic induction, $\boldsymbol{\omega}$ the angular velocity). The ϵ_k are determined by the transformation properties of the thermodynamical forces under reversal of motion

$$X_k(\boldsymbol{B}, \boldsymbol{\omega} \dots) = \epsilon_k X_k(-\boldsymbol{B}, -\boldsymbol{\omega} \dots). \tag{70}$$

A derivation of Onsager–Casimir reciprocal relations from a statistical background can be found in [15], and on a phenomenological basis in [16,17].

Because of linear constitutive Eq. (68), the entropy production of (67) is a quadratic form of the forces. The second law of thermodynamics (67) requires that L_{ik} is a positive definite matrix.

A lot of examples belonging to thermodynamics of irreversible processes can be found in [18].

3.5. Rational thermodynamics

Like thermodynamics of irreversible processes rational thermodynamics is a non-equilibrium theory in field formulation. However, the presuppositions are different from those of TIP.
- Rational thermodynamics obeys the material axioms which will be discussed in Section 4.1 strictly.
- Entropy and temperature are primitive concepts, that means nothing is said about how to define or to measure these quantities.
- The existence of the fields of specific entropy $s(\boldsymbol{x}, t)$, entropy flux density $\boldsymbol{\Phi}(\boldsymbol{x}, t)$, and entropy production $\sigma(\boldsymbol{x}, t)$ as constitutive quantities is assumed. According to (32) these fields have to satisfy the dissipation inequality which is local in time (with $r \equiv 0$).

$$\frac{\partial}{\partial t}(\varrho s) + \nabla \cdot (\boldsymbol{v}\varrho s + \boldsymbol{\Phi}) = \sigma \geq 0, \quad \forall \boldsymbol{x}, t. \tag{71}$$

There is a special exploitation of the dissipation inequality, named after Coleman and Noll (see Section 4).
- The *principle of equipresence* states that all constitutive quantities depend on the same set of variables.
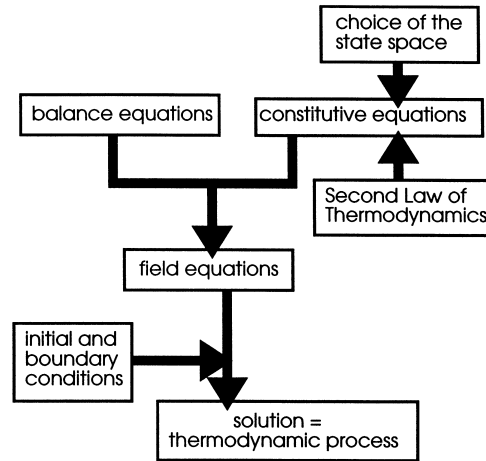
Fig. 2. The balance equations and the constitutive equations are the set of field equations to be solved.

There are two Handbook articles in which rational thermodynamics is considered [19,20]. The scheme how rational thermodynamics operates is given in Fig. 2.

As an example of a non-equilibrium state space, we choose that of simple heat conduction

$$Z = \{\varrho, \Theta, \nabla\Theta\}. \tag{72}$$

Here, Θ is a non-specified non-equilibrium temperature. The constitutive equation for a scalar quantity like the internal energy is given by the representation theorem

$$\varepsilon(\varrho, \Theta, \nabla\Theta) = e_0(\varrho, \Theta) + e_1(\varrho, \Theta)\nabla\Theta \cdot \nabla\Theta + \text{higher orders of } (\nabla\Theta), \tag{73}$$

$$\boldsymbol{q}(\varrho, \Theta, \nabla\Theta) = q_1(\varrho, \Theta, \nabla\Theta \cdot \nabla\Theta)\nabla\Theta. \tag{74}$$

In linear approximation, we obtain Fourier's law of heat conduction

$$\boldsymbol{q}(\varrho, \Theta, \nabla\Theta) = -\kappa\nabla\Theta, \tag{75}$$

and the internal energy results in

$$\varepsilon(\varrho, \Theta, \nabla\Theta) = e_0(\varrho, \Theta), \tag{76}$$

The balance of internal energy for an incompressible fluid ($\varrho = $ const.) at rest ($\boldsymbol{v} = 0$) without radiation absorption r reads according to (27)

$$\varrho\frac{\partial\varepsilon}{\partial t} + \nabla \cdot \boldsymbol{q} = 0. \tag{77}$$

With the constitutive equations in linear approximation we end up with ($\kappa = $ const.)

$$\varrho\frac{\partial\varepsilon}{\partial\Theta}\frac{\partial\Theta}{\partial t} - \kappa\nabla \cdot \nabla\Theta = 0. \tag{78}$$

The final equation is the usual heat conduction equation with the heat capacity c.

$$\varrho c \frac{\partial}{\partial t} \Theta - \kappa \Delta \Theta = 0. \tag{79}$$

This differential equation is a parabolic one. (For a classification of differential equations, see [21]). The problem is that parabolic equations allow for infinite speed of propagation of disturbances which does not represent a physical correct description. These propagation problems in classical non-equilibrium thermodynamics were the motivation for the development of extended thermodynamics.

3.6. Extended thermodynamics

In extended thermodynamics, fluxes are included into the state space. We distinguish between two forms of extended thermodynamics which differ in exploiting the dissipation inequality (71). Extended thermodynamics as further development of rational thermodynamics exploiting the dissipation inequality by Liu's procedure [22,23] (see Section 4.6), and extended irreversible thermodynamics exploiting the dissipation inequality as usual as in TIP [24]. In both forms, heat flux density and stress tensor (or the trace and the symmetric traceless part of the stress tensor) are included into state space.

According to extended irreversible thermodynamics, we consider the simple example of a heat conducting rigid body which was already treated in (72) by use of different state space variables

$$Z = \{\varrho, \varepsilon, \boldsymbol{q}\}. \tag{80}$$

As already mentioned, the exploitation of the dissipation inequality is analogous to the procedure in classical TIP. Consequently, it is presupposed that a generalized Gibbs equation holds which additionally includes the heat flux density

$$\frac{\mathrm{d}s(\varrho, \varepsilon, \boldsymbol{q})}{\mathrm{d}t} = \frac{1}{\Theta} \left(\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} - \frac{p}{\varrho^2} \frac{\mathrm{d}\varrho}{\mathrm{d}t} + 2a\Theta \boldsymbol{q} \cdot \frac{\mathrm{d}\boldsymbol{q}}{\mathrm{d}t} \right). \tag{81}$$

With the assumptions

$$\boldsymbol{\Phi} = \frac{\boldsymbol{q}}{\Theta}, \qquad r = 0, \quad \text{and} \quad \boldsymbol{T} \text{ symmetric}, \tag{82}$$

the dissipation inequality reads

$$\sigma = \varrho \frac{\mathrm{d}s}{\mathrm{d}t} + \nabla \cdot \boldsymbol{\Phi} = \varrho \frac{\mathrm{d}s}{\mathrm{d}t} + \frac{\nabla \cdot \boldsymbol{q}}{\Theta} - \frac{1}{\Theta^2} \nabla \Theta \cdot \boldsymbol{q} = \frac{\varrho}{\Theta} \left(\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} - \frac{p}{\varrho^2} \frac{\mathrm{d}\varrho}{\mathrm{d}t} + 2a\Theta \boldsymbol{q} \cdot \frac{\mathrm{d}\boldsymbol{q}}{\mathrm{d}t} \right)$$

$$+ \frac{1}{\Theta} \nabla \cdot \boldsymbol{q} - \frac{1}{\Theta^2} \nabla \Theta \cdot \boldsymbol{q} = \frac{1}{\Theta} (\boldsymbol{T} : \nabla \boldsymbol{v} + p \nabla \cdot \boldsymbol{v} + 2a\Theta \boldsymbol{q} \cdot \frac{\mathrm{d}\boldsymbol{q}}{\mathrm{d}t} - \frac{1}{\Theta} \nabla \Theta \cdot \boldsymbol{q}$$

$$= \frac{1}{\Theta} \left(\underbrace{\overline{\boldsymbol{T}}}_{\text{flux}} : \underbrace{\overline{\nabla \boldsymbol{v}}}_{\text{force}} + \underbrace{(p + \tfrac{1}{3}\operatorname{tr}(\boldsymbol{T}))}_{\text{flux}} \underbrace{\nabla \cdot \boldsymbol{v}}_{\text{force}} + \underbrace{\boldsymbol{q}}_{\text{flux}} \cdot \underbrace{\left(2a\Theta \frac{\mathrm{d}\boldsymbol{q}}{\mathrm{d}t} - \frac{1}{\Theta} \nabla \Theta \right)}_{\text{force}} \right). \tag{83}$$

As in TIP, the expression for the entropy production is a sum of products of fluxes and forces. The choice of linear constitutive equations between the fluxes and forces results in

$$\overline{\boxed{\boldsymbol{T}}} = 2\mu\,\overline{\boxed{\nabla\boldsymbol{v}}}\,, \tag{84}$$

$$p + \tfrac{1}{3}\operatorname{tr}(\boldsymbol{T}) = \lambda\nabla\cdot\boldsymbol{v}, \tag{85}$$

$$\boldsymbol{q} = -\kappa\nabla\Theta - 2\varrho\Theta^2 a\dot{\boldsymbol{q}}. \tag{86}$$

Eq. (86) is called *Cattaneo equation of heat conduction* [25] which generates a finite speed of propagation of disturbances.

In the other version of extended thermodynamics, additional balance equations for the fluxes are used. In a purely phenomenological theory, the validity of such balance equations for the fluxes are ansatzes. Such balance equations can be derived from kinetic theory, including even higher order fluxes into the state space [23,26]. However, this derivation starts from Boltzmann's equation [23,27] which is valid only for dilute gases.

Using the state space

$$Z = \{\varrho, \varepsilon, \boldsymbol{T}, \boldsymbol{q}\} \tag{87}$$

the balance equations are

$$\frac{\mathrm{d}\varrho}{\mathrm{d}t} + \varrho\nabla\cdot\boldsymbol{v} = 0, \tag{88}$$

$$\varrho\frac{\mathrm{d}\boldsymbol{v}}{\mathrm{d}t} - \nabla\cdot\boldsymbol{T}^{\mathrm{T}} = \varrho\boldsymbol{f}, \tag{89}$$

$$\varrho\frac{\mathrm{d}(\varepsilon + (1/2)\boldsymbol{v}\cdot\boldsymbol{v})}{\mathrm{d}t} - \nabla\cdot\boldsymbol{q} = \boldsymbol{T}:\nabla\boldsymbol{v} + r, \tag{90}$$

$$\frac{\mathrm{d}\boldsymbol{q}}{\mathrm{d}t} + \nabla\cdot\boldsymbol{L} = \boldsymbol{G}, \tag{91}$$

$$\frac{\mathrm{d}\boldsymbol{T}}{\mathrm{d}t} + \nabla\cdot\boldsymbol{M} = \boldsymbol{N}\cdot \tag{92}$$

The fluxes $\boldsymbol{L}$ and $\boldsymbol{M}$, as well as the productions $\boldsymbol{G}$ and $\boldsymbol{N}$ are constitutive quantities. Considering $\boldsymbol{T}$ and $\boldsymbol{q}$ as additional wanted fields, the need of additional constitutive equations cannot be avoided. Often, it is assumed for the higher order fluxes and productions, that constitutive equations linear in the non-equilibrium variables stress tensor and heat flux density are sufficient.

The state space of extended thermodynamics includes fluxes, but no gradients or time derivatives of variables. It can be proved that using constitutive functions defined on this state space, the balance equations form a hyperbolic system of partial differential equations [28]. Such systems of differential equations allow for finite speeds of disturbances.

The different choices of state spaces presented in this section are summarized in Table 1.

Table 1
Different state spaces belonging to special versions of thermodynamics

	Thermostatics	Internal variables	TIP	Rational thermodynamics	Extended thermodynamics
State space	$\{\boldsymbol{n}, \boldsymbol{a}, T\}$ or $\{\boldsymbol{n}, \boldsymbol{a}, \varepsilon\}$	$\{\boldsymbol{n}, \boldsymbol{a}, T, \nabla\boldsymbol{n}, \nabla\boldsymbol{a}, \nabla T, \alpha_k, \dots\}$	$\{\boldsymbol{n}, \boldsymbol{a}, T\}$	$\{\boldsymbol{n}, \boldsymbol{a}, T, \varepsilon, \nabla\varepsilon, \dots, \dot{n}, \dot{a}, \dot{T}\}$	$\{\boldsymbol{n}, \boldsymbol{a}, \varepsilon, \boldsymbol{q}, \boldsymbol{T}\}$
Additional assumptions	Equilibrium	Rate equations for the internal variables	Local equilibrium, linear constitutive laws $\Phi = \boldsymbol{q}/T$	s, Φ, σ: primitive concepts	Balance equation for $\boldsymbol{q}, \boldsymbol{T}$
Advantage and disadvantage	Reversible processes only	Avoids history-dependent constitutive equations	Easy to handle	Non-equilibrium temperature not defined	Finite speed of propagation

4. Constitutive theory

4.1. Material axioms

In this section, we now put the question 'how to obtain constitutive equations?' This question can be answered in two different ways: we can make ansatzes for the constitutive equations compatible with the second law. Examples for such ansatzes can be found in [29]. The other way is to formulate *material axioms*. Instead of a special ansatz material axioms give standardized procedures for constructing (and classifying) classes of materials and constitutive equations belonging to them.

We now formulate

Material axioms: Constitutive equations have to satisfy the following:
1. The second law, and if necessary its additionals.
2. Transformation properties by changing the observer.
3. The material-symmetry.
4. Additionally, state spaces have to be chosen such that finite speed of wave propagation is guaranteed.

In continuum, thermodynamics, the second law is represented by the in time local dissipation inequality (32)

$$\dot{\varrho}s + \nabla \cdot \boldsymbol{\Phi} - \gamma = \sigma \geq 0, \qquad \boldsymbol{\Phi} := \kappa + \frac{\boldsymbol{q}}{\Theta}, \qquad \gamma = \frac{r}{\Theta}. \tag{93}$$

Here, Θ is a non-equilibrium temperature, such as the *contact temperature* of the discrete system in consideration [30,6]. Changing the observer demands *covariance* in relativistic theories or *objectivity* in non-relativistic theories. Material symmetry is described by *isotropy groups*. Hyperbolicity in extended thermodynamics is enforced by constructing a *symmetric hyperbolic* system of partial differential equations from the balances and the constitutive equations [23].

4.2. An example

4.2.1. The state space

For more elucidation, a simple example is now considered. We choose a large state space consisting of mass density, internal energy, their gradients and the velocity gradient

$$Z = (\varrho, \varepsilon, \boldsymbol{v}, \nabla\varrho, \nabla\varepsilon, \nabla\boldsymbol{v}), \tag{94a}$$

$$Z = (\varrho, \varepsilon, \nabla\varrho, \nabla\varepsilon, \nabla\boldsymbol{v}), \tag{94b}$$

which belongs to an acceleration insensitive fluid because the acceleration is not included into Z. Eq. (94b) is caused by material axiom 2 which will be discussed in more detail in Section 4.2.2. The second equation states, that constitutive properties do not depend on the material velocity, because material properties should not depend on the motion of the observer. Different from state space the five wanted fields are as usual. Because the state space Z is the domain of the constitutive equations we obtain for the pressure tensor $\boldsymbol{P} \equiv -\boldsymbol{T}$ and for the heat flux density

$$\boldsymbol{P}(\boldsymbol{x}, t) = \mathcal{P}(\varrho(\boldsymbol{x}, t), \varepsilon(\boldsymbol{x}, t), \nabla\varrho(\boldsymbol{x}, t), \nabla\varepsilon(\boldsymbol{x}, t), \nabla\boldsymbol{v}(\boldsymbol{x}, t)), \tag{95}$$

$$\boldsymbol{q}(\boldsymbol{x}, t) = \mathcal{Q}(\varrho(\boldsymbol{x}, t), \varepsilon(\boldsymbol{x}, t), \nabla\varrho(\boldsymbol{x}, t), \nabla\varepsilon(\boldsymbol{x}, t), \nabla\boldsymbol{v}(\boldsymbol{x}, t)). \tag{96}$$

We here pre-suppose that the fluid in consideration does not have an internal spin, as we can find it for liquid crystals. If there is no internal spin, the pressure tensor is symmetric according to (21)

$$P(x, t) = P^{\mathrm{T}}(x, t). \tag{97}$$

4.2.2. Material frame indifference

We now apply material axiom 2 "Transformation properties by changing the observer". In non-relativistic theories, changing the observer is described by an Euclidean transformation of space–time described in general by a time-dependent proper orthogonal transformation $Q(t)$ and by a time dependent translation $c(t)$ [31]. Physical quantities show different transformation behavior with changing the observer. So mass density and internal energy are of scalar behavior, that means, they are invariant, they have the same value for all observers. Other quantities transform as tensors of different order. So, entropy flux density, heat flux density, and gradients of scalars are vectors (tensors of first order), the symmetric part of the velocity gradient and the stress tensor are tensors of second order. In more detail, we have

$$\varrho \to \varrho, \qquad \varepsilon \to \varepsilon, \tag{98}$$

$$\boldsymbol{\Phi} \to \boldsymbol{Q} \cdot \boldsymbol{\Phi}, \qquad q \to \boldsymbol{Q} \cdot q, \tag{99}$$

$$\nabla\varrho \to \boldsymbol{Q} \cdot \nabla\varrho, \qquad \nabla\varepsilon \to \boldsymbol{Q} \cdot \nabla\varepsilon, \tag{100}$$

$$(\nabla v)^s \to \boldsymbol{Q} \cdot (\nabla v)^s \cdot \boldsymbol{Q}^{\mathrm{T}}, \tag{101a}$$

$$P \to \boldsymbol{Q} \cdot P \cdot \boldsymbol{Q}^{\mathrm{T}}. \tag{101b}$$

Here, the arrow ($\to$) denotes changing the observer, and ( )^s is the symmetric part of a tensor of second order.

Now, in principle, we know, how physical quantities transform with changing the observer, and the question arises, what happens with the constitutive equations such as (95) and (96)? Because different observers considering the same material, see the same constitutive mapping the material axiom 2 states

4.2.2.1. Material Frame Indifference: Constitutive mappings are observer-invariant. In more detail material frame indifference means

1. Quantities of the state space and of the range of the constitutive equations transform as tensors with changing the observer.
2. The constitutive mapping is observer-invariant, that means, it is the same for all observers.

Consequently, the material velocity v and the antisymmetric part of the pressure tensor $(\nabla v)^a$ cannot be included in the state space, because these quantities do not transform as tensors under changing the observer. The constitutive mappings themselves may depend on the acceleration of the motion of the material with respect to an arbitrary frame of reference, but this dependence is also the same for all observers [32].

For (94)–(96), the axiom of material frame indifference induces

$$\boldsymbol{Q} \cdot P \cdot \boldsymbol{Q}^{\mathrm{T}} = \mathcal{P}(\varrho, \varepsilon, \boldsymbol{Q} \cdot \nabla\varrho, \boldsymbol{Q} \cdot \nabla\varepsilon, \boldsymbol{Q} \cdot (\nabla v)^s \cdot \boldsymbol{Q}^{\mathrm{T}}), \tag{102}$$

$$\boldsymbol{Q} \cdot q = \mathcal{Q}(\varrho, \varepsilon, \boldsymbol{Q} \cdot \nabla\varrho, \boldsymbol{Q} \cdot \nabla\varepsilon, \boldsymbol{Q} \cdot (\nabla v)^s \cdot \boldsymbol{Q}^{\mathrm{T}}). \tag{103}$$

Analogously, we obtain for the entropy flux density

$$\boldsymbol{Q} \cdot \boldsymbol{\Phi} \rightarrow \mathcal{F}(\varrho, \varepsilon, \boldsymbol{Q} \cdot \nabla \varrho, \boldsymbol{Q} \cdot \nabla \varepsilon, \boldsymbol{Q} \cdot (\nabla \boldsymbol{v})^s \cdot \boldsymbol{Q}^{\mathrm{T}}). \tag{104}$$

4.2.3. The balances

In the balance equations for momentum (15) and internal energy (29), we find the expressions $\nabla \cdot \boldsymbol{P}$ and $\nabla \boldsymbol{q}$ which we obtain from (95) and (96) by using the chain rule, as we discussed in (52). Thus, (15) and (29) result in

$$\varrho \dot{\boldsymbol{v}} + \frac{\partial \boldsymbol{P}}{\partial \varrho} \cdot \nabla \varrho + \frac{\partial \boldsymbol{P}}{\partial \varepsilon} \cdot \nabla \varepsilon + \frac{\partial \boldsymbol{P}}{\partial \nabla \varrho} : \nabla \nabla \varrho + \frac{\partial \boldsymbol{P}}{\partial \nabla \varepsilon} : \nabla \nabla \varepsilon + \frac{\partial \boldsymbol{P}}{\partial (\nabla \boldsymbol{v})^s} : \cdot \nabla (\nabla \boldsymbol{v})^s - \varrho \boldsymbol{f} = \boldsymbol{0}, \tag{105}$$

$$\varrho \dot{\varepsilon} + \frac{\partial \boldsymbol{q}}{\partial \varrho} \cdot \nabla \varrho + \frac{\partial \boldsymbol{q}}{\partial \varepsilon} \cdot \nabla \varepsilon + \frac{\partial \boldsymbol{q}}{\partial \nabla \varrho} : \nabla \nabla \varrho + \frac{\partial \boldsymbol{q}}{\partial \nabla \varepsilon} : \nabla \nabla \varepsilon + \frac{\partial \boldsymbol{q}}{\partial (\nabla \boldsymbol{v})^s} : \cdot \nabla (\nabla \boldsymbol{v})^s + \boldsymbol{P} : (\nabla \boldsymbol{v})^s - r = 0. \tag{106}$$

The dissipation inequality (93) results in

$$\varrho \left[\frac{\partial s}{\partial \varrho} \dot{\varrho} + \frac{\partial s}{\partial \varepsilon} \dot{\varepsilon} + \frac{\partial s}{\partial \nabla \varrho} \cdot (\dot{\nabla} \varrho) + \frac{\partial s}{\partial \nabla \varepsilon} \cdot (\dot{\nabla} \varepsilon) + \frac{\partial s}{\partial (\nabla \boldsymbol{v})^s} : ((\dot{\nabla} \boldsymbol{v})^s) \right]$$

$$+ \frac{\partial \boldsymbol{\Phi}}{\partial \varrho} \cdot \nabla \varrho + \frac{\partial \boldsymbol{\Phi}}{\partial \varepsilon} \cdot \nabla \varepsilon + \frac{\partial \boldsymbol{\Phi}}{\partial \nabla \varrho} : \nabla \nabla \varrho + \frac{\partial \boldsymbol{\Phi}}{\partial \nabla \varepsilon} : \nabla \nabla \varepsilon + \frac{\partial \boldsymbol{\Phi}}{\partial (\nabla \boldsymbol{v})^s} : \cdot \nabla (\nabla \boldsymbol{v})^s - \frac{r}{\Theta} \geq 0. \tag{107}$$

The three balance equations for mass (13a), for momentum (105), for internal energy (106), and the dissipation inequality (107) can be written in matrix form

$$\boldsymbol{A} \boldsymbol{y} = \boldsymbol{C} \tag{108a}$$

$$\boldsymbol{B} \boldsymbol{y} \geq \boldsymbol{D}. \tag{108b}$$

If we introduce the so-called *higher derivatives*, that are the derivatives of the state space variables (94)

$$\boldsymbol{y}^{\mathrm{T}} = (\dot{\varrho}, \dot{\varepsilon}, \dot{\boldsymbol{v}}, (\dot{\nabla} \varrho), (\dot{\nabla} \varepsilon), ((\dot{\nabla} \boldsymbol{v})^s), \nabla \nabla \varrho, \nabla \nabla \varepsilon, \nabla (\nabla \boldsymbol{v})^s), \tag{109}$$

($^{\mathrm{T}}$ denotes the transposed matrix), then the matrices $\boldsymbol{A}$ and $\boldsymbol{C}$ become

$$\boldsymbol{A} = \begin{pmatrix} 1 & 0 & \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{0} & \varrho \boldsymbol{1} & \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{0} & \frac{\partial \boldsymbol{P}}{\partial \nabla \varrho} & \frac{\partial \boldsymbol{P}}{\partial \nabla \varepsilon} & \frac{\partial \boldsymbol{P}}{\partial (\nabla \boldsymbol{v})^s} \\ 0 & \varrho & \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{0} & \boldsymbol{0} & \frac{\partial \boldsymbol{q}}{\partial \nabla \varrho} & \frac{\partial \boldsymbol{q}}{\partial \nabla \varepsilon} & \frac{\partial \boldsymbol{q}}{\partial (\nabla \boldsymbol{v})^s} \end{pmatrix}, \tag{110}$$

$$\boldsymbol{C} = \begin{pmatrix} -\varrho \boldsymbol{1} : (\nabla \boldsymbol{v})^s \\ \varrho \boldsymbol{f} - \dfrac{\partial \boldsymbol{P}}{\partial \varrho} \cdot \nabla \varrho - \dfrac{\partial \boldsymbol{P}}{\partial \varepsilon} \cdot \nabla \varepsilon \\ r - \boldsymbol{P} : (\nabla \boldsymbol{v})^s - \dfrac{\partial \boldsymbol{q}}{\partial \varrho} \cdot \nabla \varrho - \dfrac{\partial \boldsymbol{q}}{\partial \varepsilon} \cdot \nabla \varepsilon \end{pmatrix}. \tag{111}$$

The matrices $\boldsymbol{B}$ and $\boldsymbol{D}$ forming the dissipation inequality (93) and (108b) are

$$\boldsymbol{B} = \left(\varrho \frac{\partial s}{\partial \varrho} \quad \varrho \frac{\partial s}{\partial \varepsilon} \quad \boldsymbol{0} \quad \varrho \frac{\partial s}{\partial \nabla \varrho} \quad \varrho \frac{\partial s}{\partial \nabla \varepsilon} \quad \varrho \frac{\partial s}{\partial (\nabla \boldsymbol{v})^s} \quad \frac{\partial \boldsymbol{\Phi}}{\partial \nabla \varrho} \quad \frac{\partial \boldsymbol{\Phi}}{\partial \nabla \varepsilon} \quad \frac{\partial \boldsymbol{\Phi}}{\partial (\nabla \boldsymbol{v})^s} \right), \tag{112}$$

$$\boldsymbol{D} = \left(\frac{r}{\Theta} - \frac{\partial \boldsymbol{\Phi}}{\partial \varrho} \cdot \nabla \varrho - \frac{\partial \boldsymbol{\Phi}}{\partial \varepsilon} \cdot \nabla \varepsilon \right). \tag{113}$$

This simple example demonstrates, that because the balance equations and also the dissipation inequality are linear in the derivatives and ∇, we get, after having applied the chain rule, linear Eq. (108) in the higher derivatives $\boldsymbol{y}$. Because of the chosen large state space $\boldsymbol{A}, \boldsymbol{C}, \boldsymbol{B}$, and $\boldsymbol{D}$ are *state functions* defined on the state space (in this example on (94)), and $\boldsymbol{y}$ is beyond the state space variables. As we can see in the special example $\boldsymbol{A}, \boldsymbol{C}, \boldsymbol{B}$, and $\boldsymbol{D}$ contain derivatives of the constitutive equations with respect to the state variables. Consequently they depend on the constitutive equations which are not yet fixed.

4.3. Class of materials

We are not only interested in a special constitutive equation, but we are looking for a class of materials which is defined as follows

Definition. All constitutive equations defined on the chosen large state space satisfying the balance equations and the dissipation inequality determine the *class of materials*

In principle there are two possibilities excluding each other to find this class of materials:
1. For fixed $\boldsymbol{A}, \boldsymbol{C}, \boldsymbol{B}$, and $\boldsymbol{D}$ the dissipation inequality excludes certain $\boldsymbol{y}$, i.e. certain process directions in state space (represented by the higher derivatives) are not allowed.
2. The $\boldsymbol{A}, \boldsymbol{C}, \boldsymbol{B}$, and $\boldsymbol{D}$ have to be determined so that all process directions are possible, that means, whatever $\boldsymbol{y}$ may be, the dissipation inequality is always satisfied.

Without additional physical tools there is no possibility to decide which of both cases is the correct one. Consequently we need an amendment to the second law for deciding, how to exploit the dissipation inequality (108b) with respect to the balance equations (108a). This amendment to the second law is the *no-reversible direction axiom* which we will discuss now.

4.4. No-reversible direction axiom

According to 1. and 2. we have to look for a criterion, if constitutive properties can exclude process directions in state space, or if constitutive properties are restricted in such a way, that all process directions in state space are allowed. The no-reversible direction axiom enforces case (2), that means, that for all materials and to each fixed process direction in state space initial conditions are possible, so that the process runs along the prescribed process direction. A detailed discussion of that axiom is rather sophisticated [33], but here we will give a shortened version sufficient for clarifying the problem.

We consider an arbitrary material at a fixed state $Z(\boldsymbol{x}, t)$ [fixed position, fixed time, local]. The coefficients in the balance equations (108a) and the dissipation inequality (108b) are

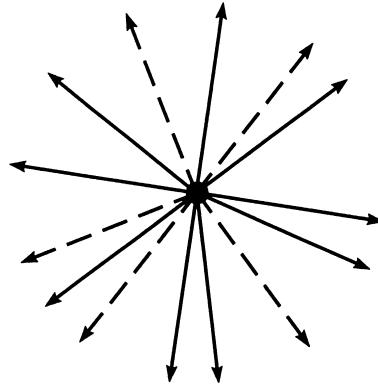$$\boldsymbol{A}(Z), \ \boldsymbol{C}(Z), \ \boldsymbol{B}(Z), \ \boldsymbol{D}(Z) \tag{114}$$

Fig. 3. At fixed state Z, there are directional, representing directions which are allowed ($\rightarrow$) or forbidden ($---$). 'Allowed' means in agreement with the dissipation inequality, and 'forbidden' is in contradiction to it.

We now presuppose that case (1) may be possible.

Assumption. At arbitrary, but fixed Z there are allowed and forbidden directions in state space (Fig. 3).

May $\boldsymbol{y}^1$ be an *allowed* process direction as in (109). Then according to (108)

$$\boldsymbol{A}\boldsymbol{y}^1 = \boldsymbol{C}, \quad \boldsymbol{B}\boldsymbol{y}^1 \geq \boldsymbol{D} \tag{115}$$

is valid. If $\boldsymbol{y}^2$ is a *forbidden* process direction, we have

$$\boldsymbol{A}\boldsymbol{y}^2 = \boldsymbol{C}, \quad \boldsymbol{B}\boldsymbol{y}^2 < \boldsymbol{D}. \tag{116}$$

We now prove the following

Proposition. *A consequence of* (115) *and* (116) *is the statement. There exist a reversible process direction* $\alpha\boldsymbol{y}^1 + (1-\alpha)\boldsymbol{y}^2$ *for each arbitrary, but fixed state. The real number α satisfies*

$$0 < \alpha := \frac{\boldsymbol{D} - \boldsymbol{B}\boldsymbol{y}^2}{\boldsymbol{B}(\boldsymbol{y}^1 - \boldsymbol{y}^2)} < 1. \tag{117}$$

Proof. Multiplying (115) with $\alpha > 0$ and (116) with $\beta > 0$, we obtain by addition of them

$$\boldsymbol{A}(\alpha\boldsymbol{y}^1 + \beta\boldsymbol{y}^2) = (\alpha + \beta)\boldsymbol{C}, \quad \alpha + \beta \doteq 1, \tag{118}$$

$$\boldsymbol{B}[\alpha\boldsymbol{y}^1 + (1 - \alpha)\boldsymbol{y}^2] \doteq \boldsymbol{D}. \tag{119}$$

By the demand $\alpha + \beta \doteq 1$ the process direction $\alpha\boldsymbol{y}^1 + (1-\alpha)\boldsymbol{y}^2$ in (118) satisfies the balance equations. α is determined by (119) from which immediately (117) follows. The inequalities in (117) are induced by (115) and (116). From (119) results that $\alpha\boldsymbol{y}^1 + (1-\alpha)\boldsymbol{y}^2$ is a reversible process direction. $\qquad\square$

By this proposition we proved the existence of at least one reversible process direction, if at an arbitrary non-equilibrium state Z of both kinds of allowed and forbidden process directions exists. By arguments of

continuity we conclude the existence, not only of a reversible direction, but also of a piece of a reversible trajectory. Because we are in non-equilibrium, we have to exclude such reversible trajectories by the *no-reversible-direction*.

Axiom ([34]). Except in equilibrium subspace reversible process directions in state space do not exist.

A consequence of this axiom is the fact that in non-equilibrium *all* process directions are either allowed or forbidden, but no non-equilibrium state exists with both kinds of process directions because then according to (117) a reversible process direction can be constructed. By the no-reversible direction axiom and the proposition (117) we have proved the

Proposition. *If Z is no trap, the inclusion*

$$\wedge y : A(Z)y = C(Z) \rightarrow B(Z)y \geq D(Z) \tag{120}$$

is valid, that means, all solutions of the balance equations satisfy the dissipation inequality.

This special formulation of the second law after having used the no-reversible direction axiom is named to Coleman and Mizel [35], who used (120) as an ad-hoc formulation.

By this proposition restrictions for the A, C, B, and D result. These restrictions characterize the class of materials we are looking for.

4.5. Coleman-Noll technique

Using this technique the inclusion (120) is enforced by

$$B(Z) = 0 \wedge D(Z) \leq 0, \tag{121}$$

$$A(Z) \text{ and } C(Z) \text{ are not restricted} \tag{122}$$

But this choice is only one possibility among other ones. The class of materials found by this 'technique' is in general too small.

4.6. Liu technique

We start out with

Proposition (Liu's Proposition [36,37]). *By use of the inclusion* (120) *the following statement is valid:* [36,37] *In large state spaces constitutive equations satisfy the Liu relations*

$$B(Z) = \lambda(Z)A(Z), \tag{123}$$

$$\lambda(Z)C(Z) \geq D(Z). \tag{124}$$

Here the state function λ is only unique, if A has its maximal rank. The entropy production density

$$\sigma := \lambda C - D \geq 0 \tag{125}$$

is independent of the process direction.

For the proof of Liu's proposition we refer to the literature [33]. A corollary results immediately from Liu's proposition:

Corollary. *For an arbitrary process direction $\boldsymbol{w}$ which need not satisfy the balance equations we have*

$$\boldsymbol{B}\boldsymbol{\omega} - \boldsymbol{\lambda}(\boldsymbol{A}\boldsymbol{\omega} - \boldsymbol{C}) \geq \boldsymbol{D}. \tag{126}$$

4.7. Example continued

4.7.1. Liu relations

For the example in Section 4.2 we calculated the coefficients of the balance equations and those of the dissipation inequality (110)–(113). According to Liu's proposition these coefficients have to satisfy Liu's relations (123) and (124). Because $\boldsymbol{A}$ has three rows we obtain for

$$\boldsymbol{\lambda} = (\lambda_1, \ \boldsymbol{\lambda}_2, \ \lambda_3). \tag{127}$$

Then (123) results in nine equations

$$\lambda_1 = \varrho \frac{\partial s}{\partial \varrho}, \tag{128}$$

$$\varrho \lambda_3 = \varrho \frac{\partial s}{\partial \varepsilon}, \tag{129}$$

$$\varrho \boldsymbol{\lambda}_2 = \boldsymbol{0}, \tag{130}$$

$$\boldsymbol{0} = \varrho \frac{\partial s}{\partial \nabla \varrho}, \tag{131}$$

$$\boldsymbol{0} = \varrho \frac{\partial s}{\partial \nabla \varepsilon}, \tag{132}$$

$$\boldsymbol{0} = \varrho \frac{\partial s}{\partial (\nabla \boldsymbol{v})^s}, \tag{133}$$

$$\boldsymbol{\lambda}_2 \cdot \frac{\partial \boldsymbol{P}}{\partial \nabla \varrho} + \lambda_3 \frac{\partial \boldsymbol{q}}{\partial \nabla \varrho} = \frac{\partial \boldsymbol{\Phi}}{\partial \nabla \varrho}, \tag{134}$$

$$\boldsymbol{\lambda}_2 \cdot \frac{\partial \boldsymbol{P}}{\partial \nabla \varepsilon} + \lambda_3 \frac{\partial \boldsymbol{q}}{\partial \nabla \varepsilon} = \frac{\partial \boldsymbol{\Phi}}{\partial \nabla \varepsilon}, \tag{135}$$

$$\boldsymbol{\lambda}_2 \cdot \frac{\partial P}{\partial (\nabla \boldsymbol{v})^s} + \lambda_3 \frac{\partial \boldsymbol{q}}{\partial (\nabla \boldsymbol{v})^s} = \frac{\partial \boldsymbol{\Phi}}{\partial (\nabla \boldsymbol{v})^s}, \tag{136}$$

By (111) and (113) the dissipation inequality (124) results in

$$-\lambda_1 \varrho \boldsymbol{1} : (\nabla \boldsymbol{v})^s + \boldsymbol{\lambda}_2 \cdot \left[\varrho \boldsymbol{f} - \frac{\partial \boldsymbol{P}}{\partial \varrho} \cdot \nabla \varrho - \frac{\partial \boldsymbol{P}}{\partial \varepsilon} \cdot \nabla \varepsilon \right]$$
$$+ \lambda_3 \left[r - \boldsymbol{P} : (\nabla \boldsymbol{v})^s - \frac{\partial \boldsymbol{q}}{\partial \varrho} \cdot \nabla \varrho - \frac{\partial \boldsymbol{q}}{\partial \varepsilon} \cdot \nabla \varepsilon \right] \geq \frac{r}{\Theta} - \frac{\partial \boldsymbol{\Phi}}{\partial \varrho} \cdot \nabla \varrho - \frac{\partial \boldsymbol{\Phi}}{\partial \varepsilon} \cdot \nabla \varepsilon. \tag{137}$$

We now exploit Liu's relations. According to the chosen state space (94) we obtain from (131) to (133) that the specific entropy depends only on mass density and on specific internal energy

$$s = \boldsymbol{S}(\varrho, \varepsilon). \tag{138}$$

From (128) and (129) follows immediately

$$\lambda_1 = \mathcal{L}_1(\varrho, \varepsilon), \tag{139a}$$

$$\lambda_3 = \mathcal{L}_3(\varrho, \varepsilon). \tag{139b}$$

Consequently the quantities s, λ_1, and λ_3 depend only on equilibrium variables also in non-equilibrium. This fact is connected to a statement which played historically an essential role. In linear irreversible thermodynamics the hypothesis of *local equilibrium* (see (64)) was formulated: The state space is spanned by the equilibrium variables also in non-equilibrium. According to (130) and (139), (134)–(136) result in

$$\frac{\partial}{\partial \nabla \varrho}[\boldsymbol{\Phi} - \lambda_3 \boldsymbol{q}] = \mathbf{0}, \quad \frac{\partial}{\partial \nabla \varepsilon}[\boldsymbol{\Phi} - \lambda_3 \boldsymbol{q}] = \mathbf{0}, \quad \frac{\partial}{\partial (\nabla \boldsymbol{v})^s}[\boldsymbol{\Phi} - \lambda_3 \boldsymbol{q}] = \mathcal{O} \tag{140}$$

from which follows immediately because of the chosen state space (94)

$$\boldsymbol{\Phi} - \lambda_3 \boldsymbol{q} = \mathcal{K}(\varrho, \varepsilon). \tag{141}$$

4.7.2. Material frame indifference

We now have all tools for exploiting (141) by the principle of material frame indifference. By use of (103), (104) and (139) for the original observer ($\boldsymbol{Q}=\boldsymbol{1}$) (141) writes:

$$\mathcal{F}(\varrho, \varepsilon, \nabla \varrho, \nabla \varepsilon, (\nabla \boldsymbol{v})^s) - \mathcal{L}_3(\varrho, \varepsilon)\mathcal{Q}(\varrho, \varepsilon, \nabla \varrho, \nabla \varepsilon, (\nabla \boldsymbol{v})^s) = \mathcal{K}(\varrho, \varepsilon). \tag{142}$$

Because of the principle of material frame indifference the mappings $\mathcal{F}$, $\mathcal{L}_3$, $\mathcal{Q}$, and $\mathcal{K}$ are observer invariant. Therefore, (141) written down for the changed observer runs as follows:

$$\mathcal{F}(\varrho, \varepsilon, \boldsymbol{Q} \cdot \nabla \varrho, \boldsymbol{Q} \cdot \nabla \varepsilon, \boldsymbol{Q} \cdot (\nabla \boldsymbol{v})^s \cdot \boldsymbol{Q}^{\mathrm{T}}) - \mathcal{L}_3(\varrho, \varepsilon)\mathcal{Q}(\varrho, \varepsilon, \boldsymbol{Q} \cdot \nabla \varrho, \boldsymbol{Q} \cdot \nabla \varepsilon, \boldsymbol{Q} \cdot (\nabla \boldsymbol{v})^s \cdot \boldsymbol{Q}^{\mathrm{T}})$$
$$= \mathcal{K}(\varrho, \varepsilon), \tag{143}$$

or according to (141)

$$\boldsymbol{Q} \cdot \boldsymbol{\Phi} - \lambda_3 \boldsymbol{Q} \cdot \boldsymbol{q} = \mathcal{K}(\varrho, \varepsilon), = \boldsymbol{Q} \cdot \mathcal{K}(\varrho, \varepsilon), \quad \wedge \boldsymbol{Q}. \tag{144}$$

Because this equation is valid for all $\boldsymbol{Q}$ (for all observers) we obtain by use of (141)

$$\mathcal{K}(\varrho, \varepsilon) = \mathbf{0} \rightarrow \boldsymbol{\Phi}(\varrho, \varepsilon, \nabla \varrho, \nabla \varepsilon, (\nabla \boldsymbol{v})^s) = \lambda_3(\varrho, \varepsilon)\boldsymbol{q}(\varrho, \varepsilon, \nabla \varrho, \nabla \varepsilon, (\nabla \boldsymbol{v})^s). \tag{145}$$

We now have to exploit the dissipation inequality (137) which according to (130) can be written in the form

$$-[\lambda_1 \varrho \boldsymbol{1} + \lambda_3 \boldsymbol{P}] : (\nabla \boldsymbol{v})^s - \left[\lambda_3 \frac{\partial \boldsymbol{q}}{\partial \varrho} - \frac{\partial \boldsymbol{\Phi}}{\partial \varrho}\right] \cdot \nabla \varrho - \left[\lambda_3 \frac{\partial \boldsymbol{q}}{\partial \varepsilon} - \frac{\partial \boldsymbol{\Phi}}{\partial \varepsilon}\right] \cdot \nabla \varepsilon + \left(\lambda_3 - \frac{1}{\Theta}\right) r \geq 0. \tag{146}$$

Because we have

$$\lambda_3 \frac{\partial \boldsymbol{q}}{\partial \varrho} - \frac{\partial \boldsymbol{\Phi}}{\partial \varrho} = \frac{\partial}{\partial \varrho}[\lambda_3 \boldsymbol{q} - \boldsymbol{\Phi}] - \boldsymbol{q} \frac{\partial \lambda_3}{\partial \varrho} = -\boldsymbol{q} \frac{\partial \lambda_3}{\partial \varrho}. \tag{147}$$

Here the last equation stems from (145). Because $\boldsymbol{P}$ was presupposed to be symmetric we obtain

$$\lambda_1 \varrho \boldsymbol{1} + \lambda_3 \boldsymbol{P} =: \boldsymbol{F}(\varrho, \varepsilon, \nabla \varrho, \nabla \varepsilon, (\nabla \boldsymbol{v})^s) = \boldsymbol{F}^\top. \tag{148}$$

Consequently we obtain by (147) and by the analogous equation for ε

$$\sigma := -[\lambda_1 \varrho \boldsymbol{1} + \lambda_3 \boldsymbol{P}] : (\nabla \boldsymbol{v})^s + \boldsymbol{q} \cdot \nabla \lambda_3(\varrho, \varepsilon) + \left(\lambda_3 - \frac{1}{\Theta}\right) r \geq 0. \tag{149}$$

For continuing the exploitation of the dissipation inequality we need the equilibrium conditions.

4.7.3. Equilibrium conditions

The preconceived opinion that in equilibrium all quantities are time independent and that there are no gradients turns quickly out as being wrong, what a simple example demonstrates. If there is a gravitation field, we have a gradient of mass density also in equilibrium, and if an observer is freely falling in this gravitation field, he sees that the mass density is changing in time although the system is in equilibrium. Consequently time independence and vanishing gradients cannot be used as equilibrium conditions, if no additional conditions are taken into account.

First of all we want to formulate equilibrium condition with respect to a special observer. Having done so, we can transform them to arbitrary observers.

Equilibrium conditions. A system is called *to be in equilibrium*, if there exist an observer $\Sigma^\dagger$ so that the velocity field is constant, all material time derivatives $(66)_2$, all non-convective fluxes (12), and all production and supply terms (10) are zero

$$\boldsymbol{v}^\dagger \equiv \boldsymbol{c} = \text{const}, \tag{150a}$$

$$\frac{\mathrm{d}^\dagger}{\mathrm{d}t} \equiv 0, \tag{150b}$$

$$\boldsymbol{q}^\dagger \equiv \boldsymbol{0}, \qquad \boldsymbol{\Phi}^\dagger \equiv \boldsymbol{0}, \tag{151}$$

$$r^\dagger \equiv 0, \qquad \sigma^\dagger \equiv 0. \tag{152}$$

Changing the observer from $\Sigma^\dagger$ to an arbitrary one all equilibrium conditions except (150a) remain valid, because the material time derivative is the observer independent time derivative of the rest observer, and non-convective fluxes are also observer independent. Consequently we obtain the equilibrium conditions for an arbitrary observer by replacing the † by $^{\text{eq}}$

$$\partial_t + \boldsymbol{v}^{\text{eq}} \cdot \nabla = \frac{\mathrm{d}^{\text{eq}}}{\mathrm{d}t} \equiv 0, \tag{153}$$

$$\boldsymbol{q}^{\text{eq}} \equiv \boldsymbol{0}, \tag{154a}$$

$$\boldsymbol{\Phi}^{\text{eq}} \equiv \boldsymbol{0}, \tag{154b}$$

$$r^{\text{eq}} \equiv 0, \tag{155a}$$

$$\sigma^{\text{eq}} \equiv 0. \tag{155b}$$

According to (101a) $(\nabla \boldsymbol{v})^s$ is a quantity which transforms homogeneously by changing the observer [38], the equilibrium conditions with regard to the dissipation inequality (149) are

$$(\nabla \boldsymbol{v})^{s\,\dagger} \equiv \boldsymbol{0} \rightarrow (\nabla \boldsymbol{v})^{s\,\mathrm{eq}} \equiv \boldsymbol{0}, \tag{156a}$$

$$\boldsymbol{q}^{\mathrm{eq}} \equiv \boldsymbol{0}, \tag{156b}$$

$$r^{\mathrm{eq}} = 0. \tag{156c}$$

Because of the following

Proposition ([39]). *If* $\boldsymbol{X} \cdot \boldsymbol{f}(\boldsymbol{X}) \geq 0$ *and* $\boldsymbol{f}$ *is continuous at* $\boldsymbol{X}=0$, *then* $\boldsymbol{f}(0)=\boldsymbol{0}$ *follows*, we obtain from (149) and from the equilibrium conditions (156) the following relations

$$\lambda_1^{\mathrm{eq}} \varrho \mathbf{1} + \lambda_3^{\mathrm{eq}} \boldsymbol{P}^{\mathrm{eq}} \equiv \boldsymbol{0}, \tag{157a}$$

$$(\nabla \lambda_3)^{\mathrm{eq}} \equiv \boldsymbol{0}, \tag{157b}$$

$$\lambda_3^{\mathrm{eq}} - \left(\frac{1}{\Theta}\right)^{\mathrm{eq}} \equiv 0. \tag{157c}$$

Because according to (139) the λ-s depend only on the equilibrium variables ϱ and ε we can omit the mark $^{\mathrm{eq}}$ for them.

4.7.4. Discussion

Introducing the large *state space* (94) for a five-fold problem

$$Z := (\varrho, \varepsilon, \nabla\varrho, \nabla\varepsilon, (\nabla\boldsymbol{v})^s), \tag{158}$$

we obtain by Liu technique a *specific entropy* (138) which is independent of the gradients even in non-equilibrium

$$s = \mathcal{S}(\varrho, \varepsilon). \tag{159}$$

According to (145) we obtain for the e*ntropy flux density*

$$\boldsymbol{\Phi}(\varrho, \varepsilon, \nabla\varrho, \nabla\varepsilon, (\nabla\boldsymbol{v})^s) = \lambda_3(\varrho, \varepsilon)\boldsymbol{q}(\varrho, \varepsilon, \nabla\varrho, \nabla\varepsilon, (\nabla\boldsymbol{v})^s). \tag{160}$$

The form of the *non-equilibrium pressure tensor* follows from (157a)

$$\boldsymbol{P}(Z) = p(\varrho, \varepsilon)\mathbf{1} + \boldsymbol{V}(Z), \tag{161}$$

with the static pressure

$$p(\varrho, \varepsilon) := -\frac{\lambda_1}{\lambda_3}\varrho, \tag{162}$$

and with the *dissipative part of the pressure tensor*

$$\boldsymbol{V}(Z), \tag{163a}$$

$$\boldsymbol{V}^{\mathrm{eq}} = \boldsymbol{0}. \tag{163b}$$

Because of (139b), (157b) results in

$$\frac{\partial \lambda_3}{\partial \varrho} \nabla \varrho + \frac{\partial \lambda_3}{\partial \varepsilon} \nabla \varepsilon = \mathbf{0}. \tag{164}$$

If now the internal energy is uniform in equilibrium, the same will follow for the mass density and vice versa

$$(\nabla \varepsilon)^{\text{eq}} = \mathbf{0} \leftrightarrow (\nabla \varrho)^{\text{eq}} = \mathbf{0}. \tag{165}$$

Otherwise the gradients of the mass density and of the internal energy are coupled by (164) also in equilibrium.

From (157c) we obtain for the *non-equilibrium temperature* Θ introduced in (93)

$$\frac{1}{\Theta}(Z) = \frac{1}{T}(\varrho \varepsilon) - \tau(Z), \qquad \tau^{\text{eq}} = 0, \tag{166}$$

with the reciprocal thermostatic temperature

$$\frac{1}{T}(\varrho, \varepsilon) := \lambda_3. \tag{167}$$

By (161), (162), (166), and (167) the entropy production density (149) results in

$$\sigma = -\frac{1}{T} \mathbf{V}(Z) : (\nabla \mathbf{v})^s + \mathbf{q}(Z) \cdot \nabla \frac{1}{T} + \tau(Z) r(Z) \geq 0. \tag{168}$$

The entropy balance Eq. (93) becomes by (161) and (145)

$$\varrho \dot{s} + \nabla \cdot \frac{\mathbf{q}}{T} = -\frac{1}{T} \mathbf{V} : (\nabla \mathbf{v})^s + \mathbf{q} \cdot \nabla \frac{1}{T} + \frac{r}{T}. \tag{169}$$

Inserting here the balance Eq. (13a), (15) and (29) we obtain

$$\varrho \dot{s} = \frac{\varrho}{T} \dot{\varepsilon} - \frac{p}{\varrho T} \dot{\varrho}, \tag{170}$$

which is consistent with (128) and (129).

Because of the equilibrium conditions (154a), (155a), (163b), (156a), (157b) and (166a) the non-linear constitutive equations can be written down

$$r(Z) = \mathbf{L}^{11}(Z) : (\nabla \mathbf{v})^s + \mathbf{L}^{12}(Z) \frac{1}{T} + L^{13}(Z) \tau, \tag{171}$$

$$\mathbf{q}(Z) = \mathcal{L}^{21}(Z) : (\nabla \mathbf{v})^s + \mathbf{L}^{22}(Z) \cdot \nabla \frac{1}{T} + \mathbf{L}^{23}(Z) \tau, \tag{172}$$

$$\mathbf{V}(Z) = \mathcal{L}^{31}(Z) : (\nabla \mathbf{v})^s + \mathcal{L}^{32}(Z) \cdot \nabla \frac{1}{T} + \mathbf{L}^{33}(Z) \tau. \tag{173}$$

This system of 100 constitutive equations

$$\begin{pmatrix} \mathbf{L}^{11}(Z) & \mathbf{L}^{12}(Z) & L^{13}(Z) \\ \mathcal{L}^{21}(Z) & \mathbf{L}^{22}(Z) & \mathbf{L}^{23}(Z) \\ \mathcal{L}^{31}(Z) & \mathcal{L}^{32}(Z) & \mathbf{L}^{33}(Z) \end{pmatrix} \tag{174}$$

determines the class of materials compatible with the chosen state space (94). The number of functions and their tensor orders are

	Tensor order	Number of functions
$\boldsymbol{L}^{11}(Z)$	2	6
$\boldsymbol{L}^{12}(Z)$	1	3
$L^{13}(Z)$	0	1
$\mathcal{L}^{21}(Z)$	3	18
$\boldsymbol{L}^{22}(Z)$	2	9
$\boldsymbol{L}^{23}(Z)$	1	3
$\mathcal{L}^{31}(Z)$	4	36
$\mathcal{L}^{32}(Z)$	3	18
$\boldsymbol{L}^{33}(Z)$	2	6

(175)

These 100 functions are not arbitrary, because they have to satisfy the dissipation inequality (168). After having chosen these functions compatible with the dissipation inequality the constitutive Eqs. (171)–(173) are inserted into the balance equations of mass, momentum, and internal energy together with the constitutive Eq. (162) for the static pressure $p(\varrho,\varepsilon)$. Then these balances have to be solved with respect to initial conditions and to constraints. The solution consists of the wanted fields $\varrho(\boldsymbol{x}, t)$, $\varepsilon(\boldsymbol{x}, t)$, $\boldsymbol{v}(\boldsymbol{x}, t)$. The thermostatic equation of state (162)

$$\frac{p(\varrho, \varepsilon)}{\varrho T} = -\lambda_1 = -\varrho \frac{\partial s}{\partial \varrho} \tag{176}$$

represents together with (129) and (167) a differential equation for the specific entropy.

Fundamentals of all these results are the choice of the state space, the dissipation inequality and its exploitation by Liu technique based on the no-reversible direction axiom, the principle of frame indifference, and the equilibrium conditions. By choice of the state space the class of materials follows straight forward by the exploitation of the dissipation inequality. Of course, in general the class of materials contains more than only one material, because one scalar inequality — the dissipation inequality — is a weak constraint. Consequently further ansatzes for the constitutive equations of a special material have to be made compatible with this class of materials.

Thus, the procedure for obtaining constitutive equations is clearly divided into two steps: constructing the class of materials by choosing a state space, and by making ansatzes to determine a special material of this class. In doing so, the first step cannot be omitted, because the result, that e.g. the specific entropy (159) does not depend on gradients of the state space, cannot be concluded by an ansatz. Also the form of the dissipation inequality (168) including the thermostatic temperature can only be derived by the first step of the procedure and not by an ansatz. Although the first step looks less effective — because here 100 functions remain arbitrary — this step is unrenouncable, because before making ansatzes we need the corresponding class of materials.

5. Mesoscopic theory

Beyond the quantities whose balance equations are mentioned above, complex materials need more variables for their unique description. Examples for these additional quantities are internal variables [40,11], order and damage parameters [41,42], Cosserat triads [43], directors [44,45], and alignment and conformation tensors [46,47]. In principle, there are two possibilities for including these additional quantities into the theoretical continuum description: one can introduce additional fields and their balance equations defined on space–time, or the additional quantities can be introduced as variables extending space–time to the so-called *mesoscopic space* on which now the balances of mass, momentum etc. are defined. The first possibility for describing complex materials by introducing additional fields has a long history in continuum theory. Starting out with the first contribution of the Cosserat brothers [48,49], the development of mechanics of generalized continua is lasting since today [50–52]. The second possibility introducing the mesoscopic space is called the *mesoscopic concept* [53] which stems historically from the theory of liquid crystals [41,44–46,54–56] by taking the orientation distribution function of the molecules into consideration [13,57,58].

5.1. Mesoscopic concept

As discussed above, the mesoscopic concept introduces the mesoscopic space

$$(\boldsymbol{m}, \boldsymbol{x}, t) \in \mathcal{M} \times \mathbb{R}^3 \times \mathbb{R}^1, \tag{177}$$

on which the balances are defined. Here, $\boldsymbol{m} \in \mathcal{M}$ is a set of mesoscopic variables which is an element of a suitable manifold $\mathcal{M}$ on which an integration can be defined.

Beyond the use of additional variables $\boldsymbol{m}$, the mesoscopic concept introduces a statistical element, the so-called *mesoscopic distribution function* (MDF) $f(\boldsymbol{m}, \boldsymbol{x}, t)$ generated by the different values of the mesoscopic variables of the molecules in a volume element

$$f(\boldsymbol{m}, \boldsymbol{x}, t) \equiv f(\cdot), \quad (\cdot) \equiv (\boldsymbol{m}, \boldsymbol{x}, t) \in \mathcal{M} \times \mathbb{R}^3 \times \mathbb{R}^1. \tag{178}$$

The MDF is defined on the mesoscopic space (177) describing the distribution of $\boldsymbol{m}$ in a volume element around $\boldsymbol{x}$ at time t, and therefore, it is always normalized

$$\int f(\boldsymbol{m}, \boldsymbol{x}, t) \, \mathrm{d}\mathcal{M} = 1. \tag{179}$$

Now, the fields such as mass density, momentum density, specific internal energy etc. are defined on the mesoscopic space. For distinguishing these fields from the usual macroscopic ones, we add the word 'mesoscopic'. Consequently, the *mesoscopic mass density* is defined by

$$\varrho(\cdot) := \varrho(\boldsymbol{x}, t) f(\cdot). \tag{180}$$

Here, $\varrho(\boldsymbol{x}, t)$ is the macroscopic mass density. By use of (179), we obtain

$$\varrho(\boldsymbol{x}, t) = \int \varrho(\boldsymbol{m}, \boldsymbol{x}, t) \, \mathrm{d}\mathcal{M}. \tag{181}$$

This equation shows that the system can be formally treated as a mixture by regarding all particles in a volume element of the same mesoscopic variables as one component of the system having the partial

mass density $\varrho(\cdot)$ [58]. Here, the 'component index' m is a continuous one. Because the mixture theory is well developed [59,60], *mesoscopic balance equations* can be written down very easily [61].

Other mesoscopic fields defined on the mesoscopic space are the *mesoscopic material velocity* $v(\cdot)$ of the particles belonging to the mesoscopic variable m at time t in a volume element around x, the *external mesoscopic acceleration* $k(\cdot)$, the *mesoscopic stress tensor* $T(\cdot)$, and the *mesoscopic heat flux density* $q(\cdot)$, etc.

5.2. Mesoscopic balances

5.2.1. Global mesoscopic balances

First of all, we write down a general global mesoscopic balance equation [13] which has the following form:

$$\frac{\mathrm{d}}{\mathrm{d}t} \int X(\cdot) \, \mathrm{d}\mathcal{M} \, \mathrm{d}^3 x = Z^{\mathrm{tot}}, \tag{182}$$

$$Z^{\mathrm{tot}} = \int [\Sigma(\cdot) + \nabla_x \cdot S(\cdot) + \nabla_m \cdot R(\cdot)] \, \mathrm{d}M \, \mathrm{d}^3 x. \tag{183}$$

Here, $X(\cdot)$ *is the balanced quantity*, $\Sigma(\cdot)$ the volume part of production and supply, and $S(\cdot)$ and $R(\cdot)$ are the fluxes through the surface in position space and on the manifold $\mathcal{M}$, respectively. The total change Z^{tot} is the sum of the production and the total flux over the boundary in mesoscopic space.

The global mesoscopic balance equation (182) can be transformed into a mesoscopic one which is local in position, time, and in the set of mesoscopic variables. For this purpose, we need a generalized *Reynolds transport theorem* (7) (without interfaces) [13]

$$\frac{\mathrm{d}}{\mathrm{d}t} \int \Phi(\cdot) \, \mathrm{d}\mathcal{M} \, \mathrm{d}^3 x = \int \left[\frac{\partial}{\partial t} \Phi(\cdot) + \nabla_x \cdot [v(\cdot)\Phi(\cdot)] + \nabla_m \cdot [u(\cdot)\Phi(\cdot)] \right] \mathrm{d}\mathcal{M} \, \mathrm{d}^3 x. \tag{184}$$

Here, the independent field $u(\cdot)$, defined on the mesoscopic space, describes the change in time of the set of mesoscopic variables: with respect to m, the *mesoscopic change velocity* $u(\cdot)$ is the analogue to the mesoscopic material velocity $v(\cdot)$ referring to x; if a molecule is characterized by (m, x, t), then for $\Delta t \to 0$, it is characterized by $(m+u(\cdot)\Delta t, x+v(\cdot)\Delta t, t+\Delta t)$. Besides the usual spatial gradient, the gradient with respect to the set of mesoscopic variables appears in (184) by which we can transform the global mesoscopic balance equation (182) as usual into a local one.

5.2.2. Local mesoscopic balances

Presupposing the global balances, we obtain by use of (184) local balance equations [62] which are defined on the mesoscopic space and which are therefore denoted as *local mesoscopic balances*. The general shape of these balances is

$$\frac{\partial}{\partial t} X(\cdot) + \nabla_x \cdot [v(\cdot)X(\cdot) - S(\cdot)] + \nabla_m \cdot [u(\cdot)X(\cdot) - R(\cdot)] = \Sigma(\cdot). \tag{185}$$

As already discussed in Section 2.2, the special balances are obtained by a special identification of $X(\cdot)$ by which an interpretation of $S(\cdot)$ and $R(\cdot)$ follows.

Especially, the mesoscopic balances of mass and momentum are [61]

$$\frac{\partial}{\partial t}\varrho(\cdot) + \nabla_x \cdot \{\varrho(\cdot)\boldsymbol{v}(\cdot)\} + \nabla_m \cdot \{\varrho(\cdot)\boldsymbol{u}(\cdot)\} = 0. \tag{186}$$

$$\frac{\partial}{\partial t}[\varrho(\cdot)\boldsymbol{v}(\cdot)] + \nabla_x \cdot [\boldsymbol{v}(\cdot)\varrho(\cdot)\boldsymbol{v}(\cdot) - \boldsymbol{T}^\top(\cdot)] + \nabla_m \cdot [\boldsymbol{u}(\cdot)\varrho(\cdot)\boldsymbol{v}(\cdot) - \mathcal{T}^\top(\cdot)] = \varrho(\cdot)\boldsymbol{k}(\cdot). \tag{187}$$

Here, $\boldsymbol{k}(\cdot)$ is the external acceleration, $\boldsymbol{T}^\top(\cdot)$ the transposed Cauchy stress tensor, and $\mathcal{T}^\top(\cdot)$ the transposed stress tensor on $\mathcal{M}$. Other mesoscopic balances can be found in [63].

According to the definition of the mesoscopic mass density (180), we obtain from the mesoscopic mass balance (186) a balance of the MDF $f(\cdot)$ by inserting its definition

$$\frac{\partial}{\partial t} f(\cdot) + \nabla_x \cdot [\boldsymbol{v}(\cdot)f(\cdot)] + \nabla_m \cdot [\boldsymbol{u}(\cdot)f(\cdot)] + f(\cdot)\left[\frac{\partial}{\partial t} + \boldsymbol{v}(\cdot) \cdot \nabla_x\right] \ln \varrho(\boldsymbol{x}, t) = 0. \tag{188}$$

Because this balance equation of the mesoscopic distribution function includes the macroscopic field of the mass density (181), it is not independent of the macroscopic mass balance defined on $\mathbb{R}^3$. Therefore, the mesoscopic rate equation for the MDF already contains macroscopic quantities influencing its time rate. This can be interpreted as an influence of a 'mean field' on the mesoscopic motion.

5.3. Order parameters and constitutive equations

Using the set $\boldsymbol{m}$ of mesoscopic variables, we can introduce the family of the macroscopic *fields of order parameters* which is defined by different moments of the MDF

$$1 = \int f(\cdot)\,\mathrm{d}\mathcal{M}, \tag{189}$$

$$\boldsymbol{A}(\boldsymbol{x}, t) := \int f(\cdot)\boldsymbol{m}\,\mathrm{d}\mathcal{M}, \tag{190}$$

$$\boldsymbol{a}(\boldsymbol{x}, t) := \int f(\cdot)\overline{\boldsymbol{mm}}\,\mathrm{d}\mathcal{M}, \tag{191}$$

$$\underline{\boldsymbol{a}}_4(\boldsymbol{x}, t) := \int f(\cdot)\overline{\boldsymbol{mmmm}}\,\mathrm{d}\mathcal{M}, \tag{192}$$

$$\underline{\boldsymbol{a}}_N(\boldsymbol{x}, t) := \int f(\cdot)\overline{\boldsymbol{m}\ldots N\ \text{times}\ldots\boldsymbol{m}}\,\mathrm{d}\mathcal{M}, \text{ etc.} \tag{193}$$

Here, the symbol $\overline{\quad}$ denotes as in (56) the traceless symmetric part of the tensor under the bracket [64].

These fields of order parameters describe macroscopically the mesoscopic state of the system introduced by $\boldsymbol{m}$ and its MDF $f(\cdot)$. Consequently, these fields are the link between the mesoscopic background description of the system and its extended description by additional macroscopic fields.

In a purely macroscopic phenomenological theory, the order parameters are internal variables, and relaxation equations for them are postulated [18,65]. Bearing in mind the mesoscopic background, equations of motion for these variables can be derived starting out with the differential equation (188) of the

MDF. We multiply (188) with $\overline{m_{\mu_1}\ldots m_{\mu_\ell}}$, integrate over the manifold $\mathcal{M}$ and obtain

$$\int \frac{\partial}{\partial t}[f(\cdot)\overline{m_{\mu_1} \ldots m_{\mu_\ell}}] \, d\mathcal{M}$$

$$+ \int \nabla_x \cdot [\boldsymbol{v}(\cdot)f(\cdot)\overline{m_{\mu_1} \ldots m_{\mu_\ell}}] \, d\mathcal{M} + \int \overline{m_{\mu_1} \ldots m_{\mu_\ell}} \nabla_m \cdot [\boldsymbol{u}(\cdot)f(\cdot)] \, d\mathcal{M}$$

$$+ \int f(\cdot)\overline{m_{\mu_1} \ldots m_{\mu_\ell}} \left[\frac{\partial}{\partial t} \ln \rho(\boldsymbol{x}, t) + \boldsymbol{v}(\cdot) \cdot \nabla_x \ln \rho(\boldsymbol{x}, t) \right] d\mathcal{M} = 0. \tag{194}$$

We suppose that the mesoscopic manifold $\mathcal{M}$ is time-independent. Then, the time derivative and the derivative with respect to position can be interchanged with the integration over $\mathcal{M}$. We split the mesoscopic velocity into the macroscopic velocity and the deviation from this average

$$\boldsymbol{v}(\cdot) = \boldsymbol{v}(\boldsymbol{x}, t) + \delta\boldsymbol{v}(\cdot). \tag{195}$$

Introducing the definition of the order parameters (193), we obtain

$$\frac{\partial}{\partial t}\underline{\boldsymbol{a}}_\ell + \nabla_x \cdot \left[\boldsymbol{v}(\boldsymbol{x}, t)\underline{\boldsymbol{a}}_\ell + \int (\delta\boldsymbol{v}(\cdot)f(\cdot)\overline{m_{\mu_1} \ldots m_{\mu_\ell}}) \, d\mathcal{M} \right]$$

$$+ \int \overline{m_{\mu_1} \ldots m_{\mu_\ell}} \nabla_m \cdot [\boldsymbol{u}(\cdot)f(\cdot)] \, d\mathcal{M} + \underline{\boldsymbol{a}}_\ell \left[\frac{\partial}{\partial t} \ln \rho(\boldsymbol{x}, t) + \boldsymbol{v}(\boldsymbol{x}, t) \cdot \nabla_x \ln \rho(\boldsymbol{x}, t) \right]$$

$$+ \nabla_x \ln \rho(\boldsymbol{x}, t) \cdot \int (\delta\boldsymbol{v}(\cdot)f(\cdot)\overline{m_{\mu_1} \ldots m_{\mu_\ell}}) \, d\mathcal{M} = 0. \tag{196}$$

For writing down constitutive equations, a *state space* has to be introduced [66]. In mesoscopic theories, there are different possibilities for doing that: a state space of purely mesoscopic variables, a mixed one consisting of mesoscopic and macroscopic variables, or one containing only macroscopic variables can be introduced. Because the constitutive theory of mesoscopic continuum physics is in development [67,68], its presentation today is out of the scope of this sketch.

6. Generic

During the last 15 years, a bracket formalism of dissipative continuum physics has been developed which is shortly denoted as GENERIC [1]. It has been applied to different problems of continuum thermodynamics, often in this way, that a well-known problem was reformulated in GENERIC formalism. The fundamental structure of GENERIC describing isolated discrete systems is determined by four building blocks [69–74]: the set $\boldsymbol{Z}$ of the variables of the system, two potentials (total energy and total entropy), two in general operator-valued matrices, and the state space. The equations of motion have the special GENERIC form

$$\dot{\boldsymbol{Z}} = \mathcal{L}\frac{\delta E^{\text{tot}}}{\delta \boldsymbol{Z}} + \mathcal{M}\frac{\delta S}{\delta \boldsymbol{Z}}. \tag{197}$$

Here, δ/δ denotes the functional derivative. In GENERIC, $\boldsymbol{Z}$ is the set of independent variables required for a complete description of the non-equilibrium system, E^{tot} and S are its total energy and its total entropy expressed in terms of the variables $\boldsymbol{Z}$, and $\mathcal{L}$ and $\mathcal{M}$ are the matrices mentioned above.

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[1] General equation for the non-equilibrium reversible–irreversible coupling.

Beyond (197), the complementary degeneracy conditions

$$\mathcal{L}\frac{\delta S(\mathbf{Z})}{\delta \mathbf{Z}} = \mathbf{0} \tag{198}$$

and

$$\mathcal{M}\frac{\delta E^{\text{tot}}(\mathbf{Z})}{\delta \mathbf{Z}} = \mathbf{0} \tag{199}$$

are satisfied by $\mathcal{L}$ and $\mathcal{M}$. The requirement that the gradient $\delta S(\mathbf{Z})/\delta \mathbf{Z}$ is in the null space of $\mathcal{L}$ expresses the reversible nature of the *L*-contribution to dynamics. The demand that the gradient $\delta E^{\text{tot}}(\mathbf{Z})/\delta \mathbf{Z}$ is in the null space of $\mathcal{M}$ expresses the conservation of the total energy by the *M*-contribution to dynamics. The two parts

$$\dot{\mathbf{Z}}^{\text{rev}} := \mathcal{L}\frac{\partial E^{\text{tot}}}{\partial \mathbf{Z}}, \qquad \dot{\mathbf{Z}}^{\text{irr}} := \mathcal{M}\frac{\partial S}{\partial \mathbf{Z}}, \tag{200}$$

contributing to the time evolution of $\mathbf{Z}$ generated by the total energy E^{tot} and by the total entropy S are called the *reversible and irreversible contributions* to dynamics.

A first possibility to construct $\mathcal{L}$ is to use the existence of a generator $G(\mathbf{Z})$ having the property

$$\mathcal{L}\frac{\delta G(\mathbf{Z})}{\delta \mathbf{Z}} = \mathbf{v} \cdot \frac{\partial \mathbf{Z}}{\partial \mathbf{x}}. \tag{201}$$

On the right-hand side, we find the velocity field $\mathbf{v}$ and the spatial gradient of the variables $\mathbf{Z}$.

General properties of $\mathcal{L}$ and $\mathcal{M}$ are discussed easily in terms of two symmetric and antisymmetric brackets

$$[A, B] := \left\langle \frac{\delta A}{\delta \mathbf{Z}}, \mathcal{L}\frac{\delta B}{\delta \mathbf{Z}} \right\rangle \doteq -[B, A] \rightarrow [A, A] = 0, \tag{202}$$

$$\{A, B\} := \left\langle \frac{\delta A}{\delta \mathbf{Z}}, \mathcal{M}\frac{\delta B}{\delta \mathbf{Z}} \right\rangle \doteq \{B, A\}, \tag{203a}$$

$$\{A, A\} \dot{\geq} 0. \tag{203b}$$

Here, $\langle , \rangle$ denotes a scalar product and A and B are sufficiently regular real-valued functionals on $\mathbf{Z}$. From (202), it follows that $\mathcal{L}$ is antisymmetric, whereas we have to demand the symmetry of $\mathcal{M}$ which cannot be concluded from (203). The antisymmetric bracket is presupposed to satisfy the Jacobi identity

$$[A, [B, C]] + [B, [C, A]] + [C, [A, B]] \doteq 0. \tag{204}$$

According to (197), (202) and (203), we can rewrite the time evolution of A as

$$\dot{A}(\mathbf{Z}) = \frac{\delta A}{\delta \mathbf{Z}} \cdot \dot{\mathbf{Z}} = [A, E^{\text{tot}}] + \{A, S\}. \tag{205}$$

For $\mathbf{Z} = \int \mathbf{Z} \mathrm{d}^3 x$, we immediately obtain

$$\dot{\mathbf{Z}} = [\mathbf{Z}, E^{\text{tot}}] + \{\mathbf{Z}, S\}. \tag{206}$$

According to (198), (199), (203b) and (205), we obtain the time rate of the total energy and that of the total entropy of the isolated system

$$\dot{E}^{\text{tot}} = [E^{\text{tot}}, E^{\text{tot}}] + \{E^{\text{tot}}, S\} = 0, \tag{207}$$

$$\dot{S} = [S, E^{\text{tot}}] + \{S, S\} = \{S, S\} \geq 0. \tag{208}$$

This inequality represents the second law of thermodynamics.

Conventional non-equilibrium thermodynamics starts out with the chosen set of variables, the balance equations, and the dissipation inequality. The entropy is a constitutive quantity which is restricted by the dissipation inequality. A special microscopic foundation of non-equilibrium thermodynamics may be desirable, but is not necessary for its performance.

GENERIC contains more free quantities than conventional non-equilibrium thermodynamics. According to (197), we have to know the set $\mathbf{Z}$ of the variables of the system and its total energy $E^{\text{tot}}(\mathbf{Z})$. Additionally, we need the matrices $\mathcal{L}$ and $\mathcal{M}$, perhaps from a microscopic background theory, and the entropy $S(\mathbf{Z})$ to obtain the equations of motion of $\mathbf{Z}$ given by (197). But usually, there is no microscopic background theory available, and we have to ask how to obtain $\mathcal{L}$, $\mathcal{M}$ and $S(\mathbf{Z})$ in that case.

There are in principle two different possibilities for interpreting the GENERIC formalism. Assuming that, starting out with a microscopic background theory, the setting of GENERIC formalism described above can be 'proved'. Then, the GENERIC form of the balance equations (197) is much more specific than those in conventional thermodynamics. They always can be decomposed into a reversible and an irreversible part (200) which are additive. Two matrices, a symmetric and an antisymmetric one, can be calculated from the microscopic background which determine the irreversible and the reversible part of the balances. There are two 'potentials', the total energy and the total entropy of the isolated system in consideration. The derivatives of the potentials to the system's variables determine their time rates according to (197). The total energy is given by the structure of the system; the total entropy is determined by differential equations for its first derivatives to the system's variables which are generated by one of the degeneracy conditions. The balance equations are derived microscopically.

The second interpretation does not share the optimistic view that a microscopic derivation of the GENERIC setting, although perhaps possible in general, can be afforded in each special case. From this point of view, the starting point of GENERIC is the same as in conventional thermodynamics: the known balance equations which have to be written in the form of the equations of motion (197), and now, we have to determine $\mathcal{L}$, $\mathcal{M}$ and $S(\mathbf{Z})$. That is not uniquely possible in general, because there are not enough macroscopic equations for determining these quantities. But this non-uniqueness does not influence the physical results, because the input comprises only the conventional balance equations and their GENERIC splitting (200) which is enforced by the microscopic background. Therefore, the proof that GENERIC can be derived in principle from such a microscopic background is absolutely necessary for its convincing application.

But if we assume that the GENERIC setting can be founded microscopically, then we have a more detailed input into non-equilibrium thermodynamics: the reversible–irreversible splitting of the balances and the unknown degeneracy conditions in conventional thermodynamics. In this case, GENERIC may be easier to handle than the conventional theory.

Acknowledgements

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