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An Amendment to the Second Law

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Introduction

In continuum thermodynamics the usual form of the Second Law (SL) is local in time and position and runs as follows: *The entropy production density is not negative at each position for all times.* This statement is not unique, because after having inserted the constitutive equations into the balance equations we can differently interpret as follows:
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.*
The consequences of these two interpretations of the SL are totally different. Statement i) means that the constitutive equations have to be restricted in such a way that all mathematical solutions of the balance equations must satisfy the SL. Consequently i) means restriction of material properties by the SL. Statement ii) means that there are solutions of the balance equations which do not exist in nature because they do not satisfy the SL. Consequently ii) means restriction of processes by the SL.

Obviously only one of the statements i) and ii) can be true, but which of them? This question can not be decided by the formulation of the SL given above, because the terms "process" and "constitutive equation" are not included in this formulation. Thus we need some more knowledge for deciding what is the true statement, i) or ii). This "some more" is an amendment to the SL, because it has to contain more than in SL is stated.

In the following it is derived that the (nearly self-evident, but never formulated) amendment

There are no reversible process directions in non-equilibrium allows to prove statement i). As a consequence the entropy production density is a function of state. The connection between this amendment and the stronger CM-formulation of the second law is discussed. Additional constraints for the constitutive equations, called Liu equations and residual dissipation inequality, are consequences of the amendment.

1. Balances and Constitutive Equations

The M *basic fields* of continuum thermodynamics $u_A(\boldsymbol{x},t)$ satisfy balance equations [8], [3]

$$\partial_t u_A + \partial_j \Phi^j_A = r_A, \qquad A = 1,2,....,M. \tag{1}$$

Here the $\Phi^j_A(\boldsymbol{x},t)$ and the $r_A(\boldsymbol{x},t)$ are the fluxes and the supply and production terms belonging to the $u_A(\boldsymbol{x},t)$. This system of partial differential equations of first order for the basic fields can only be solved, if the fluxes and the supply and production terms are known by constitutive equations [8]. But these constitutive equations are only indirectly given as fields, because the fluxes and the supply and production terms depend on other fields $\boldsymbol{z}(\boldsymbol{x},t)$, called the *state* of the system.

As a simple example we consider the field of the heat flux density $\boldsymbol{q}(\boldsymbol{x},t)$ which depends on the temperature gradient $\partial_j T(\boldsymbol{x},t)$, so that we have

$$\boldsymbol{q}(\boldsymbol{x},t) = \mathcal{Q}(\partial_j T(\boldsymbol{x},t),....). \tag{2}$$

Here $\partial_j T(\boldsymbol{x},t)$ belongs to the state of the system.

Consequently, by dependence of the constitutive equations on other fields than the basic ones $u_A(\boldsymbol{x},t)$, we have to introduce the *state space* [4] which in general can be chosen almost freely. Here we restrict ourselves to a 5ω-dimensional state space consisting of ω fields $z_\alpha(\boldsymbol{x},t)$ and their first derivatives

$$\boldsymbol{z} = (z_\alpha, \partial_j z_\alpha, \partial_t z_\alpha)(\boldsymbol{x},t), \qquad \alpha = 1,2,...,\omega. \tag{3}$$

Thus we have to know the constitutive equations

$$\Phi^j_A = \mathcal{F}^j_A(\boldsymbol{z}(\boldsymbol{x},t)), \tag{4}$$

$$r_A = \mathcal{R}_A(\boldsymbol{z}(\boldsymbol{x},t)), \tag{5}$$

$$u_A = \mathcal{U}_A(\boldsymbol{z}(\boldsymbol{x},t)). \tag{6}$$

According to these constitutive equations the partial derivatives ∂_j in (1) have to be performed by use of the chain rule

$$\partial_j \Phi^j_A = \frac{\partial \mathcal{F}^j_A}{\partial \boldsymbol{z}} \cdot \partial_j \boldsymbol{z}. \tag{7}$$

Inserting the constitutive equations (4) - (6) into (1) we obtain

$$\frac{\partial \mathcal{U}_A}{\partial \boldsymbol{z}} \cdot \partial_t \boldsymbol{z} = -\frac{\partial \mathcal{F}^j_A}{\partial \boldsymbol{z}} \cdot \partial_j \boldsymbol{z} + \mathcal{R}_A(\boldsymbol{z}). \tag{8}$$

Using (3) we obtain from (8) differential equations for the $z_\alpha(\boldsymbol{x}, t)$ which we call the *balances on state space*

$$\begin{aligned} &\frac{\partial \mathcal{U}_A}{\partial z_\alpha} \partial_t z_\alpha + \frac{\partial \mathcal{U}_A}{\partial \partial_t z_\alpha} \partial_t \partial_t z_\alpha + \frac{\partial \mathcal{U}_A}{\partial \partial_k z_\alpha} \partial_t \partial_k z_\alpha + \\ &+ \frac{\partial \mathcal{F}^j_A}{\partial z_\alpha} \partial_j z_\alpha + \frac{\partial \mathcal{F}^j_A}{\partial \partial_t z_\alpha} \partial_j \partial_t z_\alpha + \frac{\partial \mathcal{F}^j_A}{\partial \partial_k z_\alpha} \partial_j \partial_k z_\alpha = \mathcal{R}_A(z_\beta, \partial_j z_\beta, \partial_t z_\beta). \end{aligned} \tag{9}$$

After having introduced the constitutive equations into the balance equations (1) we obtain the balances on the state space (9) which have to be solved by posing suitable constraints and initial conditions. Especially the initial conditions depend on the choice of the state space (3). Some possibilities of choosing the state space are discussed in the next section.

2. Different Types of State Spaces

The easiest case is, if the basic fields themselves span the state space [1]

$$\boldsymbol{z} = (u_A(\boldsymbol{x}, t)). \tag{10}$$

The balances on the state space (9) become in this case

$$\partial_t u_A + \frac{\partial \mathcal{F}^j_A}{\partial u_B} \partial_j u_B = \mathcal{R}_A(u_C). \tag{11}$$

Other choices of state spaces are

$$\boldsymbol{z} = (u_A, \partial_j u_A)(\boldsymbol{x}, t), \tag{12}$$

[1] This is the state space of Extended Thermodynamics, because in this case $\boldsymbol{q}(\boldsymbol{x}, t)$ belongs to the basic fields.

$$\boldsymbol{z} = (u_A, \partial_j u_A, \partial_t u_A)(\boldsymbol{x}, t), \tag{13}$$

$$\boldsymbol{z} = (u_B, z_\beta, \partial_j u_B, \partial_j z_\beta, \partial_t z_\beta)(\boldsymbol{x}, t). \tag{14}$$

Especially the balances on the state space (13) which we consider here are

$$\partial_t u_A + \frac{\partial \mathcal{F}_A^j}{\partial u_B}\partial_j u_B + \frac{\partial \mathcal{F}_A^j}{\partial \partial_t u_B}\partial_j \partial_t u_B + \frac{\partial \mathcal{F}_A^j}{\partial \partial_k u_B}\partial_j \partial_k u_B = \mathcal{R}_A(u_C, \partial_j u_C, \partial_t u_C). \tag{15}$$

Up to now the second law was not taken into account which is formulated in the next section.

3. Dissipation Inequality

In continuum thermodynamics the second law is represented by the dissipation inequality [9]

$$\partial_t(\rho s) + \partial_j(v^j \rho s + \Psi^j) = \sigma \geq 0. \tag{16}$$

Here the specific entropy s and the entropy flux density Ψ^j are constitutive quantities

$$s = \mathcal{S}(\boldsymbol{z}(\boldsymbol{x}, t)), \qquad \Psi^j = \mathcal{P}(\boldsymbol{z}(\boldsymbol{x}, t)). \tag{17}$$

Inserting these constitutive equations into (16) we obtain the *dissipation inequality on the state space*

$$\begin{aligned} &\frac{\partial \rho s}{\partial z_\alpha}\partial_t z_\alpha + \frac{\partial \rho s}{\partial \partial_t z_\alpha}\partial_t \partial_t z_\alpha + \frac{\partial \rho s}{\partial \partial_k z_\alpha}\partial_t \partial_k z_\alpha + \\ &+ \frac{\partial (v^j \rho s + \Psi^j)}{\partial z_\alpha}\partial_j z_\alpha + \frac{\partial (v^j \rho s + \Psi^j)}{\partial \partial_t z_\alpha}\partial_j \partial_t z_\alpha + \frac{\partial (v^j \rho s + \Psi^j)}{\partial \partial_k z_\alpha}\partial_j \partial_k z_\alpha = \sigma. \end{aligned} \tag{18}$$

The problem now is to solve the balances on the state space (9) taking into account the dissipation inequality (18). By posing initial conditions and constraints a solution of (9) may satisfy (18) everywhere or may not. If it does not satisfy (18) for all $(\boldsymbol{x}, t)$ this solution of (9) does not exist in nature because the second law is violated. Now it is very cumbersome to solve (9), and after having got a solution to prove, that this solution satisfies the second law (18) for all $(\boldsymbol{x}, t)$. Therefore we need a necessary and sufficient condition to recognize, whether a solution of (9) does satisfy (18) or does not. This condition is easy to obtain, as we will demonstrate later.

4. The Higher Derivatives

The balances and the dissipation inequality on the state space have a special shape which is now discussed. After having inserted the constitutive equations and performed the differentiations ∂_t and ∂_j in the balance equations (1) and in the dissipation inequality (16) 10ω so-called *higher derivatives*

$$\boldsymbol{y} = (\partial_t \partial_t z_\alpha, \partial_t \partial_k z_\alpha, \partial_j \partial_k z_\alpha)(\boldsymbol{x}, t) \tag{19}$$

appear in (9) and (18). Because the coefficients in (9) and (18), and (17) do not depend on the higher derivatives according to (4) - (6), these relations are linear in the higher derivatives. Thus the balances on the state space (9) and (18) can be written briefly as [5]

$$A(\boldsymbol{z}) \cdot \boldsymbol{y} = \boldsymbol{C}(\boldsymbol{z}), \quad \boldsymbol{B}(\boldsymbol{z}) \cdot \boldsymbol{y} \geq D(\boldsymbol{z}). \tag{20}$$

Here the coefficients $A(\boldsymbol{z}(\boldsymbol{x}, t))$ and $\boldsymbol{B}(\boldsymbol{z}(\boldsymbol{x}, t))$ are given by the derivatives of the constitutive equations

$$\frac{\partial \mathcal{U}_A}{\partial \partial_t z_\alpha}, \frac{\partial \mathcal{U}_A}{\partial \partial_k z_\alpha}, \frac{\partial \mathcal{F}^j_A}{\partial \partial_t z_\alpha}, \frac{\partial \mathcal{F}^j_A}{\partial \partial_k z_\alpha},$$
$$\frac{\partial \rho s}{\partial \partial_t z_\alpha}, \frac{\partial \rho s}{\partial \partial_k z_\alpha}, \frac{\partial (v^j \rho s + \Psi^j)}{\partial \partial_t z_\alpha}, \frac{\partial (v^j \rho s + \Psi^j)}{\partial \partial_k z_\alpha}.$$

The other coefficients $\boldsymbol{C}(\boldsymbol{z}(\boldsymbol{x}, t))$ and $D(\boldsymbol{z}(\boldsymbol{x}, t))$ include all other terms which are not multiplied by higher derivatives.

We now consider (global) initial conditions suitable to the balances (9) on the state space. Because (9) is a system of differential equations of second order in time the initial conditions are

$$z_\alpha(\boldsymbol{x}, t_0) = \Lambda_\alpha(\boldsymbol{x}), \qquad \partial_t z_\alpha(\boldsymbol{x}, t_0) = \Xi_\alpha(\boldsymbol{x}). \tag{21}$$

From these initial conditions follows immediately by differentiation to ∂_j

$$\partial_j z_\alpha(\boldsymbol{x}, t_0) = \partial_j \Lambda_\alpha(\boldsymbol{x}), \qquad \partial_j \partial_k z_\alpha(\boldsymbol{x}, t_0) = \partial_j \partial_k \Lambda_\alpha(\boldsymbol{x}), \tag{22}$$

$$\partial_j \partial_t z_\alpha(\boldsymbol{x}, t_0) = \partial_j \Xi_\alpha(\boldsymbol{x}). \tag{23}$$

The balance equations (9) determine the ω second time derivatives $\partial_t \partial_t z_\alpha(\boldsymbol{x}, t_0)$, if the matrix $\partial \mathcal{U}_A / \partial \partial_t z_\alpha$ is regular. Consequently not all the higher derivatives are determined by the balance equations $(20)_1$ -here a system of linear algebraic equations- because 9ω of the 10ω higher derivatives are given by the initial conditions $\boldsymbol{z}(\boldsymbol{x}, t_0)$. Thus the kernel of $A(\boldsymbol{z})$ is non-trivial, and we have k linearly independent $\boldsymbol{y}^k$ satisfying $(20)_1$

$$A(\boldsymbol{z}) \cdot \boldsymbol{y}^k = \boldsymbol{C}(\boldsymbol{z}), \quad k = 1, 2, ..., \ \text{dimker} \leq 10\omega. \tag{24}$$

We now consider (local) initial conditions at an arbitrary, but fixed event $(\boldsymbol{x}_0, t_0)$

$$z_\alpha(\boldsymbol{x}_0, t_0) = \zeta_\alpha, \quad \partial_t z_\alpha(\boldsymbol{x}_0, t_0) = \xi_\alpha, \tag{25}$$

and

$$\partial_j z_\alpha(\boldsymbol{x}_0, t_0) = \mu_{j\alpha}, \quad \partial_j \partial_k z_\alpha(\boldsymbol{x}_0, t_0) = \nu_{jk\alpha}, \quad \partial_j \partial_t z_\alpha(\boldsymbol{x}_0, t_0) = \kappa_{j\alpha}. \tag{26}$$

The 14ω real numbers ζ_α,...,$\kappa_{j\alpha}$ can be chosen freely. According to (21) to (23) these chosen numbers correspond to a a special global initial condition

$$\Lambda_\alpha(\boldsymbol{x}_0) = \zeta_\alpha, \quad \Xi_\alpha(\boldsymbol{x}_0) = \xi_\alpha, \tag{27}$$

$$\partial_j \Lambda_\alpha(\boldsymbol{x}_0) = \mu_{j\alpha}, \quad \partial_j \partial_k \Lambda_\alpha(\boldsymbol{x}_0) = \nu_{jk\alpha}, \quad \partial_j \Xi_\alpha(\boldsymbol{x}_0) = \kappa_{j\alpha}. \tag{28}$$

Changing the values of these 14ω real numbers independently of each other, i.e. changing the local initial conditions, means that also the global initial conditions have to be changed according to (27) and (28).

Now we can formulate the necessary and sufficient condition mentioned above at the end of section 3: Instead of solving the balances (9) on the state space globally and inserting them into the dissipation inequality (18) for testing the sign, we can can solve the algebraic problem (24) for arbitrary $(\boldsymbol{x}_0, t_0)$ and insert its (not unique) solution into

$$\boldsymbol{B}(\boldsymbol{z}) \cdot \boldsymbol{y}^k \geq D(\boldsymbol{z}) \tag{29}$$

for testing the sign. Consequently the algebraic (local) version (20) of the balance equations and of the dissipation inequality is a suitable tool for exploiting the dissipation inequality which we will discuss in the next section.

5. Exploitation of the Dissipation Inequality

As we mentioned in the introduction, the question arises, if each solution of the balance equations satisfies the dissipation inequality. The usual formulation of the second law (16) does not make any statement about that. This

fact can be formulated by two statements excluding each other:
i) *All (local) solutions of the balance equations have to satisfy the SL*

$$\forall_k \{\boldsymbol{y}^k \mid A \cdot \boldsymbol{y}^k = \boldsymbol{C}\} \longrightarrow \{\boldsymbol{B} \cdot \boldsymbol{y}^k \geq D\}, \tag{30}$$

or
ii) *There are (local) solutions of the balance equations which satisfy the SL, and others which do not*

$$\exists_k \{\boldsymbol{y}^k \mid A \cdot \boldsymbol{y}^k = \boldsymbol{C}\} \longrightarrow \{\boldsymbol{B} \cdot \boldsymbol{y}^k \geq D\} \wedge \tag{31}$$

$$\wedge \exists_n \{\boldsymbol{y}^n \mid A \cdot \boldsymbol{y}^n = \boldsymbol{C}\} \longrightarrow \{\boldsymbol{B} \cdot \boldsymbol{y}^n < D\}. \tag{32}$$

To decide what statement is the correct one, we will formulate an amendment of the second law in the next section. For that purpose the following proposition is needed which is not proved here:

PROPOSITION 1. ([5]) *If there are (local) solutions $\boldsymbol{y}^l$ and $\boldsymbol{y}^m$ of different signs of entropy production density (case ii))*

$$\boldsymbol{B} \cdot \boldsymbol{y}^l \geq D \text{ and } \boldsymbol{B} \cdot \boldsymbol{y}^m < D, \tag{33}$$

then (local) solutions

$$\boldsymbol{Y} := \sum_j \alpha_j \boldsymbol{y}^j, \quad \sum_j \alpha_j = 1, \quad \alpha_j \in I\!R, \quad \boldsymbol{B} \cdot \boldsymbol{Y} = D \tag{34}$$

exist. Because of the equality in $(34)_4$ the higher derivatives $\boldsymbol{Y}$ represent a reversible direction *in state space.*

6. Non-Reversible Direction Axiom

If a state $\boldsymbol{z}(\boldsymbol{x}, t)$ has higher derivatives $\boldsymbol{y}^j$ of different signs of entropy production density, also a higher derivative $\boldsymbol{Y}$ of vanishing entropy production exists according to proposition *I* which is called reversible direction. Because this lemma is valid for each state a reversible process can be generated starting out with an arbitrary non-equilibrium state. Thus we obtain the strange fact that a reversible process is passing through each state, independently of being an equilibrium one or a non-equilibrium one. But by experience non-equilibrium states can only be passed by irreversible process directions (higher derivatives belonging to positive entropy production density). Consequently no reversible process direction exists in non-equilibrium states. Thus we formulate [6], [7] the

NON-REVERSIBLE-DIRECTION AXIOM: *Except in equilibrium reversible process directions in state space do not exist.*

This axiom excludes (32) for non-equilibrium states because otherwise reversible process direction could be constructed according to proposition I (34). Consequently reversible process directions appear only in connection with equilibrium states (not exactly defined here), and only (30) is valid. Thus the dissipation inequality is a constraint not for excluding processes, but a constraint for the constitutive equations: The constitutive equations, i.e. the $A(\boldsymbol{z})$, $\boldsymbol{B}(\boldsymbol{z})$, $\boldsymbol{C}(\boldsymbol{z})$, and $D(\boldsymbol{z})$, cannot be independent of each other, but must have the property that the entropy production density is not negative for all solutions of the balance equations. This is the CM-formulation of the second law [1] which presupposes the validity of (30) and which therefore do not need the non-reversible direction axiom.

7. CONSEQUENCES OF THE AMENDMENT

Presupposing the amendment the following propositions can be proved:

PROPOSITION 2. ([5]) *The entropy production density is a function of state and does not depend on the higher derivatives*

$$0 \leq \boldsymbol{B}(\boldsymbol{z}) \cdot \boldsymbol{y} - D(\boldsymbol{z}) =: \sigma(\boldsymbol{z}). \tag{35}$$

PROPOSITION 3. ([2]) *There exist functions of state $\boldsymbol{\Lambda}(\boldsymbol{z})$ so that the* Liu equations

$$\boldsymbol{\Lambda} \cdot A = \boldsymbol{B} \tag{36}$$

and the residual dissipation inequality

$$\boldsymbol{\Lambda} \cdot \boldsymbol{C} \geq D \tag{37}$$

are valid.

PROPOSITION 4. *If A is of maximal rank*

$$A \cdot A^{-} = 1, \tag{38}$$

the second law and its amendment yield constraints for the constitutive equations

$$\boldsymbol{B} \cdot A^{-} \cdot \boldsymbol{C} \geq D. \tag{39}$$

These constraints for the constitutive equations have to be taken into account in (20) before solving the balance equations (9).

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