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Terminology and classification of special versions of continuum thermodynamics

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Contemporary controversies concerning the foundations of thermodynamics are rooted not only in different sets of concepts and principles, but also in terminology and semantics. Here, some remarks are made for a possible unifying thermodynamical terminology. We deal only with the continuum formulation of different non-equilibrium thermodynamical theories [1]-[4]. Introducing the concepts of balance equations, quantities describing a thermodynamical system, state vector, basic or wanted fields, internal variables, constitutive mappings (with some remarks on the methods to obtain them), we classify special versions of non-equilibrium continuum thermodynamics by the choice of their state spaces together with different basic assumptions.

In a field formulation of thermodynamics, the quantities describing a thermodynamical system are in general n time-dependent fields $\mathbf{a}(\mathbf{x},t)$ which satisfy *balance equations* [1]-[3]

$$\partial_t(\rho\mathbf{a}) + \nabla\cdot(\mathbf{v}\rho\mathbf{a} + \mathbf{\Phi}) = \mathbf{\Sigma}. \tag{1}$$

Here $\rho(\mathbf{x},t)$ is the field of the mass density, $\mathbf{v}(\mathbf{x},t)$ the material velocity, $\mathbf{\Phi}$ the conductive fluxes belonging to $\mathbf{a}$, and $\mathbf{\Sigma}$ the sum of the production and supply terms of $\mathbf{a}$. In general, the $\mathbf{a}$ are not the *basic fields* (wanted fields) which have to be determined for solving the problem under consideration. The balance equations (1) are undetermined, because there are n equations for more than n quantities. Consequently, for obtaining a closed system of differential equations, we need *constitutive equations*, additional equations defining the *constitutive fields* which depend on the *state space* $\mathbf{z}(\mathbf{x},t)$ which is defined as the domain of the constitutive mappings. In general, the variables of the state space are different from those of the wanted fields. Inserting constitutive equations into the balance equations, we obtain the so-called *balances on the state space* which is a system of differential equations often highly non-linear, whose order depends on the constitutive equations.

The balances on the state space govern the evolution of the wanted fields which have to satisfy the *second law of thermodynamics*. In continuum thermodynamics this is represented by the (Clausius -Duhem) *dissipation inequality*. The choice of the state space determines the *class of materials*. The state space may include the gradients

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and the time derivatives of the wanted fields and *additional variables* $\boldsymbol{\alpha}(\mathbf{x},t)$ for which also additional *evolution equations*, often called *rate equations*, are necessary

$$\partial_t(\rho\boldsymbol{\alpha}) + \nabla\cdot(\mathbf{v}\rho\boldsymbol{\alpha} + \boldsymbol{\Psi}) = \boldsymbol{\Xi}. \tag{2}$$

Here $\boldsymbol{\Psi}$ is the field of the conductive flux belonging to $\boldsymbol{\alpha}$ and $\boldsymbol{\Xi}$ is the sum of the production and supply terms. At one point in the state space, the values of the basic fields and their corresponding gradients and time derivatives are independent variables. If in (2) the additional variables $\boldsymbol{\alpha}$ are the so called *internal variables*, we need a (microscopic or molecular) model for their interpretation [2].

The form of the constitutive equations can be obtained by using material axioms. Because constitutive mappings are defined on the state space, differentiations with respect to space and time have to be performed by use of the chain rule. After having performed these differentiations, the system of balances on the state space and the dissipation inequality can be represented in the following matrix formulation

$$\mathbf{A}\cdot\mathbf{Y} = \mathbf{C}, \qquad \mathbf{B}\cdot\mathbf{Y} \geq \mathbf{D}. \tag{3}$$

The column $\mathbf{Y}$ contains the *higher derivatives* of state space variables which are not included in the state space. The other matrices $\mathbf{A},\mathbf{B},\mathbf{C}$ and $\mathbf{D}$ contain constitutive state functions depending on the state space variables only [4].

The second law of thermodynamics (SL), represented by the dissipation inequality $(3)_2$, is in field formulation local in time and position and runs as follows:

The entropy production density $\sigma := \mathbf{B}\cdot\mathbf{Y} - \mathbf{D} \geq 0$ *is not negative at each position for all times .*

This statement is not complete, because the balances on the state space $(3)_1$ can be differently exploited by the dissipation inequality $(3)_2$ [1]-[3]:

i) all solutions of the balance equations have to satisfy the SL, or
ii) there are solutions of the balance equations which satisfy the SL, and others which do not.

Statement i) means, that the constitutive equations have to be restricted in such a way that all solutions of the balance equations satisfy the SL which is *material-selective* in this case. Statement ii) means, that there are solutions of the balance equations which do not exist in nature, because they do not satisfy the SL which is now *process-selective* interpreted. Both the statements are excluding each other. For deciding which of them is the correct one, we need an *amendment to the second law*:

Except in equilibrium, there are no reversible process directions in the state space.

Using this amendment, it is possible to prove the *Coleman-Mizel formulation of the second law* (statement i))

$$\mathbf{A}\cdot\mathbf{Y} = \mathbf{C} \quad\Longrightarrow\quad \mathbf{B}\cdot\mathbf{Y} \geq \mathbf{D} \quad \text{is valid for all } \mathbf{Y}. \tag{4}$$

By this induction, restrictions arise for the matrices $\mathbf{A},\mathbf{C},\mathbf{B}$ and $\mathbf{D}$ which characterize the class of materials we are looking for.

There are two techniques to exploit (4), the *Coleman-Noll technique* and the *Liu procedure*. Correctly applied, both the procedures yield the same result for lower dimensional state spaces (see [5]):

In large state spaces, there exist state space functions $\mathbf{\Lambda}(\mathbf{z})$ so that the constitutive equations satisfy the following relations

$$\mathbf{\Lambda}(\mathbf{z}) \cdot \mathbf{A}(\mathbf{z}) = \mathbf{B}(\mathbf{z}), \qquad \mathbf{\Lambda}(\mathbf{z}) \cdot \mathbf{C}(\mathbf{z}) \geq \mathbf{D}(\mathbf{z}). \tag{5}$$

The row of state functions $\mathbf{\Lambda}$ is only unique, if $\mathbf{A}(\mathbf{z})$ is of maximal rank. The entropy production density σ is independent of the higher derivatives $\mathbf{Y}$ and is therefore a function of state.

Balances and constitutive equations have to satisfy transformation properties by changing the observer described by Euclidean transformations in non-relativistic theories. Because no observer is distinguished, these relations are *observer-invariant*, that means, they are of the same shape for arbitrary observers [6]. Quantities which transform as tensor components under changing the observer are called *objective*. Beyond the SL, the observer-invariant constitutive equations have to satisfy the principle of *material frame indifference*. This principle states [6]:

i) constitutive mappings are observer-independent,
ii) state space variables and quantities in the range of the constitutive mappings transform as tensors under changing the observer,
iii) constitutive mappings depend on the motion with respect to an arbitrarily chosen standard frame of reference [6], but
iv) uniform motions of the material with respect to the standard frame of reference do not influence constitutive properties.

We now classify some special versions of non-equilibrium thermodynamics: In *thermodynamics of irreversible processes* (TIP) the following assumptions are made: The state space is the equilibrium subspace. This presupposition is called the *hypothesis of local equilibrium*, thus banishing gradients and time derivatives from the state space. The entropy flux density is given by $\mathbf{\Phi} = \mathbf{q}/T$ in case of one component materials. Also in non-equilibrium, the time rate of the entropy satisfies the equilibrium Gibbs fundamental equation. The entropy production has the form of a sum of products of fluxes J_i and forces X_i , $\sigma = \Sigma_i J_i X_i \geq 0$. Fluxes and forces are connected by linear constitutive equations resulting in a quadratic form for the entropy production $\sigma = \sum L_{ik} X_i X_k$. The coefficients L_{ik} form a positive definite, in general not symmetric matrix according to the SL.

The assumptions made in *rational thermodynamics* are different from those of the TIP: Entropy and temperature are primitive concepts, that means, nothing is said about how to define (or to measure) these quantities in non-equilibrium. The fields of specific entropy $s(\mathbf{x}, t)$, entropy flux density $\mathbf{\Phi}(\mathbf{x}, t)$ and entropy production density $\sigma(\mathbf{x}, t)$ are assumed as constitutive quantities which have to satisfy the dissipation inequality which is exploited by Coleman/Noll or Liu procedure. The principle of equipresence states that all constitutive quantities depend on the same set of variables, thus introducing the state space. The constitutive equations are given by the representation theorems beloging to the chosen state space.

Extended thermodynamics is characterized by the following assumptions: Dissipative fluxes are included in the state space, but no gradients or time derivatives appear. We distinguish between two forms of extended thermodynamics which differ mainly in exploiting the dissipation inequality and in treating Gibbs fundamental equation [1]-[4]: *Rational extended thermodynamics* as further development of rational thermodynamics, exploits the dissipation inequality by use of Liu or Coleman and Noll technique. *Extended irreversible thermodynamics* stemming from TIP, exploits the dissipation inequality as it is usual in TIP . Because dissipative fluxes are used in extended thermodynamics, additional balance equations for fluxes are needed, may be as ansatzes or in the framework of a class of materials. It can be proved that using the state space of extended thermodynamics, the balance equations on the state space form a hyperbolic system of partial differential equations that only allow for finite speeds of disturbances.

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