

Article

Entropy Production and Equilibrium Conditions of General-Covariant Spin Systems

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Abstract: In generalizing the special-relativistic one-component version of Eckart's continuum thermodynamics to general-relativistic space-times with Riemannian or post-Riemannian geometry as presented by Schouten (Schouten, J.A. *Ricci-Calculus*, 1954) and Blagojevic (Blagojevic, M. *Gauge Theories of Gravitation*, 2013) we consider the entropy production and other thermodynamical quantities, such as the entropy flux and the Gibbs fundamental equation. We discuss equilibrium conditions in gravitational theories, which are based on such geometries. In particular, thermodynamic implications of the non-symmetry of the energy-momentum tensor and the related spin balance equations are investigated, also for the special case of general relativity.

Keywords: spin systems; general-covariant entropy production; general-covariant equilibrium conditions

1. Introduction

The special-relativistic version of continuum thermodynamics (CT) was founded by Eckart [1] in the form of the special-relativistic theory of irreversible processes. CT is based (i) on the conservation law of the particle number and on the balance equation of the energy-momentum tensor and (ii) on the dissipation inequality and the Gibbs fundamental equation. In order to incorporate CT into general relativity (GR) and other gravitational theories all based on curved space-times, as a first step, one has to go over to the general-covariant formulation of CT, which is performed here.

The paper is devoted to the derivation of the entropy production and equilibrium conditions in general-covariant continuum thermodynamics (GCCT). Starting out with an entropy identity [2], a tool to construct entropy flux and production, as well as gr-Gibbs and gr-Gibbs-Duhem equations more consequently, different forms of the entropy production are considered for discussing non-dissipative materials and equilibria, which both are characterized by vanishing entropy production. For defining equilibrium beyond the vanishing entropy production, additionally "supplementary equilibrium conditions" are required [2]. The material-independent equilibrium condition, that the four-temperature vector is a Killing field, is rediscovered also for gravitational theories beyond GR, including a spin part in the state space.

The paper is organized as follows: First, the general-covariant shape of the energy-momentum and spin CT-balances are written down and entropy flux and production, gr-Gibbs and gr-Gibbs-Duhem equations are derived. Furthermore, non-dissipative materials and equilibria of spin materials are investigated with regard to the resulting constitutive constraints. Finally, equilibrium conditions for Frenkel materials are derived.

2. General-Covariant Continuum Physics

2.1. The Balance Equations

The balance equations of energy-momentum and spin of phenomenological GCCT in a curved space-time (the comma denotes partial and the semicolon covariant derivatives, round brackets the symmetric part of a tensor, square brackets its asymmetric part) are [2]:

$$T^{bc}_{;b} = G^c + k^c, \quad T^{bc} \neq T^{cb}, \quad S^{cba}_{;c} = H^{ba} + m^{ba} \quad (1)$$

$$\text{with } S^{cba} = -S^{cab}, \quad m^{ba} = -m^{ab} \quad \text{and} \quad H^{ba} = -H^{ab} \quad (2)$$

Here, T^{ab} is the, in general, non-symmetric energy-momentum tensor of CT and S^{cba} the current of spin density, often denoted in brief as spin tensor. The G^c and H^{bc} are internal source terms, the Geo-SMEC-terms (geometry-spin-momentum-energy-coupling) [2], which are caused by the choice of a special space-time geometry and by a possible coupling between energy-momentum, spin and geometry.

For non-isolated systems, $k^c \neq 0$ denotes an external force density, and $m^{ab} \neq 0$ is an external momentum density. As in the continuum theory of irreversible processes [3,4], the balance Equation (1) must be supplemented by those of particle number and entropy density:

$$N^k_{;k} = 0, \quad S^k_{;k} = \sigma + \varphi \quad (3)$$

(N^k particle flux density, S^k entropy four-vector, σ entropy production, φ entropy supply). The second law of thermodynamics is taken into account by the demand that the entropy production has to be non-negative at each event and for arbitrary materials after having inserted the constitutive equations into the expression of the entropy production:

$$\sigma \geq 0 \quad (4)$$

The (3 + 1)-splits of the tensors in Equations (1) and (3) are:

$$N^k = \frac{1}{c^2} n u^k, \quad n := N^k u_k, \quad (n u^k)_{;k} = 0 \quad (5)$$

$$T^{kl} = \frac{1}{c^4} e u^k u^l + \frac{1}{c^2} u^k p^l + \frac{1}{c^2} q^k u^l + t^{kl} \quad (6)$$

$$p^l u_l = 0, \quad q^k u_k = 0, \quad t^{kl} u_k = 0, \quad t^{kl} u_l = 0 \quad (7)$$

$$S^{kab} = \left(\frac{1}{c^2} s^{ab} + \frac{2}{c^4} u^{[a} \Xi^{b]} \right) u^k + s^{kab} + \frac{2}{c^2} u^{[a} \Xi^{kb]} =: u^k \Phi^{ab} + \Psi^{kab} \quad (8)$$

$$\Xi^b u_b = 0, \quad \Xi^{kb} u_k = \Xi^{kb} u_b = 0, \quad s^{ab} u_a = s^{ab} u_b = 0 \quad (9)$$

$$S^k = \frac{1}{c^2} s u^k + s^k, \quad s := S^k u_k, \quad s^k := h^k_l S^l \quad (10)$$

Here, the divergence-free particle number flux density N^k is chosen according to Eckart [1], and the projector perpendicular to the four-velocity u^k , respectively u_i , is introduced:

$$h^i_k = \delta^i_k - \frac{1}{c^2} u^i u_k, \quad h^i_k u_i = 0, \quad h^i_k u^k = 0 \quad (11)$$

and Equation (9) results in:

$$\Xi^b h^j_b = \Xi^j, \quad \Xi^{kb} h^j_k = \Xi^{jb}, \quad \Xi^{kb} h^j_b = \Xi^{kj} \quad (12)$$

By splitting the stress tensor into its diagonal and its traceless parts:

$$t^{kl} = -ph^{kl} + \pi^{kl}, \quad \pi^{kl}h_{kl} = 0, \quad t^{kl}h_{kl} = t^k_k =: -3p \tag{13}$$

we introduce the pressure p and the friction tensor π^{kl} .

According to Equations (6) and (7), we obtain:

$$u_l T^{kl} = q^k + \frac{1}{c^2} e u^k \tag{14}$$

Starting out with Equation (8), it holds:

$$\Xi^c = S^{abc} u_a u_b, \quad \Xi^{mc} = S^{abc} h_a^m u_b \tag{15}$$

resulting in:

$$\Xi^{mc} + \frac{1}{c^2} \Xi^c u^m = S^{mbc} u_b \tag{16}$$

Taking Equation (12) into account, we obtain:

$$S^{mbc} u_b h_c^j = S^{mbj} u_b \tag{17}$$

The (3 + 1)-split of tensors is a usual tool in relativistic continuum physics. The (3 + 1)-components, generated by the split, have physical significance, which originally is hidden in the unsplit tensor Equations (5) to (10). Thus, we generate by (3 + 1)-split the following covariant quantities: the particle number density n , the energy density e , the momentum flux density p^l , the energy flux density q^k , the stress tensor t^{kl} , the spin density s^{ab} , the spin density vector Ξ^b , the couple stress s^{kab} , the spin stress Ξ^{kb} , the entropy density s and the entropy flux density s^k .

It is clear that these quantities are not independent of each other. Especially here, we are interested in expressions for the entropy density and the entropy flux density, which we are going to construct in the next section by use of a special procedure starting out with the entropy identity [2]. Some further hints can be found in the Appendix.

2.2. The Entropy Identity

For defining the entropy density s and the entropy flux density s^k , which determine the entropy four-vector according to Equation (10)₁, we add suitable zeros to the entropy four-vector, a procedure that paves the way for defining s and s^k later on. The entropy identity results by multiplying Equations (5)₁, (14) and (16) with the present arbitrary quantities κ , λ and Λ_c , which are suitably chosen below; Equation (10)₁ becomes:

$$\begin{aligned} S^k &\equiv \frac{1}{c^2} s u^k + s^k + \kappa \left[N^k - \frac{1}{c^2} n u^k \right] + \\ &+ \lambda \left[u_l T^{kl} - q^k - \frac{1}{c^2} e u^k \right] + \Lambda_c \left[S^{kbc} u_b - \Xi^{kc} - \frac{1}{c^2} \Xi^c u^k \right] = \end{aligned} \tag{18}$$

$$\begin{aligned} &= \frac{1}{c^2} s u^k - \kappa \frac{1}{c^2} n u^k - \lambda \frac{1}{c^2} e u^k - \frac{1}{c^2} \Lambda_c \Xi^c u^k + \\ &+ \kappa N^k + \lambda u_l T^{kl} + \Lambda_c S^{kbc} u_b + \left(s^k - \lambda q^k - \Lambda_c \Xi^{kc} \right) \end{aligned} \tag{19}$$

This entropy identity does not take the entire energy-momentum and spin tensor into account, but only their contractions with u_l according to Equation (18).

That means that the contractions with h_{kl} are not included in the entropy identity, resulting in the consequence that more than one entropy identity can be established, if other secondary conditions are taken into consideration. A generalization of the entropy identity is obtained by replacing κ , λ and Λ_c by tensors of higher order.

An entropy vector regarding the spin of the system is also constructed by kinetic approaches of the equilibrium theory of spin systems [5,6]. Interestingly, in the latter paper, a spin vector was derived that satisfies the entropy identity Equation (19). This spin vector is that one that is also mostly used in phenomenological considerations.

Because the entropy identity is not unique, the entropy production and later on also s and s^k are not unique, either: changing the entropy identity results in changing the material. Here, we start out with the special entropy identity Equation (18).

Because the part of Λ_c that is parallel to u^c does not contribute to the last term of Equation (18) and, consequently, not to the entropy identity, we can demand:

$$\Lambda_c u^c \doteq 0 \tag{20}$$

without restricting the generality. The identity Equation (19) becomes another one by differentiation:

$$\begin{aligned} S^k{}_{;k} \equiv & \left[\frac{1}{c^2} (s - \kappa n - \lambda e - \Lambda_c \Xi^c) u^k \right]_{;k} + \\ & + (\kappa N^k)_{;k} + (\lambda u_m T^{km})_{;k} + (\Lambda_c S^{kbc} u_b)_{;k} + \\ & + (s^k - \lambda q^k - \Lambda_c \Xi^{kc})_{;k} \end{aligned} \tag{21}$$

This identity changes into the entropy production, if according to Equations (3)₂ and (10)₁, s , s^k and φ are specified. For achieving that, we now rearrange the five terms of Equation (21).

Introducing the covariant time derivative ($\dot{\Xi} := \Xi_{;k} u^k$ is the relativistic analogue of the non-relativistic material time derivative $d\Xi/dt$, which describes the time rates of a rest-observer; therefore, $\dot{\Xi}$ is observer independent and zero in equilibrium [7,8]):

$$\dot{\Xi} := \Xi_{;k} u^k \tag{22}$$

and using the balance Equations (3)₁ and (1)_{1,3}, the entropy identity Equation (21) becomes:

$$\begin{aligned} S^k{}_{;k} \equiv & \frac{1}{c^2} \left(\dot{s} - \dot{\kappa} n - \kappa \dot{n} - \dot{\lambda} e - \lambda \dot{e} - \dot{\Lambda}_c \Xi^c - \Lambda_c \dot{\Xi}^c \right) + \\ & + \frac{1}{c^2} (s - \kappa n - \lambda e - \Lambda_c \Xi^c) u^k{}_{;k} + \kappa_{;k} \frac{1}{c^2} n u^k + \\ & + (\lambda u_m)_{;k} T^{km} + \lambda u_m (G^m + k^m) + \\ & + (\Lambda_c u_b)_{;k} S^{kbc} + \Lambda_c u_b (H^{bc} + m^{bc}) + \\ & + (s^k - \lambda q^k - \Lambda_c \Xi^{kc})_{;k} \end{aligned} \tag{23}$$

The covariant time derivative Equation (22) can be replaced by the Lie derivative \mathcal{L}_u because:

$$(A^p B_p)^\bullet = \mathcal{L}_u(A^p B_p) \tag{24}$$

is valid, and we apply the covariant time derivative only on scalars according to the first row of Equation (23). Consequently, concerning the time derivative appearing in the entropy identity, we can use the covariant time derivative Equation (22) or the Lie derivative, both along u^k .

Taking Equations (6), (13) and (14) into account, the fourth term of Equation (23) becomes:

$$\begin{aligned} (\lambda u_m)_{;k} T^{km} &= \lambda_{;k} \left(q^k + \frac{1}{c^2} e u^k \right) + \lambda u_{m;k} \left(\frac{1}{c^2} u^k p^m - p h^{km} + \pi^{km} \right) = \\ &= \lambda_{;k} q^k + \frac{1}{c^2} \dot{\lambda} e + \frac{1}{c^2} \lambda \dot{u}_m p^m - \lambda p u^k_{;k} + \lambda u_{m;k} \pi^{km} \end{aligned} \tag{25}$$

We now transform the sixth term of the entropy identity Equation (23) by taking Equations (8) and (20) into account:

$$\begin{aligned} (\Lambda_c u_b)_{;k} S^{kbc} &= (\Lambda_c u_b) \cdot \Phi^{bc} + (\Lambda_c u_b)_{;k} \Psi^{kbc} = \\ &= \left(\dot{\Lambda}_c u_b + \Lambda_c \dot{u}_b \right) \left(\frac{1}{c^2} s^{bc} + \frac{1}{c^4} (u^b \Xi^c - u^c \Xi^b) \right) + \\ &\quad + \left(\Lambda_{c;k} u_b + \Lambda_c u_{b;k} \right) \left(s^{kbc} + \frac{1}{c^2} (u^b \Xi^{kc} - u^c \Xi^{kb}) \right) = \\ &= \dot{\Lambda}_c \frac{1}{c^2} \Xi^c + \Lambda_c \dot{u}_b \frac{1}{c^2} s^{bc} + \Lambda_{c;k} \Xi^{kc} + \Lambda_c u_{b;k} s^{kbc} \end{aligned} \tag{26}$$

Inserting Equations (25) and (26) into Equation (23) results in:

$$\begin{aligned} S^k_{;k} &\equiv \frac{1}{c^2} \left(\dot{s} - \kappa \dot{n} - \lambda \dot{e} - \Lambda_c \dot{\Xi}^c \right) + \\ &\quad + \frac{1}{c^2} \left(s - \kappa n - \lambda e - \Lambda_c \Xi^c - \lambda c^2 p \right) u^k_{;k} + \\ &\quad + \lambda_{;k} q^k + \frac{1}{c^2} \lambda \dot{u}_m p^m + \lambda u_{m;k} \pi^{km} + \lambda u_m (G^m + k^m) + \\ &\quad + \Lambda_c \dot{u}_b \frac{1}{c^2} s^{bc} + \Lambda_{c;k} \Xi^{kc} + \Lambda_c u_{b;k} s^{kbc} + \Lambda_c u_b (H^{bc} + m^{bc}) + \\ &\quad + \left(s^k - \lambda q^k - \Lambda_c \Xi^{kc} \right)_{;k} \equiv \sigma + \varphi \end{aligned} \tag{27}$$

As already mentioned, the entropy identity has to be transferred into the expression for the entropy production by specifying the entropy flux s^k , the entropy density s , the entropy supply φ and the three for the present arbitrary quantities κ , λ and Λ_c .

Obviously, Equation (27) contains terms of different kinds: a divergence of a vector perpendicular to u^k (the last term of Equation (27)), time derivatives of intensive quantities (the first row of Equation (27)), two terms stemming from the field equations (last terms of the third and fourth row of Equation (27)), three terms containing spin (3 + 1)-components (in the fourth row of Equation (27)) and three further terms containing (3 + 1)-components of the energy-momentum tensor (in the third row of Equation (27)). This structure of the entropy identity allows one to choose a state space and, by virtue of it, to define the entropy density, the entropy supply, the entropy flux, the gr-Gibbs equation and the gr-Gibbs–Duhem equation, which all are represented in the next sections.

2.3. The Entropy Supply

If the system under consideration is isolated, the external sources vanish:

$$k^m \doteq 0, \quad m^{bc} \doteq 0 \tag{28}$$

and with them also the entropy supply:

$$\varphi \equiv 0 \tag{29}$$

Thus, because the entropy supply is generated by external sources, we define:

$$\varphi := \lambda u_m k^m + \Lambda_c u_b m^{bc} \tag{30}$$

This definition is made in such a way that external sources do not appear in the entropy production. Consequently, the entropy supply is given by the last terms in the third and fourth row of Equation (27).

2.4. State Space, Gr-Gibbs Equation and Entropy Flux

We now choose a state space that belongs to a one-component spin system in local equilibrium and which is spanned by the particle number n , the energy density e and the spin density vector Ξ_c :

$$\boxtimes = (n, e, \Xi_c) \tag{31}$$

Local equilibrium means: the state at each event is described by a set of equilibrium variables, which change from event to event, generating gradients of equilibrium variables, causing irreversible processes. According to Equations (15) and (16), the three-indexed spin is only partly taken into account, namely by Ξ_c and Ξ^{kc} . Here, Ξ_c is an independent state variable, whereas Ξ^{kc} represents a constitutive property according to Equation (36).

The gr-Gibbs equation is given by the covariant time derivative of the entropy density s , which is composed of covariant time derivatives belonging to the chosen state space. Such covariant time derivatives appear only in the first row of Equation (27) (the acceleration \dot{u}_m is not a material property, but one of the kinematical invariants). Consequently, we define:

$$\dot{s} := \kappa \dot{n} + \lambda \dot{e} + \Lambda_c \dot{\Xi}^c \tag{32}$$

and the split of the entropy identity into the gr-Gibbs equation and entropy density later on depends on the choice of the time derivative, although the entropy identity is independent of this choice.

Up to here, the quantities κ , λ , Λ_c introduced into the entropy identity Equation (18) are unspecified. Taking the gr-Gibbs Equation (32) into consideration, such a specification is now possible: λ is the reciprocal rest-temperature:

$$\lambda := \frac{1}{T} \tag{33}$$

κ is proportional to the chemical potential:

$$\kappa := -\frac{\mu}{T} \tag{34}$$

and Λ_c is analogous to Equation (34) proportional to a spin potential:

$$\Lambda_c := -\frac{\mu_c}{T} \tag{35}$$

These quantities, as all of the others that do not belong to the state space variable Equation (31), are constitutive quantities describing the material by constitutive equations. These constitutive quantities are:

$$\mathbf{M} = (T, \mu, \mu_c, p^k, q^k, p, \pi^{km}, s^{km}, s^{ckm}, \Xi^{km}) \tag{36}$$

They all, including the entropy density s and the entropy flux density s^k , are functions of the state space variables:

$$\mathbf{M} = \mathcal{M}(\boxtimes) \tag{37}$$

These constitutive equations are out of scope of this paper (for how to use the constitutive equations in connection with the field equations, see [9]).

Because of Equation (33), the term λq^k is as in CT a part of the entropy flux. Consequently, we define the entropy flux density according to the last row of Equation (27):

$$s^k := \lambda q^k + \Lambda_c \Xi^{kc} \tag{38}$$

Taking Equation (36) into consideration, the entropy flux density is also a constitutive quantity.

2.5. Entropy Density and the Gr-Gibbs–Duhem Equation

According to the second row of the entropy identity Equation (27), we define the entropy density:

$$s := \kappa n + \lambda e + \Lambda_c \Xi^c + \lambda c^2 p \tag{39}$$

This definition has to be in accordance with the gr-Gibbs Equation (32). As usual in non-relativistic thermostatics, we demand a gr-Gibbs–Duhem equation of the intensive variables:

$$\dot{\kappa} n + \dot{\lambda} (e + c^2 p) + \dot{\Lambda}_c \Xi^c + \lambda c^2 \dot{p} = 0 \tag{40}$$

2.6. The Entropy Production

Inserting the entropy supply Equation (30), the entropy flux Equation (38), the gr-Gibbs Equation (32) and the entropy density Equation (39) into the entropy identity Equation (27), we obtain the entropy production:

$$\begin{aligned} \sigma = & \lambda_{,k} q^k + \frac{1}{c^2} \lambda \dot{u}_m p^m + \lambda u_{m;k} \pi^{km} + \lambda u_m G^m + \\ & + \Lambda_c \dot{u}_b \frac{1}{c^2} s^{bc} + \Lambda_{c;k} \Xi^{kc} + \Lambda_c u_{b;k} s^{kbc} + \Lambda_c u_b H^{bc} \end{aligned} \tag{41}$$

We get by taking Equations (7)₁ and (10)₃ into account:

$$\frac{1}{c^2} \lambda \dot{u}_m p^m + \Lambda_c \dot{u}_b \frac{1}{c^2} s^{bc} = - \frac{1}{c^2} u_m (\lambda \dot{p}^m + \Lambda_c \dot{s}^{mc}) \tag{42}$$

Starting out with the RHS of Equation (42) and with the Geo-SMEC-terms of Equation (41), we obtain:

$$\begin{aligned} - \frac{1}{c^2} u_m (\lambda \dot{p}^m + \Lambda_c \dot{s}^{mc}) + \lambda u_m G^m + \Lambda_c u_b H^{bc} = \\ = u_m \left[\lambda \left(G^m - \frac{1}{c^2} \dot{p}^m \right) + \Lambda_c \left(H^{mc} - \frac{1}{c^2} \dot{s}^{mc} \right) \right] \end{aligned} \tag{43}$$

and the entropy production Equation (41) results in:

$$\begin{aligned} \sigma = & \lambda_{,k} q^k + \Lambda_{c;k} \Xi^{kc} + u_{m;k} \left(\lambda \pi^{km} + \Lambda_c s^{kmc} \right) + \\ & + u_m \left[\lambda \left(G^m - \frac{1}{c^2} \dot{p}^m \right) + \Lambda_c \left(H^{mc} - \frac{1}{c^2} \dot{s}^{mc} \right) \right] \end{aligned} \tag{44}$$

an expression that belongs to a general-covariant one-component spin system. The entropy production depends on the Geo-SMEC-terms of the balance equations, that means the same material has different entropy productions in space-times of different theories. Entropy flux and density, gr-Gibbs and the gr-Gibbs–Duhem equation do not depend on Geo-SMEC-terms, because the energy-momentum and spin tensor are independent of the Geo-SMEC-terms: that is obvious, because the (3 + 1)-split Equations (6) and (8) are valid for all space-times.

3. Further Forms of Entropy Production

The gradient of the velocity can be decomposed into its kinematical invariants: symmetric traceless shear σ_{nm} , expansion Θ , anti-symmetric rotation ω_{nm} and acceleration \dot{u}_n [10]:

$$u_{l;k} = \sigma_{lk} + \omega_{lk} + \Theta h_{lk} + \frac{1}{c^2} \dot{u}_l u_k \tag{45}$$

$$\sigma_{lk} = \sigma_{kl}, \omega_{lk} = -\omega_{kl}, u^l \sigma_{lk} = \sigma_{lk} u^k = u^l \omega_{lk} = \omega_{lk} u^k = 0 \tag{46}$$

$$\sigma_k^k = \omega_k^k = 0, \Theta := u_k^k \tag{47}$$

Using Equation (45), the third term of Equation (41) can be replaced by:

$$\lambda u_{m;k} \pi^{km} = \lambda \sigma_{mk} \pi^{(km)} + \lambda \omega_{mk} \pi^{[km]} \tag{48}$$

We now derive another shape of the entropy production: starting out with the entropy identity Equation (21), we obtain the entropy production by taking the entropy flux Equation (38), the entropy density Equation (39), the energy-momentum balance Equation (1)₁ and the particle balance Equations (3)₁ and (5)₁ into account. Inserting these quantities, we obtain for isolated systems:

$$\sigma = \frac{1}{c^2} \left[\lambda c^2 p u^k \right]_{;k} + \dot{\kappa} \frac{1}{c^2} n + (\lambda u_m)_{;k} T^{km} + \lambda u_m G^m + \left(\Lambda_c u_b S^{kbc} \right)_{;k} \tag{49}$$

and the first term of Equation (49) is:

$$\frac{1}{c^2} \left[\lambda c^2 p u^k \right]_{;k} = (\lambda p)^\bullet + \lambda p u^k_{;k} \tag{50}$$

For the sequel, we need an additional expression whose validity is independent of the entropy production because it represents an identity:

$$\begin{aligned} (\lambda u_m)_{;k} \left(\frac{1}{c^4} e u^k u^m - p h^{km} \right) &= (\lambda_{;k} u_m + \lambda u_{m;k}) \left(\frac{1}{c^4} e u^k u^m - p h^{km} \right) = \\ &= \frac{e}{c^2} \lambda^\bullet - \lambda p u^k_{;k} \end{aligned} \tag{51}$$

The sum of Equations (49) and (51) results in:

$$\begin{aligned} \sigma &= (\lambda p)^\bullet + \frac{e}{c^2} \lambda^\bullet + \dot{\kappa} \frac{1}{c^2} n + \\ &+ (\lambda u_m)_{;k} \left(T^{km} - \frac{1}{c^4} e u^k u^m + p h^{km} \right) + \\ &+ \lambda u_m G^m + \left(\Lambda_c u_b \right)_{;k} S^{kbc} + \Lambda_c u_b H^{bc} \end{aligned} \tag{52}$$

Replacing the first two terms by the gr-Gibbs–Duhem equation Equation (40), we obtain by taking Equation (26) into account:

$$\begin{aligned} \sigma &= -\frac{1}{c^2} \dot{\Lambda}_c \Xi^c + (\lambda u_m)_{;k} \left(T^{km} - \frac{1}{c^4} e u^k u^m + p h^{km} \right) + \\ &+ \lambda u_m G^m + \left(\Lambda_c u_b \right)_{;k} S^{kbc} + \Lambda_c u_b H^{bc} = \end{aligned} \tag{53}$$

$$\begin{aligned} &= (\lambda u_m)_{;k} \left(T^{km} - \frac{1}{c^4} e u^k u^m + p h^{km} \right) + \lambda u_m G^m + \\ &+ \Lambda_c u_b \left(H^{bc} - \frac{1}{c^2} \dot{s}^{bc} \right) + \Lambda_{c;k} \Xi^{kc} + \Lambda_c u_{b;k} s^{kbc} \end{aligned} \tag{54}$$

Here, in contrast to Equation (44), the heat flux q^k and the friction tensor π^{km} do not appear. They are replaced by the first term of Equation (54) describing the deviation of the material from a perfect one. The second row represents the influence of the chosen state space Equation (31) on the entropy production.

We now consider the thermodynamical results: if we start out with the entropy identity for which the last term of Equation (18) is set to zero $\Lambda_c \equiv 0$ [11].

By doing so, Ξ^{kc} and especially Ξ^c do not appear any more in the entropy identity, and consequently, they are withdrawn from the procedure. The entropy identity changes, and the state space Equation (31) transforms into:

$$\boxtimes_0 = (n, e) \tag{55}$$

which characterizes a spin-free material in contrast to Equation (31). The entropy production Equation (54) becomes:

$$\sigma_0 = (\lambda u_m)_{;k} \left(T^{km} - \frac{1}{c^4} e u^k u^m + p h^{km} \right) + \lambda u_m G^m \tag{56}$$

and the entropy flux Equation (38) is:

$$s_0^k = \lambda q^k \tag{57}$$

The gr-Gibbs equation Equation (32) becomes:

$$\dot{s}_0 = \kappa \dot{n} + \lambda \dot{e} \tag{58}$$

and the entropy density Equation (39) is:

$$s_0 = \kappa n + \lambda e + c^2 \lambda p \tag{59}$$

Finally, the gr-Gibbs–Duhem equation Equation (40) results in:

$$\dot{\kappa} n + \dot{\lambda} (e + c^2 p) + \dot{p} c^2 \lambda = 0 \tag{60}$$

The thermodynamical quantity Equations (56) to (60) based on the chosen state space as a comparison with Equations (31), (32), (39) and (40) is demonstrated. Consequently, the thermodynamical quantities are not “absolute”; they belong to a thermodynamical scheme implemented by a chosen state space. The spin does not appear in the thermodynamical quantity Equations (56) to (60) in contrast to Equations (31), (32), (39) and (40). Furthermore, the regard of the spin balance Equation (1)₃ is different: the entropy production Equation (54) takes it explicitly into account, whereas spin parts do not appear in Equation (56) [12]. Here, the spin is a constitutive quantity and not a state space variable. For the sequel, we use the state space Equation (31) because of its generality and consider the restricted state space Equation (55) as a special case.

The special case Equation (55) can be easily obtained by the setting $\Lambda_c \doteq 0$. Especially in GR, the energy-momentum tensor is symmetric, and the external sources and the Geo-SMEC-terms are zero. Thus, Equation (54) results in:

$$\sigma_0^{GR} = \frac{1}{2} \left[(\lambda u_m)_{;k} + (\lambda u_k)_{;m} \right] \left(T^{km} - \frac{1}{c^4} e u^k u^m + p h^{km} \right) \tag{61}$$

Consequently, the entropy production vanishes in GR for perfect materials or/and if the space-time allows that the four-temperature vector is a Killing field. This is the well-known result derived in [12], which is here worked out using a more general aspect. More details in connection with equilibrium will be discussed in Section 5.1.

4. Non-Dissipative Materials

As already mentioned, the entropy production depends always on a chosen state space. Thus, Equation (54) belongs to Equation (31), and for Equations (56) to (55), the entropy production depends on the material and on the space-time, a statement that is also valid for its zero. A non-dissipative material is characterized by vanishing entropy production Equation (54), even in the case of non-equilibrium (vanishing entropy production is necessary, but not sufficient for equilibrium), independently of the specially-chosen space-time. Consequently, by definition, all processes of non-dissipative materials are reversible (reversible “processes” are trajectories in the state space consisting of equilibrium states), and therefore, these materials are those of thermostatics. If the state space is changed, it may be that a non-dissipative material becomes dissipative, because changing the state space means changing the material.

Starting out with Equation (54), we point out a set of conditions that is sufficient that a material is non-dissipative, that means its entropy production vanishes independently of the space-time. These conditions are generated by setting individual terms in Equation (54) to zero. First, the non-dissipative material is perfect:

$$T_{\text{ndiss}}^{kl} \doteq \frac{1}{c^4} e u^k u^l - p h^{kl}, \quad \longrightarrow \quad T_{\text{ndiss}}^{[kl]} = 0, \quad (62)$$

for which the first term of Equation (54) vanishes. Furthermore, the second term must vanish:

$$G_{\text{ndiss}}^m \doteq 0 \quad (63)$$

that means the Geo-SMEC-term of the energy-momentum balance has to be zero.

The second row of Equation (54) depends on Λ_c , which introduces according to the last term of Equation (18) a spin part explicitly into the state space Equation (31). There are now two possibilities for vanishing the second row of Equation (54):

$$H_{\text{ndiss}}^{bc} = 0, \quad \overset{\bullet}{s}_{\text{ndiss}}{}^{bc} = 0, \quad \Psi_{\text{ndiss}}^{kbc} = 0 \quad (64)$$

or second:

$$\Lambda_c^{\text{ndiss}} = 0 \quad (65)$$

If now Λ_c vanishes in Equation (54), and consequently also in Equation (18), spin terms cannot appear in the state space, with the result that we have to choose the state space Equation (55) instead of Equation (31).

Finally, we proved two statements that presuppose different state spaces for non-dissipative materials.

■ Proposition I: The five altogether sufficient conditions characterizing non-dissipative materials are: (i) the material is perfect; (ii) the Geo-SMEC-terms of the energy-momentum and of the spin balance vanish; (iii) the spin is $S_{\text{ndiss}}^{kbc} = u^k \Phi_{\text{ndiss}}^{bc}$; (iv) the spin density Equation (64)₂ is covariantly constant; and (v) the state space is spanned by the particle number, the energy density and the spin density vector Ξ_c . ■

■ Proposition II: The three altogether sufficient conditions characterizing non-dissipative materials are: (i) the material is perfect; (ii) the Geo-SMEC-term of the energy-momentum balance vanishes; and (iii) the state space is spanned by the particle number and the energy density. ■

5. Equilibrium

5.1. Equilibrium Conditions

We start out with the question: how are equilibrium and non-dissipative materials related to each other? Concerning non-dissipative materials, we are looking for material properties enforcing vanishing entropy production for all admissible space-times. Concerning equilibria, we are asking for space-times in which materials can be at equilibrium. This is defined by equilibrium conditions, which are divided into necessary and supplementary ones [2]. The necessary ones are given by vanishing entropy production and vanishing entropy flux density:

$$\sigma^{eq} \doteq 0 \quad \wedge \quad s_{eq}^k \doteq 0 \tag{66}$$

Supplementary equilibrium conditions are given by vanishing covariant time derivatives, except that of the four-velocity:

$$\boxplus_{eq}^\bullet \doteq 0, \quad \boxplus \neq u^l \tag{67}$$

that means \dot{u}^l_{eq} is in general not zero in equilibrium. Consequently, according to Equations (32) and (40), the gr-Gibbs and the gr-Gibbs–Duhem equations are identically satisfied in equilibrium. Whereas in Section 4, the non-dissipative materials are defined independently of the admissible space-times, here, a material in a given space-time is considered, and the equilibrium condition Equations (66) and (67) are valid.

From Equation (3)₁ follows:

$$\dot{n} := n_{;k} u^k = -n u^k_{;k} \quad \longrightarrow \quad u^k_{;k} = -\frac{\dot{n}}{n} \tag{68}$$

According to Equations (67)₁ and (68)₃, the divergence of the four-velocity, that is the expansion Equation (47)₂, vanishes in equilibrium for arbitrary space-times and materials:

$$u^k_{;k}{}^{eq} = 0 \tag{69}$$

Starting out with the identity Equation (51) and taking Equations (67) and (69) into account, we obtain for all equilibria:

$$(\lambda u_m)_{;k}{}^{eq} \left(\frac{1}{c^4} e u^k u^m - p h^{km} \right)^{eq} = 0 \tag{70}$$

Because the second bracket of Equation (70) is never zero, the four-temperature vector λu_m is independent of the material a Killing vector in equilibrium:

$$\left[(\lambda u_m)_{;k} + (\lambda u_k)_{;m} \right]^{eq} = 0 \tag{71}$$

The equilibrium condition Equations (69) and (71) are induced by Equation (67)₁ independently of the entropy production and the material. Especially, Equation (71) is the well-known necessary condition for defining thermodynamic equilibrium. It can be found in textbooks on phenomenological and kinetic theories. Using solely arguments from phenomenological continuum thermodynamics, e.g., in [12], Stephani presented its derivation under the assumption of the reduced state space Equation (55) spanned by the specific internal energy and the specific volume using a symmetric and divergence-free energy-momentum tensor.

No equilibria are possible in space-times that do not allow the validity of Equations (69) or/and (71). It is obvious that the condition Equations (69) and (71) are necessary, but not sufficient for equilibrium, because they do not guarantee vanishing entropy production Equation (54) or (56), except for the case of GR according to Equation (61). Hence, vanishing entropy production in GR

means two different things: the system may be in equilibrium or the system is non-dissipative, and reversible processes occur.

The expression of the entropy production Equation (44) becomes in equilibrium by taking Equation (48) into account:

$$\begin{aligned}
 0 = & \lambda_{,k}^{eq} q_{eq}^k + \Lambda_{c;k}^{eq} \Xi_{eq}^{kc} + \\
 & + \sigma_{mk}^{eq} \left(\lambda^{eq} \pi_{eq}^{(km)} + \Lambda_c^{eq} s_{eq}^{(km)c} \right) + \omega_{mk}^{eq} \left(\lambda^{eq} \pi_{eq}^{[km]} + \Lambda_c^{eq} s_{eq}^{[km]c} \right) + \\
 & + u_m^{eq} \left(\lambda^{eq} G_{eq}^m + \Lambda_c^{eq} H_{eq}^{mc} \right)
 \end{aligned} \tag{72}$$

From Equations (38) and (66)₂ follows:

$$q_{eq}^k = -\frac{1}{\lambda^{eq}} \Lambda_c^{eq} \Xi_{eq}^{kc} \longrightarrow \lambda_{,k}^{eq} q_{eq}^k = -\frac{\lambda_{,k}^{eq}}{\lambda^{eq}} \Lambda_c^{eq} \Xi_{eq}^{kc} \tag{73}$$

Inserting Equation (73) into Equation (46) results in:

$$\begin{aligned}
 0 = & \Xi_{eq}^{kc} \left(\Lambda_{c;k}^{eq} - \frac{\lambda_{,k}^{eq}}{\lambda^{eq}} \Lambda_c^{eq} \right) + \\
 & + \sigma_{mk}^{eq} \left(\lambda^{eq} \pi_{eq}^{(km)} + \Lambda_c^{eq} s_{eq}^{(km)c} \right) + \omega_{mk}^{eq} \left(\lambda^{eq} \pi_{eq}^{[km]} + \Lambda_c^{eq} s_{eq}^{[km]c} \right) + \\
 & + u_m^{eq} \left(\lambda^{eq} G_{eq}^m + \Lambda_c^{eq} H_{eq}^{mc} \right)
 \end{aligned} \tag{74}$$

In contrast to the material-independent equilibrium condition Equations (69) and (71), the equilibrium condition Equations (72) to (74) depend on material and space-time. Each of these three condition is necessary for equilibrium, and altogether, they are sufficient for equilibrium, because the field equation Equation (1) and the entropy supply Equation (30) are taken into account.

Another shape of Equation (74) can be derived from Equation (54) by taking Equation (71) into account:

$$\begin{aligned}
 0 = & (\lambda u_m)_{;k}^{eq} T_{eq}^{[km]} + \\
 & + \Lambda_{c;k}^{eq} \Xi_{eq}^{kc} + \Lambda_c^{eq} u_{m;k}^{eq} s_{eq}^{kmc} + u_m^{eq} \left(\lambda^{eq} G_{eq}^m + \Lambda_c^{eq} H_{eq}^{mc} \right)
 \end{aligned} \tag{75}$$

This equilibrium condition is satisfied in GR because the energy-momentum tensor is symmetric; both the Geo-SMEC-term vanishes and the state space Equation (55) is used. General solutions of Equations (74) and (75), that means, to find all couples, material ↔ space-time, which satisfy Equations (74) and (75), cannot be achieved. Therefore, we discuss some special cases of equilibria in the next section.

5.2. Special Equilibria

We now decompose the equilibrium condition Equation (74) into a set of terms representing special cases of equilibria, which altogether enforce the validity of Equation (74):

$$\Xi_{eq}^{kc} \left(\Lambda_{c;k}^{eq} - \frac{\lambda_{,k}^{eq}}{\lambda^{eq}} \Lambda_c^{eq} \right) \doteq 0 \tag{76}$$

$$\sigma_{mk}^{eq} \left(\lambda^{eq} \pi_{eq}^{(km)} + \Lambda_c^{eq} s_{eq}^{(km)c} \right) \doteq 0 \tag{77}$$

$$\omega_{mk}^{eq} \left(\lambda^{eq} \pi_{eq}^{[km]} + \Lambda_c^{eq} s_{eq}^{[km]c} \right) \doteq 0 \tag{78}$$

$$u_m^{eq} \left(\lambda^{eq} G_{eq}^m + \Lambda_c^{eq} H_{eq}^{mc} \right) \doteq 0 \tag{79}$$

If we do not restrict the spin material under consideration, the bracket in Equation (76) has to be zero, resulting in a differential equation for the spin potential Equation (35):

$$\lambda^{eq} \Lambda_{c;k}^{eq} - \lambda_{,k}^{eq} \Lambda_c^{eq} = 0 \tag{80}$$

Because this equilibrium condition is pretty exotic, we restrict our discussion to spin materials with vanishing Ξ^{kc} . According to Equations (8) and (73), we obtain:

$$\Xi^{kc} \doteq 0, \quad \longrightarrow \quad S^{kbc} = u^k \Phi^{bc} + s^{kbc} \quad \wedge \quad q_k^{eq} = 0 \tag{81}$$

According to Equations (77) and (78), the couple stress s^{kbc} modifies the friction tensor:

$$\Pi_{eq}^{km} := \lambda^{eq} \pi_{eq}^{km} + \Lambda_c^{eq} s_{eq}^{kmc} \tag{82}$$

and necessary material-independent equilibrium conditions are:

$$\sigma_{mk}^{eq} = 0, \quad \omega_{mk}^{eq} = 0 \tag{83}$$

Another necessary equilibrium condition is Equation (79). In connection with Equation (75), we obtain:

$$(\lambda u_m)_{;k}^{eq} T_{eq}^{[km]} + \Lambda_c^{eq} u_{m;k}^{eq} s_{eq}^{kmc} = 0 \tag{84}$$

a relation which is satisfied, if we have e.g.,

$$(\lambda u_m)_{;k}^{eq} = 0 \quad \wedge \quad s_{eq}^{kmc} = 0 \tag{85}$$

Using the state space Equations (55), (76) to (79) result in Equation (83) or:

$$\pi_{eq} = 0 \quad \wedge \quad u_m^{eq} G_{eq}^m = 0 \tag{86}$$

5.3. Frenkel Materials

Taking Equation (9)₃ into account, materials defined by the special spin:

$$\Psi_{FR}^{kbc} \doteq 0 \quad \wedge \quad \left[\Phi_{FR}^{bc} u_b \doteq 0 \quad \longrightarrow \quad \Xi_{FR}^c = 0 \right] \tag{87}$$

are called Frenkel materials. According to Equation (87)₂, Frenkel materials belong to the state space Equation (55), and their spin is:

$$S_{FR}^{kbc} = u^k s^{bc} \tag{88}$$

According to Equation (54), a necessary equilibrium condition of Frenkel materials is:

$$0 = (\lambda u_m)_{;k}^{eq} \left(T_{FR}^{km} - \frac{1}{c^4} e_{FR} u^k u^m + p h_{FR}^{km} \right)^{eq} + u_m^{eq} \lambda^{eq} G_{FR}^m \tag{89}$$

If the Frenkel material is dissipative, the equilibrium conditions are Equations (69) and (71), and according to (89):

$$(\lambda u_m)_{;k}^{eq} T_{FR}^{[km]} = 0, \quad u_m^{eq} \lambda^{eq} G_{FR}^m = 0 \tag{90}$$

and additionally according to Equations (73)₁ and (77)/(78):

$$q_{FR}^k = 0, \quad \sigma_{mk}^{eq} \lambda^{eq} \pi_{FR}^{(km)} = 0, \quad \omega_{mk}^{eq} \lambda^{eq} \pi_{FR}^{[km]} = 0 \tag{91}$$

6. Discussion

Starting out with the entropy identity derived in [2] and specifying entropy flux, entropy density and entropy supply, different expressions of the entropy production in general-relativistic space-times are determined by taking the gr-Gibbs and the gr-Gibbs–Duhem equations into account. All of these thermodynamical quantities depend on the chosen state space, which in general is more extended than that of general relativity. Beyond that, the entropy production of a general-covariant one-component spin system depends on the so-called Geo-SMEC-terms, which are located at the RHS of the balance equations, thus discriminating between different general-covariant theories.

Well-known relations of general relativity are generalized for theories based on post-Riemannian space-times. In this case, the interrelation between geometric and constitutive quantities in the expression for the entropy production becomes more complex. Consequently, the zero of the entropy production can be realized by a variety of conditions imposed on constitutive and/or geometric quantities. One condition of them is the fact that the entropy production vanishes for perfect materials, if the state space does not include spin terms and if the Geo-SMEC-term of the energy-momentum balance is zero. That is just the well-known case of general relativity.

Vanishing of entropy production is only necessary, but not sufficient for equilibrium. This necessary condition has to be complemented by “supplementary equilibrium conditions” for describing equilibrium sufficiently. Two supplementary equilibrium conditions are independent of the entropy production restricting the space-time independently of the material: the expansion vanishes, and the four-temperature vector is a Killing field. Equilibria are impossible, if one of these two conditions is not satisfied.

For defining equilibria, the time derivative plays a prominent role. There are two concepts, the Lie derivative along the four-velocity $\mathcal{L}_u \boxtimes$ and the covariant derivative along the four-velocity $\boxtimes_{;p} u^p$, which both result in the same entropy identity. Here, we use the covariant time derivative.

From the viewpoint of material theory, the conditions are interesting for which the entropy production vanishes whatever the properties of the space-time of the considered theory may be. One set of conditions for non-dissipativity is: the material is perfect; the Geo-SMEC-term of the energy-momentum balance vanishes; and the state space is spanned by particle number and energy density. That is again the special case of general relativity.

7. Conclusions

Non-equilibrium thermodynamics of spin systems, including production, flux, supply and density of entropy and Gibbs and Gibbs–Duhem equations, can be formulated covariantly by choosing a suitable state space describing a class of materials. Results of General Relativity are contained as a special case.

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Appendix

Relativistic continuum thermodynamics is a field theory defined on the four-dimensional space-time whose elements are the events. The basic assumption is that the local state at each event is specified by the primary variables: the particle flow vector N^i , the energy-momentum tensor T^{ik} , the spin tensor S^{ikl} and the four-entropy vector S^i . In the framework of special relativity, it was shown by Eckart [1] that the particle flow vector N^i has to be introduced independently of the energy-momentum tensor T^{ik} . This fact is taken over to non-flat geometries.

The primary variables obey balance equations, that of particle number, energy-momentum, spin and entropy. These balances are covariantly formulated and therefore valid for all geometries and materials. The geometry of the space-time is determined by field equations (not considered in the paper) together with the balance equations. The (3 + 1)-split of the primary variables encloses constitutive variables, which depend on the chosen material, such as the energy flux density, the stress tensor and the entropy density. These constitutive variables are defined on a chosen state space, which determines the class of materials under consideration. Changing the state space means changing the class of materials.

The entropy identity represents a tool for constructing entropy density and entropy flux density more consequentially by choosing them in accordance with the balance equations, because these appear in the entropy identity by special chosen expressions. That is the reason why the entropy identity is not unique, but depends on the material, a fact that shows that entropy density and entropy flux density are constitutive quantities.

The basic ideas of relativistic material theory stem partly from the non-relativistic theory, from the special-relativistic TIP (thermodynamics of irreversible processes) and from general relativity [13–18].

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