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Entropy Principle and Shock-Wave Propagation in Continuum Physics

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Abstract: According to second law of thermodynamics, the local entropy production must be non-negative for arbitrary thermodynamic processes. In 1996, Muschik and Ehrentraut observed that such a constraint can be fulfilled in two different ways: either by postulating a suitable form of the constitutive equations, or by selecting among the solutions of the systems of balance laws those which represent physically realizable thermodynamic processes. Hence, they proposed an amendment to the second law which assumes that reversible process directions in state space exist only in correspondence with equilibrium states. Such an amendment allowed them to prove that the restriction of the constitutive equations is the sole possible consequence of non-negative entropy production. Recently, Cimmelli and Rogolino revisited the classical result by Muschik and Ehrentraut from a geometric perspective and included the amendment in a more general formulation of the second law. Herein, we extend this result to nonregular processes, i.e., to solutions of balance laws which admit jump discontinuities across a given surface. Two applications of these results are presented: the thermodynamics of an interface separating two different phases of a Korteweg fluid, and the derivation of the thermodynamic conditions necessary for shockwave formation. Commonly, for shockwaves the second law is regarded as a restriction on the thermodynamic processes rather than on the constitutive equations, as only perturbations for which the entropy continues to grow across the shock can propagate. We prove that this is indeed a consequence of the general property of the second law of thermodynamics that restricts the constitutive equations for nonregular processes. An analysis of shockwave propagation in different thermodynamic theories is developed as well.



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1. Introduction

The classical formulation of the second law of thermodynamics for continuous systems asserts that the entropy production density is not negative in any point of the system and for all times, whatever the thermodynamic process. In 1996, Muschik and Ehrentraut investigated the consequences of the validity of the second law of thermodynamics on constitutive theories [1]. They observed that the formulation above could be interpreted either as a constraint on the constitutive equations or as a selection of the admissible thermodynamic processes. The two interpretations mentioned above have totally different consequences; hence, it is important to investigate which one is true. To achieve that task, Muschik and Ehrentraut [1] proposed the following amendment to the second law:

Postulate 1. *Except in equilibria, reversible process directions in state space do not exist.*

Presupposing its validity, the authors were able to prove the following theorem:

Theorem 1. *If Postulate 1 holds, then the second law of thermodynamics necessarily restricts the constitutive functions and not the thermodynamic processes.*

In continuum physics, the result above is known as the entropy principle [2]. It can be formulated as follows [3,4]:

Postulate 2. *The constitutive equations characterizing the properties of materials must be assigned in such a way that second law of thermodynamics is satisfied along arbitrary thermodynamic processes.*

Theorem 1 has been reformulated within a geometric perspective in [5] by applying the results in [6,7]. In [5], after defining the configuration space and the space of the higher derivatives, the authors introduce the definitions of real, ideal, and over-ideal vectors. Moreover, they provide the definitions of irreversible, reversible, and over-reversible thermodynamic process by analyzing the properties of the representative curve in the fiber bundle of the configuration spaces. In such a geometric framework, the second law of thermodynamics is reformulated in order to encompass the amendment, and a new proof of the Muschik and Ehretraut theorem is provided [5].

It is worth observing that the analysis in [1,5] is carried out under the hypothesis of regular thermodynamic processes. However, in physics, the presence of domains across which the fundamental fields and/or their derivatives may suffer jump discontinuities is very frequent. Indeed, discontinuous solutions may occur in important physical phenomena, such as, for example, phase transitions or wave propagation. In such cases, jumps of the field equations may be calculated as the difference between the limits on both sides of the discontinuity domain, which are assumed to exist and to satisfy the second law. Such a procedure assumes that the entropy principle holds on both sides of the domain of discontinuity, where the second law is presupposed to restrict the constitutive equations and not the thermodynamic processes. However, such a presupposition is not a direct consequence of the results in [1,5], as only regular processes are considered therein.

The aim of the present investigation is to fill such a gap by extending the results obtained in [5] to the case of nonregular processes. To this end, we follow the way already paved in [8,9], within the geometric framework established in [5]. As an application, we discuss the case of shockwave propagation, for which it is commonly assumed that the second law selects the admissible shocks [10]. Indeed, we show that in this case the second law restricts the constitutive equations on both sides of the shock, and that as a consequence of this restriction only shocks across which the entropy production is positive can propagate.

As a further application, we review the consequences of the second law of thermodynamics within the frame of different thermodynamic theories of continuum physics, namely, Classical Irreversible Thermodynamics (CIT) [11,12], Rational Thermodynamics (RT) [3,13], Extended Irreversible Thermodynamics (EIT) [14,15], and Rational Extended Thermodynamics (RET) [16,17].

The rest of this paper has the following layout.

In Section 2, we construct a new geometric framework for nonregular thermodynamic processes. In Section 3, we generalize the formulation of the second law of thermodynamics provided in [5] in order to encompass the case in which a domain of discontinuity is present. In Section 4, we prove the Muschik and Ehretraut theorem for nonregular processes. In Section 5, we show a useful application of the results obtained in Section 4 by developing the thermodynamics of an interface separating two Korteweg fluids. In Section 6, we discuss shockwave propagation in light of the theorems proven in Section 4. The previous results are then resumed in Section 7, wherein an analysis of the interpretation of the entropy principle in different thermodynamic theories is carried out.

2. Thermodynamic Processes from a Geometric Perspective

Let B be a continuous body obeying the following system of balance laws:

$$u_{\beta,t} + u_{\beta,j}v_j + \psi_{k,k}^\beta = r_\beta, \quad \beta = 1 \dots \omega, \tag{1}$$

with v_j as the components of the velocity field on B , ψ_k^β the components of the flux of u_β , and r_β the production of u_β . For the sake of simplicity, we assume that the supplies are absent. The fields u_β and fluxes ψ_k^β are supposed to depend on ω unknown fields $z_\alpha(x_j, t)$ as well as on their spatial derivatives $z_{\alpha,j}(x_j, t)$. The present analysis is carried out under the hypothesis that B occupies the whole space. Then, in order to solve the Cauchy problem for System (1), we must assign suitable initial conditions, namely,

$$z_\alpha(x_j, t_0) = z_{\alpha 0}(x_j), \quad \forall P \in B. \tag{2}$$

Often, System (1) may be put in the first-order quasi-linear form

$$A_0(\mathbf{u})u_{,t} + A_i(\mathbf{u})u_{,i} = \mathbf{f}(\mathbf{u}), \tag{3}$$

with the unknown N -column vector $\mathbf{u}(x, t) = (u_1, u_2, \dots, u_N)^T$, where A_0 and A_i are real $N \times N$ matrices and \mathbf{f} is also an N -column vector.

Remark 1. *It is worth observing that the number of unknown fields N depends on the state space, and that in general $N \neq \omega$.*

As consequence of the nonlinearity of System (3), nonregular solutions may be generated and may propagate in the medium as waves. A wave is a moving surface Ω represented by an equation of type

$$\Lambda(x_i, t) = 0. \tag{4}$$

The unitary normal \mathbf{n} on Ω and the normal speed V of Ω are provided by

$$\mathbf{n} = \frac{\text{grad } \Lambda}{|\text{grad } \Lambda|}, \quad V = -\frac{\frac{\partial \Lambda}{\partial t}}{|\text{grad } \Lambda|}. \tag{5}$$

Weak waves have a continuous velocity across the front and a jump in acceleration. In such a case, the unknown fields u_α , $\alpha = 1, \dots, N$ are continuous across the front and their gradients are discontinuous, with the jump pointing in the normal direction. The symbols F^+ and F^- denote the limits of F on the side of Ω , with positive and negative normals, respectively. The quantities $\Pi_\alpha = [u_{\alpha,i}]n_i$, where $[F] = F^+ - F^-$ is the jump of F along the normal, are called the amplitudes of the acceleration wave. The wave speeds and amplitudes of the acceleration waves are respectively provided by the eigenvalues λ and eigenvectors \mathbf{v} of the following eigenvalue problem:

$$(A_i n_i - \lambda A_0)\mathbf{v} = \mathbf{0}. \tag{6}$$

System (3) is said to be hyperbolic in the t -direction if $\det A_0 \neq 0$ and the problem (6) admits only real eigenvalues (characteristic speeds) and N independent right eigenvectors.

Then, for hyperbolic systems, the acceleration waves propagate with finite speed, meaning that the underlying physical theory satisfies the principle of causality, which imposes the requirement that the cause always precede the effect.

System (3) is said to be symmetric if A_0 is positive definite and $A_i = A_i^T$. Any symmetric system is hyperbolic. In addition to the finite speed of the perturbations, a further remarkable consequence of the symmetry of System (3) is the well-posedness of the Cauchy problem in the Sobolev spaces, i.e., for weak solutions [2,18].

For hyperbolic systems, shockwaves may occur, i.e., surfaces of discontinuity across which the unknown fields u_α , $\alpha = 1, \dots, N$ are also discontinuous [10].

Here and in the following, we assume that both the solution of the Cauchy problem (1)–(2) and its space and time derivatives suffer jump discontinuities across a regular surface Ω . Such a surface may be of a different nature, such as, for instance, a traveling wave or a surface separating two different phases. Moreover, Ω can be at rest, as happens, for instance, for the interface at the junction of two different materials. Then, in order to encompass as many physical situations as possible, we do not restrict our analysis only to hyperbolic systems, and consider the case of parabolic ones as well. Parabolic systems of partial differential equations arise when modeling several physical phenomena, such as, for instance, phase transitions or diffusive heat transport. A meaningful example is the classical Stefan problem, in which the boundary between two different phases moves with time, as happens during the melting of ice to water. Meantime, the evolving boundary is unknown, meaning that the Stefan problem is a free-boundary problem [19]. From a mathematical point of view, in the bulk phases the solutions of the heat equation are continuous and differentiable, while on the moving surface separating two adjacent phases the solutions of the underlying partial differential equations and its derivatives may suffer discontinuities across interfaces.

An alternative approach to using the phase transitions is provided by the phase field model for free boundaries, which consists of a system of parabolic partial differential equations in which the unknown fields represent the temperature and some order parameters, called the phase fields, characteristic of the different phases. The phase field equations may be representative of a wide range of interface problems, including the classical Stefan model [20].

Another phenomenon involving free boundaries is crystal growth. Specifically, this is a stage of the crystallization process consisting of the addition of new atoms in the characteristic arrangement of the crystalline lattice. This phenomenon is modeled by a parabolic system of partial differential equations in which the classical heat equation is coupled with the evolution equation of the order parameter, which characterizes the unknown boundary [21].

It is worth observing that for parabolic systems of partial differential equations, causality and finite speed of propagation can be achieved in a generalized sense, as pointed out by Fichera, [22], whose results have been revisited in [23].

We denote by Ω^+ the side of Ω with a positive normal, and by Ω^- the side of Ω with a negative normal. Analogously, B^+ and B^- denote the parts of B delimited by Ω^+ and Ω^- , respectively. For instance, if Ω is a travelling surface, then Ω^+ is the side of Ω with the normal directed toward the region B^+ which Ω is about to enter, and Ω^- is the side of Ω with the normal directed toward the region B^- which Ω is about to leave. In particular, if Ω is a shockwave, then B^+ denotes the region ahead the shock and B^- denotes the region behind the shock.

In this way, we have the following decomposition of B :

$$B = (B^+ \cup \Omega^+) \cup (B^- \cup \Omega^-). \tag{7}$$

Now, we consider the ω -dimensional vector space C_t spanned by the (discontinuous) solutions $z_\alpha(x_j, t)$ of Equations (1) and (2). The vector space C_t is said to be the space of the configurations at instant t . Because the solutions $z_\alpha(x_j, t)$ suffer jump discontinuities across Ω , there exist limits $z_\alpha^+(x_j, t)$ and $z_\alpha^-(x_j, t)$ of those function on Ω^+ and Ω^- , respectively. Thus, due to the decomposition in Equation (7), we have

$$C_t = (C_t(B^+) \oplus C_t(\Omega^+)) \oplus (C_t(B^-) \oplus C_t(\Omega^-)). \tag{8}$$

We assume that C_t has the structure of a finite-dimensional manifold in such a way that the total configuration space is provided by the set

$$C = \bigcup_{t \in [0, \infty]} \{t\} \times C_t, \tag{9}$$

with a the structure of a fiber bundle over the real line [6,7]. C is said to be a configuration bundle.

A vector valued function $\pi : t \in [\tau_0, \tau_0 + \tau] \subseteq \mathbb{R} \rightarrow z_\alpha(x_j, t) \in C$ is said to be a thermodynamic process π of duration τ . Moreover, $\pi = \pi(t)$ is the parametric equation of the curve Γ representative of π in C .

For $t_0 \in [\tau_0, \tau_0 + \tau]$, a vector valued function $p : t \in [t_0, \tau_0 + \tau] \subseteq \mathbb{R} \rightarrow z_\alpha(x_j, t) \in C$ is said to be a restricted thermodynamic process p with initial point t_0 and duration $\tau_0 + \tau - t_0$ [6]. Moreover, $p = p(t)$ is the parametric equation of the curve γ representative of p in C .

Remark 2. Because the functions $z_\alpha(x_j, t)$ suffer jump discontinuities across Ω , the curves $\pi(t)$ and $p(t)$ are piecewise regular.

Remark 3. For $t_0 = \tau_0$, we have $p(t) = \pi(t)$, while for $t_0 = \tau_0 + \tau$, $p(t)$ is the process of duration 0, i.e., the null process.

For any value of the time variable t , we define a state space Σ_t that is local in time as the 4ω -dimensional vector space

$$\Sigma_t = \{z_\alpha(x_j, t), z_{\alpha,j}(x_j, t)\}. \tag{10}$$

Σ_t is said to be the state space at instant t . Because of the decomposition in Equation (7), we have

$$\Sigma_t = (\Sigma_t(B^+) \oplus \Sigma_t(\Omega^+)) \oplus (\Sigma_t(B^-) \oplus \Sigma_t(\Omega^-)). \tag{11}$$

We assume that Σ_t has the structure of a finite-dimensional manifold. The total configuration space is now

$$S = \bigcup_{t \in [0, \infty]} \{t\} \times \Sigma_t, \tag{12}$$

with the structure of a fiber bundle over the real line. We call S the thermodynamic bundle.

Remark 4. The following inclusions are evident:

$$C_t \subset \Sigma_t, \quad C \subset S. \tag{13}$$

Let us now restrict our analysis to the regions B^+ and B^- only. Under the hypothesis that the functions u_β, ψ_k^β , and r_β depend continuously on their arguments in B^+ and B^- , in those regions the balance Equation (1) on the local state space Σ_t read

$$\frac{\partial u_\beta}{\partial z_\alpha} z_{\alpha,t} + \frac{\partial u_\beta}{\partial z_{\alpha,j}} z_{\alpha,jt} + \frac{\partial u_\beta}{\partial z_\alpha} z_{\alpha,j} v_j + \frac{\partial u_\beta}{\partial z_{\alpha,k}} z_{\alpha,kj} v_j + \frac{\partial \psi_k^\beta}{\partial z_\alpha} z_{\alpha,k} + \frac{\partial \psi_k^\beta}{\partial z_{\alpha,j}} z_{\alpha,jk} = r_\beta. \tag{14}$$

Equation (14) contains the space and time derivatives of the elements of $\Sigma_t(B^+)$ and $\Sigma_t(B^-)$, namely, the 10ω higher derivatives $\{z_{\alpha,t}, z_{\alpha,jt}, z_{\alpha,jk}\}$. Thus, we can define the local-in-time 10ω -dimensional vector spaces of the higher derivatives at time t as follows:

$$H_t(B^+) = \{z_{\alpha,t}(x_j, t), z_{\alpha,jt}(x_j, t), z_{\alpha,jk}(x_j, t)\}, \quad \{x_j\} \in B^+, \tag{15}$$

$$H_t(B^-) = \{z_{\alpha,t}(x_j, t), z_{\alpha,jt}(x_j, t), z_{\alpha,jk}(x_j, t)\}, \quad \{x_j\} \in B^-. \tag{16}$$

On the other hand, because the functions $u_\beta, \psi_k^\beta,$ and r_β depend continuously on their arguments, and because the limits of the functions z_α and of their space and time derivatives exist on Ω^+ and Ω^- , the limits of Equation (14) on Ω^+ and Ω^- exist as well. Consequently, we may define the spaces of the higher derivatives on Ω^+ and Ω^- , respectively, as follows:

$$H_t(\Omega^+) = \{z_{\alpha,t}(x_j, t), z_{\alpha,jt}(x_j, t), z_{\alpha,jk}(x_j, t)\}, \{x_j\} \in \Omega^+, \tag{17}$$

$$H_t(\Omega^-) = \{z_{\alpha,t}(x_j, t), z_{\alpha,jt}(x_j, t), z_{\alpha,jk}(x_j, t)\}, \{x_j\} \in \Omega^-. \tag{18}$$

In this way, the total space of the higher derivatives at time t is

$$H_t = (H_t(B^+) \oplus H_t(\Omega^+)) \oplus (H_t(B^-) \oplus H_t(\Omega^-)), \tag{19}$$

and the fiber bundle of the higher derivatives is

$$\mathcal{H} = \bigcup_{t \in [0, \infty]} \{t\} \times H_t. \tag{20}$$

The equilibrium subspaces of $H_t(B^+), H_t(\Omega^+), H_t(B^-),$ and $H_t(\Omega^-)$ are

$$\hat{E}_t(B^+) = \{z_{\alpha,jk}(x_j, t)\}, \{x_j\} \in B^+, \hat{E}_t(\Omega^+) = \{z_{\alpha,jk}(x_j, t)\}, \{x_j\} \in \Omega^+. \tag{21}$$

$$\hat{E}_t(B^-) = \{z_{\alpha,jk}(x_j, t)\}, \{x_j\} \in B^-, \hat{E}_t(\Omega^-) = \{z_{\alpha,jk}(x_j, t)\}, \{x_j\} \in \Omega^-. \tag{22}$$

Then, the total equilibrium subspace of H_t and its fibre bundle are

$$\hat{E}_t = (\hat{E}_t(B^+) \oplus \hat{E}_t(\Omega^+)) \oplus (\hat{E}_t(B^-) \oplus \hat{E}_t(\Omega^-)), \tag{23}$$

and

$$\hat{\mathcal{E}} = \bigcup_{t \in [0, \infty]} \{t\} \times \hat{E}_t, \tag{24}$$

respectively.

In B^+ and B^- , the entropy inequality on the state space reads

$$\rho \frac{\partial s}{\partial z_\alpha} z_{\alpha,t} + \rho \frac{\partial s}{\partial z_{\alpha,j}} z_{\alpha,jt} + \rho \frac{\partial s}{\partial z_\alpha} z_{\alpha,j} v_j + \rho \frac{\partial s}{\partial z_{\alpha,k}} z_{\alpha,kj} v_j + \frac{\partial J_k}{\partial z_\alpha} z_{\alpha,k} + \frac{\partial J_k}{\partial z_{\alpha,j}} z_{\alpha,jk} \geq 0, \tag{25}$$

wherein ρ is the mass density and s the specific entropy. Then, by a procedure analogous to that illustrated above, we can define the local-in-time 10ω -dimensional vector space of the higher derivatives at time t

$$W_t = (W_t(B^+) \oplus W_t(\Omega^+)) \oplus (W_t(B^-) \oplus W_t(\Omega^-)), \tag{26}$$

and the fiber bundle of the higher derivatives

$$\mathcal{W} = \bigcup_{t \in [0, \infty]} \{t\} \times W_t. \tag{27}$$

The equilibrium subspace of W_t and its fiber bundle are provided by

$$E_t = (E_t(B^+) \oplus E_t(\Omega^+)) \oplus (E_t(B^-) \oplus E_t(\Omega^-)), \tag{28}$$

and

$$\mathcal{E} = \bigcup_{t \in [0, \infty]} \{t\} \times E_t, \tag{29}$$

respectively.

Remark 5. We have defined two different spaces of the higher derivatives, one for the balance equations and another for the entropy inequality, as the main aim of the present investigation is to determine whether all the solutions of the balance laws are solutions of the entropy inequality as well, that is, whether $\mathcal{H} = \mathcal{W}$.

In B^+ and B^- , the relations in Equations (14) and (25) can be rewritten as follows:

$$\frac{\partial u_\beta}{\partial z_\alpha} z_{\alpha,t} + \frac{\partial u_\beta}{\partial z_{\alpha,j}} z_{\alpha,jt} + \left(\frac{\partial u_\beta}{\partial z_{\alpha,k}} v_j + \frac{\partial \psi_j^\beta}{\partial z_{\alpha,k}} \right) z_{\alpha,kj} = r_\beta - \frac{\partial u_\beta}{\partial z_\alpha} z_{\alpha,j} v_j - \frac{\partial \psi_j^\beta}{\partial z_\alpha} z_{\alpha,j}. \quad (30)$$

$$\rho \frac{\partial s}{\partial z_\alpha} z_{\alpha,t} + \rho \frac{\partial s}{\partial z_{\alpha,j}} z_{\alpha,jt} + \left(\rho \frac{\partial s}{\partial z_{\alpha,k}} v_i + \frac{\partial J_i}{\partial z_{\alpha,k}} \right) z_{\alpha,ki} \geq -\rho \frac{\partial s}{\partial z_\alpha} z_{\alpha,j} v_j - \frac{\partial J_i}{\partial z_\alpha} z_{\alpha,i}. \quad (31)$$

Because of our main assumptions on the constitutive quantities and the unknown fields z_α , we may calculate the limits of Equation (30) and the inequality (31) on Ω^+ and Ω^- , respectively.

By defining the $10\omega \times 1$ column vector function

$$y_\alpha \equiv \left(z_{\alpha,t}, z_{\alpha,jt}, z_{\alpha,kj} \right)^T, \quad (32)$$

on \mathcal{H} , the $\omega \times 1$ column vector

$$C_\beta \equiv r_\beta - \frac{\partial u_\beta}{\partial z_\alpha} z_{\alpha,j} v_j - \frac{\partial \psi_j^\beta}{\partial z_\alpha} z_{\alpha,j}, \quad \beta = 1 \dots \omega, \quad (33)$$

on \mathcal{S} , and the $\omega \times 10\omega$ matrix

$$A_{\beta\alpha} \equiv \left[\frac{\partial u_\beta}{\partial z_\alpha}, \frac{\partial u_\beta}{\partial z_{\alpha,j}}, \left(\frac{\partial u_\beta}{\partial z_{\alpha,k}} v_j + \frac{\partial \psi_j^\beta}{\partial z_{\alpha,k}} \right) \right], \quad (34)$$

on \mathcal{S} , the balance Equation (30) can be rearranged as follows:

$$A_{\beta\alpha}(\mathcal{S}) y_\alpha = C_\beta(\mathcal{S}), \quad y_\alpha \in \mathcal{H}. \quad (35)$$

Analogously, by defining the $10\omega \times 1$ column vector function

$$y_\alpha \equiv \left(z_{\alpha,t}, z_{\alpha,jt}, z_{\alpha,kj} \right)^T \quad (36)$$

on \mathcal{W} , the $10\omega \times 1$ column vector function

$$B_\alpha(\mathcal{S}) \equiv \left(\rho \frac{\partial s}{\partial z_\alpha}, \rho \frac{\partial s}{\partial z_{\alpha,j}}, \left(\rho \frac{\partial s}{\partial z_{\alpha,k}} v_i + \frac{\partial J_i}{\partial z_{\alpha,k}} \right) \right)^T \quad (37)$$

on \mathcal{S} , and the scalar function

$$D(\mathcal{S}) \equiv -\rho \frac{\partial s}{\partial z_\alpha} z_{\alpha,j} v_j - \frac{\partial J_i}{\partial z_\alpha} z_{\alpha,i} \quad (38)$$

on \mathcal{S} , we can write the inequality (31) as follows:

$$B_\alpha(\mathcal{S}) y_\alpha \geq D(\mathcal{S}), \quad y_\alpha \in \mathcal{W}. \quad (39)$$

Remark 6. It is worth observing that at a fixed instant t , System (35) reduces to

$$A_{\beta\alpha}(\Sigma_t) y_\alpha = C_\beta(\Sigma_t), \quad y_\alpha \in H_t, \quad (40)$$

while inequality (39) takes the form

$$B_\alpha(\Sigma_t)y_\alpha \geq D(\Sigma_t), \quad y_\alpha \in W_t. \tag{41}$$

The mathematical solutions of the Cauchy problem in Equations (2) and (35) are physically realizable if and only if they satisfy the unilateral differential constraint (39). Thus, in 1963 Coleman and Noll formulated the constitutive principle referred in Postulate 2, ensuring that all the solutions of Equation (35) fulfill inequality (39) as well [2,3]. This was the motivation of Muschik and Ehrentraut [1] in investigating whether Postulate 2 is a consequence of a general physical law or only a useful but arbitrary operational assumption.

3. Second Law of Thermodynamics for Nonregular Processes

We now consider a fixed point $P_0 \in B = (B^+ \cup \Omega^+) \cup (B^- \cup \Omega^-)$ with a vector position indicated by \mathbf{x} and a fixed instant of time which, without loss of generality, we can suppose to coincide with the initial instant t_0 . Moreover, let Σ_0 and H_0 be the vector spaces $\Sigma_t(P_0, t_0)$ and $H_t(P_0, t_0)$, respectively. When evaluated in (P_0, t_0) , the balance Equation (40) and the entropy inequality (41) yield the ω algebraic relations:

$$A_{\beta\alpha}(\Sigma_0)y_\alpha = C_\beta(\Sigma_0), \tag{42}$$

$$B_\alpha(\Sigma_0)y_\alpha \geq D(\Sigma_0). \tag{43}$$

In this way, we can regard the $\omega \times 10\omega$ matrix $A_{\beta\alpha}(\Sigma_0)$ as a linear morphism from H_0 to the ω -dimensional Euclidean vector space defined on Σ_0 . Analogously, the vector $B_\alpha(\Sigma_0)$ can be regarded as a linear application from H_0 in \mathbb{R} , so that $B_\alpha(\Sigma_0)$ belongs to the dual space H_0^* of H_0 . It is worth observing that if $A_{\beta\alpha}$ is supposed to be invertible, the algebraic relations (42) allow us to determine ω of the 10ω components of y_α . Moreover, by spatial derivation of the initial conditions (2) in B^+ and B^- , we obtain

$$z_{\alpha,jk}(x_j, t_0) = z_{\alpha 0,jk}(x_j), \tag{44}$$

which, when evaluated in P_0 , allows us to determine the further 6ω components of y_α in B^+ and B^- . Moreover, we can calculate the limits of the 6ω quantities in Equation (44) on Ω^+ and Ω^- .

However, because the initial conditions can be assigned arbitrarily, such 6ω quantities can assume arbitrary values in B^+ and B^- , and as a consequence, on Ω^+ and Ω^- . Furthermore, there are additional 3ω components of the vector y_α which remain completely arbitrary in $P_0 \in (B^+ \cup \Omega^+) \cup (B^- \cup \Omega^-)$, as System (40) and initial relations (44) allow us to determine only 7ω of the 10ω components of y_α . Thus, at initial time t_0 , at an arbitrary point $P_0 \in (B^+ \cup \Omega^+) \cup (B^- \cup \Omega^-)$ we arrive at the following conclusions as to the nature of the 10ω components of the vectors y_α which satisfy the algebraic relations (40) after the second spatial derivatives of the initial conditions (2) are assigned through the conditions (44):

- ω components are determined by Equation (40) when $A_{\beta\alpha}(\Sigma_0)$ and $C_\beta(\Sigma_0)$ are given;
- 6ω components are determined by Equation (44) when the second spatial derivatives of the initial conditions are calculated and evaluated in (P_0, t_0) ;
- 3ω components are unknown, as we do not have further relations with which to calculate them.

Remark 7. The situation described above is different than that considered in [1], where the quantities $z_{\alpha,t}$ are included in the state space. Then, Equation (1) is of the second order in time, meaning that suitable initial conditions

$$z_{\alpha,t}(x_j, t_0) = z_{\alpha,t 0}(x_j), \quad \forall P \in B. \tag{45}$$

must be provided for the time derivatives $z_{\alpha,t}$. Then, after spatial derivation of Equation (45), the 6ω relations (44) may be supplemented by the further 3ω conditions

$$z_{\alpha,tj}(x_j, t_0) = z_{\alpha,tj0}(x_j). \tag{46}$$

Thus, the 10ω components of the vectors y_α are completely determined by the balance Equation (1) and the initial conditions (2) and (46).

As we remarked in [5], we prefer to follow the standard approach of weakly nonlocal thermodynamics [2,15], which excludes the time derivatives from the state space, as such quantities are generally not invariant with respect to changes of observer [13]. Thus, the difference between the situation considered in [1] and the present one is that in their approach all the 10ω components are determined, while in our case only 7ω are determined and the remaining 3ω are completely unknown. However, what is important for our purposes is that in both cases 9ω of the 10ω components of y_α are completely arbitrary, as the initial conditions can be assigned arbitrarily. It can be observed that there exist infinite Cauchy problems yielding the relations (44) and (46), as these relations do not change when adding to the right-hand side of Equation (2) ω linear functions of the spatial coordinates and to the right-hand side of Equation (45) ω constant quantities.

Thus, due to the arbitrariness of 9ω of the 10ω components of y_α , nothing prevents the algebraic inequality (41) being violated for some y_α . As a consequence, we cannot decide a priori whether a solution y_α of the algebraic relations (40) is solution of the algebraic inequality (41) as well. The scope of the present investigation is to find the conditions, if any, that ensure that a solution y_α of the algebraic relations (40) is also a solution of the algebraic inequality (41). To achieve this task, we define the space $W_0 \subseteq H_0$ constituted by the vectors of H_0 which satisfy both Equation (40) and inequality (41), then investigate whether $W_0 \subset H_0$, or $W_0 = H_0$. In this investigation we follow the way paved by Muschik and Ehrentraut [1], who added to inequality (41) an amendment clarifying how the reversible transformations can be realized from the operative point of view. In [5], we reinterpreted this strategy within a more general approach incorporating the amendment into a new formulation of the second law of thermodynamics. In the present paper, we do the same while extending our analysis to nonregular processes.

Let us start by observing that in the real world reversible thermodynamic transformations are approximated by quasi-static ones, in which in any point $P_0 \in B$ the system is very close to thermodynamic equilibrium. From a ideal point of view, a quasi-static transformation requires an infinite time to occur, and in any point of the system the value of the state variables is constant in time.

Remark 8. *More realistic approaches which consider thermodynamic transformations occurring in a finite time can be found within the framework of finite time thermodynamics [24–26].*

If B undergoes a quasi-static transformation, in any point (P_0, t_0) the vectors of the higher derivatives are elements of E_0 . Such an observation suggests the following definitions: a vector $y_\alpha \in H_0$ is said to be

- real, if it satisfies the relation $B_\alpha(\Sigma_0)y_\alpha > D(\Sigma_0)$;
- ideal, if it satisfies the relation $B_\alpha(\Sigma_0)y_\alpha = D(\Sigma_0)$;
- over-ideal, if it satisfies the relation $B_\alpha(\Sigma_0)y_\alpha < D(\Sigma_0)$.

Based on the above definitions we can provide the following postulate.

Postulate 3. Local formulation of the second law of thermodynamics. *Let the couple (P_0, t_0) represent an arbitrary point of $B = (B^+ \cup \Omega^+) \cup (B^- \cup \Omega^-)$ at an arbitrary instant $t_0 \in [\tau_0, \tau_0 + \tau]$. Suppose B undergoes an arbitrary thermodynamic process with initial instant t_0 and duration $\tau_0 + \tau - t_0$. Then, the local space of the higher derivatives W_0 does not contain over-ideal vectors. Moreover, a vector $y_\alpha \in W_0$ is ideal if, and only if, (P_0, t_0) is in a thermodynamic equilibrium.*

According to the postulate above, in a thermodynamic process the entropy production cannot be negative in any point P_0 of B at any instant t_0 . Moreover, the entropy production can be zero only in the points of B which are in thermodynamic equilibrium. In particular, we say that the point $P_0 \in B$ at the instant t_0 is in thermodynamic equilibrium if, and only if, $W_0 = E_0$.

Remark 9. *Although the local formulation of the second law of thermodynamics prohibits over-ideal vectors being in W_0 , it does not prevent their being in H_0 . Our investigation is aimed at determining whether or not H_0 contains over-ideal vectors.*

Let us now suppose that $B = (B^+ \cup \Omega^+) \cup (B^- \cup \Omega^-)$ undergoes a thermodynamic process p with initial instant t_0 and duration $\tau_0 + \tau - t_0$, represented by a piecewise regular curve γ in \mathcal{C} . The process p is said to be:

- irreversible, if in any point of γ the vector of the higher derivatives $y_\alpha(P, t)$ is either real or ideal, and there exists at least a point of γ in which such a vector is real;
- reversible, if in any point of γ the vector of the higher derivatives $y_\alpha(P, t)$ is ideal;
- over-reversible, if there exists at least a point of γ in which the vector of the higher derivatives $y_\alpha(P, t)$ is over-ideal.

Remark 10. *Because γ is piecewise regular, in its points on Ω^+ and Ω^- the vector of the higher derivatives $y_\alpha(P, t)$ could be of different natures.*

The definitions above allow us to enunciate a further postulate.

Postulate 4. Global formulation of the second law of thermodynamics. *Over-reversible processes do not occur in nature. Moreover, a thermodynamic process is reversible if, and only if, any point $P \in B$ at any instant t is in thermodynamic equilibrium.*

Remark 11. *We note that the local formulation of the second law regards points of B^+ and B^- as well as points of Ω^+ and Ω^- . Analogously, the global formulation holds for processes occurring in the whole B , including the discontinuity surface Ω . In the absence of Ω , the process is regular, and the situation already analyzed in [5] is recovered. However, if the process involves the points of a discontinuity surface Ω , then it is nonregular and the function $p : t \in [t_0, \tau_0 + \tau] \subseteq \mathbb{R} \rightarrow z_\alpha(x_j, t) \in \mathcal{C}$ is discontinuous on Ω . Postulate 4 ensures that at every instant t and in any point P in $B = (B^+ \cup \Omega^+) \cup (B^- \cup \Omega^-)$ the space of the higher derivatives $H(P, t)$ does not contain over-ideal vectors.*

4. The Muschik and Ehrentraut Theorem for Nonregular Processes

In this section, we present a novel formulation of the Muschik and Ehrentraut theorem proven in [1]. To this end, we use the thermodynamic framework and the generalized formulations of the second law established above.

Theorem 2. *Whatever are $P_0 \in B = (B^+ \cup \Omega^+) \cup (B^- \cup \Omega^-)$ and $t_0 \in [\tau_0, \tau_0 + \tau] \subseteq \mathbb{R}$, $H_0(P_0, t_0) = W_0(P_0, t_0)$.*

Proof. As pointed out in Section 3, in the generic point (P_0, t_0) , namely, at constant values of $A_{\beta\alpha}(\Sigma_0), C_\beta(\Sigma_0), B_\alpha(\Sigma_0)$, and $D(\Sigma_0)$ and for given initial conditions (2), Equations (2), (40) and (44) do not allow us to determine the vector of the higher derivatives corresponding to the Cauchy problem (1) and (2) uniquely in (P_0, t_0) , but only ω of its 10 ω components. Thus, it is impossible to substitute such a vector into inequality (41) in order to verify by direct calculation whether or not it satisfies such a constraint. As such, we have to investigate the thermodynamic nature of y_α (real, ideal, or over-ideal) without knowing it. We start by observing that H_0 cannot contain only over-ideal vectors. In fact, if all y_α in H_0 were over-ideal, as a consequence of Postulate 3 the vector space W_0 would be empty,

and no process would be possible in (P_0, t_0) . On the other hand, due to the arbitrariness of (P_0, t_0) , no thermodynamic transformation would be possible in B in the interval of time $[t_0, \tau_0 + \tau - t_0]$. Thus, while the space H_0 may in principle contain over-ideal vectors, it should contain at least a further type of vector (ideal, real, or both).

Let us suppose that the space H_0 contains an ideal vector y_α^1 and an over-ideal vector y_α^2 . Because y_α^1 exists if and only if (P_0, t_0) is in thermodynamic equilibrium, while y_α^2 exists if and only if (P_0, t_0) is not in thermodynamic equilibrium, such a situation cannot occur. From analogous considerations it follows that it is impossible to have y_α^1 be ideal and y_α^2 be real.

However, we may have y_α^1 real and y_α^2 over-ideal, provided (P_0, t_0) is not in equilibrium. In such a case, due to the local formulation of the second law, neither y_α^1 nor y_α^2 are elements of E_0 . Thus, we can consider the linear combination of $y_\alpha^3 = \lambda y_\alpha^1 + (1 - \lambda)y_\alpha^2$ with $\lambda \in]0, 1[$. Because y_α^1 and y_α^2 are elements of H_0 , they satisfy the following algebraic equations:

$$A_{\beta\alpha}(\Sigma_0)y_\alpha^1 = C_\beta(\Sigma_0), \tag{47}$$

$$A_{\beta\alpha}(\Sigma_0)y_\alpha^2 = C_\beta(\Sigma_0). \tag{48}$$

By combination of Equation (47) multiplied by λ and Equation (48) multiplied by $(1 - \lambda)$, we obtain

$$A_{\beta\alpha}(\Sigma_0)y_\alpha^3 = C_\beta(\Sigma_0), \tag{49}$$

meaning that y_α^3 is in H_0 . On the other hand, the local entropy production corresponding to y_α^3 can be written as

$$\begin{aligned} \sigma^3 &= \lambda [B_\alpha(\Sigma_0)y_\alpha^1 - D(\Sigma_0)] + (1 - \lambda) [B_\alpha(\Sigma_0)y_\alpha^2 - D(\Sigma_0)] = \\ &= B_\alpha(\Sigma_0) [\lambda y_\alpha^1 + (1 - \lambda)y_\alpha^2] - D(\Sigma_0). \end{aligned} \tag{50}$$

Because λ is arbitrary in $]0, 1[$, nothing prevents its being chosen as

$$\lambda = \frac{D(\Sigma_0) - B_\alpha(\Sigma_0)y_\alpha^2}{B_\alpha(\Sigma_0)[y_\alpha^1 - y_\alpha^2]}. \tag{51}$$

In fact, with y_α^2 being over-ideal, we have $D(\Sigma_0) - B_\alpha(\Sigma_0)y_\alpha^2 > 0$. Moreover, with y_α^1 being real, we have $B_\alpha(\Sigma_0)[y_\alpha^1 - y_\alpha^2] > D(\Sigma_0) - D(\Sigma_0)$, namely, $B_\alpha(\Sigma_0)[y_\alpha^1 - y_\alpha^2] > 0$. Hence, $\lambda > 0$. Moreover, with y_α^1 being real, we have $B_\alpha(\Sigma_0)[y_\alpha^1 - y_\alpha^2] > D(\Sigma_0) - B_\alpha(\Sigma_0)y_\alpha^2$, hence, $\lambda < 1$.

On the other hand, it is immediately apparent that if λ is provided by Equation (51), the right-hand side of Equation (50) vanishes, and hence y_α^3 is in E_0 . However, this is impossible, as per our hypothesis the point (P_0, t_0) is not in thermodynamic equilibrium. Thus, it is impossible that there be both real and over-ideal vectors in (P_0, t_0) which are solutions of the local balance laws (40).

Furthermore, suppose that both y_α^1 and y_α^2 are real. Then, from Equation (50) it follows that $\sigma^3 > 0$, irrespective of $\lambda \in]0, 1[$. Finally, if (P_0, t_0) is a point of equilibrium, then the entropy production corresponding to y_α^1 and y_α^2 vanishes; from Equation (50), it then follows that σ^3 is zero. Thus, we can conclude that the latter two situations are physically admissible.

From the considerations above, it follows that in a point P_0 of $B = (B^+ \cup \Omega^+) \cup (B^- \cup \Omega^-)$ at a given instant t_0 , the vectors which satisfy Equation (40) cannot be of different types. Moreover, they cannot be over-ideal only, as this contradicts the local form of the second law of thermodynamics. Thus, H_0 may contain either only real vectors, in which case (P_0, t_0) is a point of non-equilibrium, or ideal vectors only, in which case (P_0, t_0) is a point of equilibrium. This conclusion proves the theorem. \square

Corollary 3. $\mathcal{H} = \mathcal{W}$.

Proof. This corollary is an immediate consequence of the arbitrariness of the initial instant t_0 and of the point P_0 . In particular, whatever we take as $t \in [\tau_0, \tau_0 + \tau]$, we can consider it as the initial instant t_0 of the restricted process of duration $\tau_0 + \tau - t_0$. Then, the considerations made in Section 3 allow us to conclude that 9ω of the 10ω components of the vectors of H_0 are completely arbitrary, meaning that the conclusions established in Theorem 2 can be applied to H_0 . This is enough to prove that for any $t \in [\tau_0, \tau_0 + \tau]$ with arbitrary τ_0 and τ , the space of the higher derivatives H_t contains only real or ideal vectors. \square

Corollary 4. *The unilateral differential constraint (25) is a restriction on the constitutive quantities $u_\beta, r_\beta, s,$ and $J_k,$ and not on the thermodynamic processes $p.$*

Proof. In fact, as a consequence of Theorem 2, any process $p : t \in [\tau_0, \tau_0 + \tau] \subseteq \mathbb{R} \rightarrow z_\alpha(x_j, t) \subseteq \mathcal{C},$ where $z_\alpha(x_j, t)$ is a discontinuous solution of the balance laws (1), can only be either irreversible or reversible, not over-reversible, because otherwise at least in a point of its representative curve γ the space of the higher derivatives H_t would contain an over-ideal point, which is against Postulate 3. Thus, the second law of thermodynamics cannot exclude some processes $p(t),$ because all those processes are admissible. On the other hand, given the state space, only suitable forms of $A_{\beta\alpha}, C_\beta, s,$ and J_k guarantee non-negative entropy production. As such, the role of the unilateral differential constraint in Equation (25) is simply to select such forms. \square

5. Thermodynamics of an Interface

In this section we consider a thin interface separating two different materials, such as, for instance, a liquid and its vapor. Due to its small thickness, it can be modeled as a two-dimensional domain, endowed with suitable material properties accounting for its actual three-dimensional nature [27].

Thermodynamics of interfaces has been widely investigated due to its applications in science and technology [28]. Our aim here is not to establish new balance equations for the interface; rather, it is to consider a more general material with respect to that considered in [27] and derive further thermodynamic properties. To achieve that task, we need the results of Section 4, which ensures that the conclusions in [1] remain valid in the presence of discontinuity surfaces. Hence, the present investigation can be considered as an application of the general result proven in Section 4.

In what follows, the interface is regarded as a singular domain across which the unknown fields suffer jump discontinuities. This physical situation may be representative of the motion of fluids in capillary channels [28–30] or of liquid–vapor phase transitions [31,32]. For the sake of simplicity, we suppose that:

1. the interface is material;
2. the interface is plane.

The first hypothesis means that the limit values of the normal component of the particle velocity in the bulk are equal, and coincide with the normal speed of the surface. Under these circumstances, the balance equations are considerably simplified [27].

The second hypothesis can be made whenever the curvature of the interface is small with respect to the area of the interface. This allows to neglect all the surface effects due to the curvature [27,28] and to use rectangular Cartesian coordinates on the interface. Let S be a plane interface with state space

$$Z_S = \{\sigma; \sigma_{,\alpha}; \varepsilon; \varepsilon_{,\alpha}\}, \tag{52}$$

where σ is the surface mass density, ε is the surface specific energy, and the symbol $f_{,\alpha}$ stands for the partial derivative of f with respect to the Cartesian surface coordinates $x_{\alpha}, \{ \alpha=1,2 \}.$ It can be observed that, due to the presence of $\sigma_{,\alpha}$ in the state space, the interface can be considered to be a Korteweg fluid [33] of the type analyzed by Dunn and Serrin in their celebrated paper [34]. Therein, the authors proposed a new form of the local balance of

energy containing the divergence of an energy extra-flux, representing the local power due to the nonlocal interactions (interstitial working) [34]. Such a power does not vanish even in the absence of heat flux. It is worth noticing that along with Müller, such a behavior can alternatively be described as an entropy extra-flux [35]. Finally, we suppose that a Korteweg fluid is present in the bulk as well, meaning that there is an energy extra-flux in the bulk.

Under the previous hypotheses, in the absence of body forces and heat supply, the balance equations for mass, linear momentum, and energy on \mathcal{S} read [27]

$$\dot{\sigma} + \sigma v_{\alpha,\beta} \delta_{\alpha\beta} = 0, \tag{53}$$

$$\sigma \dot{v}_\alpha - \tau_{\alpha\beta,\beta} v_{\alpha,\beta} + T_\alpha^n = 0, \tag{54}$$

$$\sigma \dot{\varepsilon} - \tau_{\alpha\beta} v_{\alpha,\beta} + q_{\beta,\beta} - \ell_{\beta,\beta} + h^n - l^n = 0, \tag{55}$$

where v_α denotes the components of the velocity of the points of \mathcal{S} , $\delta_{\alpha\beta}$ the components of the identity tensor on the interface, $\tau_{\alpha\beta}$ the components of the surface stress tensor, q_α the components of the surface heat flux, and ℓ_α the components of the surface energy extra-flux. Finally, a superposed dot denotes the material time derivative on the interface, namely, $\dot{f} = f_{,t} + f_{,\alpha} v_\alpha$.

In the bulk, we suppose that the fields and their derivatives suffer jump discontinuities only across \mathcal{S} , i.e., their limits on \mathcal{S}^+ and \mathcal{S}^- exist and are independent of the direction along which the limit is calculated.

Thus, in Equations (54) and (55) we use the following notation:

$$T_\alpha^n \equiv T_{\alpha 3}^+ n_3^+ - T_{\alpha 3}^- n_3^-, \tag{56}$$

$$h^n \equiv h_3^+ n_3^+ - h_3^- n_3^-, \tag{57}$$

$$l^n \equiv l_3^+ n_3^+ - l_3^- n_3^-, \tag{58}$$

with $T_{\alpha 3}$ as the components of the stress tensor along the direction x_3 , h_i as the components of the heat flux in the bulk, l_i as the components of the energy extra-flux in the bulk, and \mathbf{n} as the normal to \mathcal{S} which, since \mathcal{S} is plane, can be supposed to be parallel to the x_3 coordinate.

In the existing literature, it is assumed that these jumps are always in accordance with the second law of thermodynamics. However, such a presupposition is no longer true if the entropy inequality does not represents a constraint on the constitutive equations on both sides of the intermediate domain as well. This consideration explains why our results in Section 4 are essential when dealing with this type of discontinuity surfaces.

On the interface, the second law of thermodynamics takes the form [27]

$$\sigma \dot{\eta} + \left(\frac{q_\alpha}{T}\right)_{,\alpha} + \left(\frac{h}{\theta}\right)^n \geq 0, \tag{59}$$

where η is the specific surface entropy, T is the absolute temperature of the interface, θ is the absolute temperature in the bulk, and

$$\left(\frac{h}{\theta}\right)^n \equiv \left(\frac{h_3^+ n_3^+}{\theta^+}\right) - \left(\frac{h_3^- n_3^-}{\theta^-}\right). \tag{60}$$

The unilateral differential constraint (59) on the state space reads

$$\begin{aligned} & \sigma T \left[\frac{\partial \eta}{\partial \sigma} \dot{\sigma} + \frac{\partial \eta}{\partial \sigma_{,\gamma}} (\dot{\sigma}_{,\gamma}) + \frac{\partial \eta}{\partial \varepsilon} \dot{\varepsilon} + \frac{\partial \eta}{\partial \varepsilon_{,\gamma}} (\dot{\varepsilon}_{,\gamma}) \right] \\ & + \frac{1}{T} \left(\frac{\partial \ell_\alpha}{\partial \sigma} \sigma_{,\alpha} + \frac{\partial \ell_\alpha}{\partial \sigma_{,\beta}} \sigma_{,\beta\alpha} + \frac{\partial \ell_\alpha}{\partial \varepsilon} \varepsilon_{,\alpha} + \frac{\partial \ell_\alpha}{\partial \varepsilon_{,\beta}} \varepsilon_{,\beta\alpha} \right) \\ & - \frac{1}{T} \left(\frac{\partial T}{\partial \sigma} \sigma_{,\alpha} + \frac{\partial T}{\partial \sigma_{,\beta}} \sigma_{,\beta\alpha} + \frac{\partial T}{\partial \varepsilon} \varepsilon_{,\alpha} + \frac{\partial T}{\partial \varepsilon_{,\beta}} \varepsilon_{,\beta\alpha} \right) q_\alpha - \sigma \dot{\varepsilon} + \tau_{\alpha,\beta} v_{\alpha,\beta} \\ & - h^n + l^n + T \left(\frac{h}{\theta} \right)^n \geq 0. \end{aligned} \tag{61}$$

The inequality above must be satisfied along arbitrary thermodynamic processes [27].

According to the classical Coleman–Noll procedure for the exploitation of the entropy principle, the local balances of mass and energy (53) and (55) must be substituted into the dissipation inequality (61). Herein, in order to take into account the dependency of the constitutive equations on $\sigma_{,\gamma}$, we generalize such a procedure by substituting the evolution equation for $\sigma_{,\gamma}$ into Equation (61). Hence, we must calculate the gradient extension of Equation (53), which reads

$$\dot{\sigma}_{,\gamma} + \sigma_{,\gamma} v_{\alpha,\beta} \delta_{\alpha\beta} + \sigma v_{\alpha,\beta\gamma} \delta_{\alpha\beta} = 0, \tag{62}$$

On the other hand, it is easy to verify that

$$(\dot{\sigma}_{,\gamma}) = \dot{\sigma}_{,\gamma} - \sigma_{,\beta} v_{\beta,\gamma} = - \left(\sigma_{,\gamma} v_{\alpha,\beta} \delta_{\alpha\beta} + \sigma v_{\alpha,\beta\gamma} \delta_{\alpha\beta} + \sigma_{,\beta} v_{\beta,\gamma} \right). \tag{63}$$

After Equations (53) and (55), together with the gradient extensions (62) and (63), are substituted into the local entropy balance (61), we obtain a generalized Coleman–Noll inequality; we omit its extended expression here for the sake of concision. Then, as usual, the thermodynamic restrictions are obtained by requiring that the coefficients of the higher derivatives

$$H_S = \left\{ v_{\alpha,\beta}; v_{\alpha,\beta\gamma}; \sigma_{,\alpha\beta}; \varepsilon_{,\alpha\beta}; \dot{\varepsilon}_{,\gamma} \right\}, \tag{64}$$

which are not included in the state space, vanish. This yields the following theorem.

Theorem 5. *The unilateral differential constraint (61) is satisfied along arbitrary thermodynamic processes if, and only if, the following thermodynamic restrictions hold:*

$$\frac{\partial \eta}{\partial \varepsilon_{,\beta}} = 0, \tag{65}$$

$$\left\langle \frac{\partial \eta}{\partial \sigma_{,\beta}} \delta_{\alpha\gamma} \right\rangle_{(\beta,\gamma)} = 0, \tag{66}$$

$$\left\langle \frac{\partial \ell_\beta}{\partial \varepsilon_{,\alpha}} - \frac{1}{T} \frac{\partial T}{\partial \varepsilon_{,\beta}} q_\alpha \right\rangle = 0, \tag{67}$$

$$\left\langle \frac{\partial \ell_\beta}{\partial \sigma_{,\alpha}} - \frac{1}{T} \frac{\partial T}{\partial \sigma_{,\beta}} q_\alpha \right\rangle = 0, \tag{68}$$

$$T \sigma^2 \frac{\partial \eta}{\partial \sigma} \delta_{\alpha\beta} + T \sigma \sigma_{,\gamma} \frac{\partial \eta}{\partial \sigma_{,\gamma}} \delta_{\alpha\beta} + T \sigma \frac{\partial \eta}{\partial \sigma_{,\beta}} \sigma_{,\alpha} = \tau_{\alpha\beta}, \tag{69}$$

$$\frac{\partial \ell_\beta}{\partial \sigma} \sigma_{,\beta} + \frac{\partial \ell_\beta}{\partial \varepsilon} \sigma_{,\beta} - \frac{1}{T} \left(\frac{\partial T}{\partial \sigma} \sigma_{,\alpha} + \frac{\partial T}{\partial \varepsilon} \varepsilon_{,\alpha} \right) q_\alpha - h^n + l^n + T \left(\frac{h}{\theta} \right)^n \geq 0. \tag{70}$$

Here, the symbol $\langle \mathcal{F}_{abc\dots} \rangle_{(a,b)}$ denotes the symmetric part of the tensor function \mathcal{F} with respect to the indices a and b , while the symbol $\langle \mathcal{F}_{abc\dots} \rangle$ denotes the symmetric part with respect to all its indices.

Note that due to the introduction of the evolution equation of $\sigma_{,\gamma}$ into the entropy inequality (61), the specific entropy η can depend on $\sigma_{,\gamma}$. As a consequence, the surface stress tensor $\tau_{\alpha\beta}$ takes the form (69). Without such a substitution, the tensor $\tau_{\alpha\beta}$ would have the classical expression proven in the physics of the interfaces [28], namely,

$$\tau_{\alpha\beta} = T\sigma^2 \frac{\partial \eta}{\partial \sigma} \delta_{\alpha\beta}. \tag{71}$$

More details on this new mathematical method of exploitation of the entropy inequality can be found in [36].

6. Shockwave Propagation

In this section, we discuss the influence of second law of thermodynamics on shock wave propagation. Shock waves have been studied for a very long time [37], and constitute a cornerstone of modern physics [38]. They have several important applications in biomedicine [39] and technology [40]. In continuum physics, shockwaves arise as discontinuous solutions of first-order quasi-linear systems of balance laws [10,16]. Herein, we aim to consider their relation with the second law of thermodynamics, that is, with the requirement of non-negative entropy production for arbitrary thermodynamic processes.

For the sake of simplicity, let us consider the single scalar partial differential equation in the unknown function $u(x, t)$

$$u_{,t} + f_{,x} = 0, \tag{72}$$

where x is a scalar space coordinate, t is the time, and $f = f(u(x, t))$ is the flux of u across a plane orthogonal to direction x . Equations of this type are of considerable importance in physics, as they represent scalar balance laws. Equation (72) may admit discontinuous solutions [10], which may be interpreted in terms of several physical phenomena. A shock wave is a travelling surface across which the unknown field $u(x, t)$ suffers jump discontinuities. In the presence of discontinuous solutions across a surface, the first problem to be solved is how the solutions on adjacent sides of the surface have to be related one to the other, as well as to the speed of propagation of the surface. It can be proved that the following celebrated Rankine–Hugoniot jump condition holds [10] across the discontinuity surface:

$$f(u_+) - f(u_-) = \bar{s}(u_+ - u_-), \tag{73}$$

where u_+ and u_- denote the values of u ahead and behind the shock, respectively, and \bar{s} is the shock velocity. From the mathematical point of view, the (weak) solution of Equation (72) with the jump condition (73) is not unique [10], meaning that it is important to select among the solutions those which are physically admissible. Indeed, admissible shocks must satisfy the celebrated Lax conditions:

$$U_- > \bar{s} > U_+, \tag{74}$$

where U_- is the characteristic speed behind the shock and U_+ is the characteristic speed ahead the shock [10]. It can be proven that for perfect fluids the Lax conditions are equivalent to the entropy growth condition:

$$\sigma^+ - \sigma^- > 0, \tag{75}$$

where σ^+ is the entropy production ahead the shock and σ^- the growth behind the shock [10]. The common interpretation of this result is that for the weak solutions of balance laws, the second law of thermodynamics restricts the thermodynamic processes instead of the constitutive equations, because physically admissible shocks are only those for which the entropy production grows across the shock. Such an interpretation seems to be questionable, as it implies that a general law of nature would have different consequences on thermodynamic processes having different mathematical regularity. Thus, this problem deserves a deeper analysis in light of the results in Corollary 4. Indeed, we prove that the

second law of thermodynamics necessarily restricts the constitutive equations on both sides of the shock, and that the entropy growth conditions are a necessary consequence of that result.

Theorem 6. *The local and global formulations of the second law of thermodynamics (Postulates 3 and 4), and Theorem 2 imply that the local entropy production across a shock wave is positive.*

Proof. Let us first suppose that the shock wave is traveling into an equilibrium state. Then, the points on Ω^+ are in thermodynamic equilibrium, while the points on Ω^- are not in equilibrium. As a consequence of the local formulation of the second law (Postulate 3), at the time t_s in which the shock occurs, the vectors $y_\alpha^+(P_s, t_s)$ are ideal, and the vectors $y_\alpha^-(P_s, t_s)$ are real. Then, $\sigma^+(P_s, t_s) = 0$ if $P_s \in \Omega^+$, and $\sigma^-(P_s, t_s) > 0$ if $P_s \in \Omega^-$, meaning that $\sigma^-(P_s, t_s) - \sigma^+(P_s, t_s) > 0$.

If the shock wave is instead traveling into a nonequilibrium state, then the vectors $y_\alpha^+(P_s, t_s)$ and $y_\alpha^-(P_s, t_s)$ are both real. In such a case, let us suppose that for a given $y_\alpha^+(P_s, t_s)$ there exist vectors $y_\alpha^-(P_s, t_s)$ such that $\sigma^-(P_s, t_s) - \sigma^+(P_s, t_s) > 0$ and vectors $y_\alpha^-(P_s, t_s)$ such that $\sigma^-(P_s, t_s) - \sigma^+(P_s, t_s) < 0$. Then, due to the continuity of $\sigma^-(P_s, t_s)$ as a function of the vectors $y_\alpha^-(P_s, t_s)$ on Ω^- , necessarily there exists a vector $\hat{y}_\alpha^-(P_s, t_s) \in W_0(P_s, t_s)$ such that $\sigma^-(\hat{y}_\alpha^-(P_s, t_s)) - \sigma^+(P_s, t_s) = 0$. Thus, the thermodynamic process corresponding to the generation of this shockwave would be reversible, even though the point (P_s, t_s) is not in equilibrium, on both Ω^+ and Ω^- . Because this contradicts the global formulation of the second law (Postulate 4), such a situation is physically not realizable. As a consequence, when $y_\alpha^+(P_s, t_s)$ is assigned, the quantity $\sigma^-(P_s, t_s) - \sigma^+(P_s, t_s)$ must have the same sign, irrespective of vector $y_\alpha^-(P_s, t_s)$. On the other hand, if $\sigma^-(P_s, t_s) - \sigma^+(P_s, t_s) < 0$, with the vectors $y_\alpha^-(P_s, t_s)$ being completely arbitrary, the latter inequality could be easily violated for some y_α^- unless $\sigma^-(P_s, t_s) < 0$, irrespective of vector $y_\alpha^-(P_s, t_s)$. Hence, at instant t_s , all the vectors in the local space of the higher derivatives at point P_s of Ω^- would be over-ideal, which is against the result in Theorem 2. As a consequence, we must conclude that for arbitrary couples (P_s, t_s) , $\sigma^-(P_s, t_s) - \sigma^+(P_s, t_s) > 0$. \square

Corollary 7. *Corollary 3 implies that the total entropy production across a shock wave is positive.*

Proof. This proposition is an immediate consequence of the arbitrariness of the instant t_s and the point P_s . In fact, whatever the instant t_s at which the shockwave starts, it can be considered as the initial instant of a process $p : t \in [t_s, t_s + \tau] \subseteq \mathbb{R} \rightarrow z_\alpha(x_j, t) \subseteq \mathcal{C}$, where $z_\alpha(x_j, t)$ is a solution of the balance laws (14) in $B = [(B^+ \cup \Omega^+) \cup (B^- \cup \Omega^-)] \times [t_s, t_s + \tau]$. Thus, by Corollary 3 together with Theorem 6, we can conclude that at any instant of time $t \in [t_s, t_s + \tau]$, the entropy production across Ω is positive in any point P_s of Ω . Consequently, the total entropy production across the shock is positive. \square

7. Conclusions

In continuum physics, the second law of thermodynamics is interpreted as a restriction on the constitutive equations which characterize the material properties. An alternative interpretation regards the second law as a restriction on the thermodynamic processes. The problem of choosing among these two interpretations was solved in 1996 by Muschik and Ehretraut [1], who postulated an amendment to the second law which assumes that at a fixed instant of time and in any point of the state space, reversible process directions exist if and only if this point is in thermodynamic equilibrium. Muschik and Ehretraut proved that, presupposing the amendment, the second law of thermodynamics necessarily restricts the constitutive equations and not the thermodynamic processes. Their result has been recently revisited by Cimmelli and Rogolino [5] within a geometric framework. The latter authors proposed a generalized formulation of the second law of thermodynamics which incorporates the amendment.

In the present paper, following the way already paved in [8], we have extended the results in [5] to the case in which there are surfaces across which the unknown fields suffer

jump discontinuities. Such an investigation seems to be important for both practical and theoretical ends.

From the practical point of view, there exist several experimental situations involving discontinuous solutions of the balance laws, such as, for instance, fluid and solid interfaces in phase transitions and capillarity, or propagation of discontinuity waves.

From the theoretical point of view, such an analysis leads to a deeper look at the role of second law of thermodynamics in the propagation of shock waves. In fact, for shock waves the celebrated entropy growth conditions apparently seem to indicate that for weak solutions of balance laws the role of the second law of thermodynamics is to restrict thermodynamic processes by selecting those physical shocks which are thermodynamically admissible. This could lead to the strange conclusion that the consequences of the second law are different for different classes of regularity of the solutions of balance laws. Indeed, in this research we have proven that the second law of thermodynamics restricts the constitutive equations on both sides of the shock, and that the entropy growth across the shock is a necessary consequence of those restrictions.

For the sake of comparison, in Table 1 the results obtained in the present paper are compared with those obtained in Refs. [1,5,8].

Table 1. Comparison of the results in [1,5,8] with the results obtained in the present paper.

Results	Ref. [1]	Ref. [5]	Ref. [8]	Present Paper
Rigorous proof of the validity of the entropy principle	Yes	Yes	Yes	Yes
Geometric approach to Non-Equilibrium Thermodynamics	No	Yes	No	Yes
Generalized Second Law including Amendment	No	Yes	No	Yes
Extension of the entropy principle to Non Regular Processes	No	No	Yes	Yes
Proof of the validity of the entropy principle for shock-wave propagation	No	No	No	Yes

As a further application of the result above, we discuss its influence on the theoretical framework of the thermodynamic theories of continuum physics mentioned in Section 1. Among them, Rational Thermodynamics [13] and Extended Irreversible Thermodynamics [14] exploit the entropy principle solely within the scope of obtaining thermodynamic restrictions on the constitutive equations. Both these theories are weakly nonlocal, in the sense that the gradients of the unknown fields are allowed to enter the state space, and obtain the thermodynamic restrictions by applying rigorous mathematical methods such as the Coleman–Noll and Liu procedures [3,41]. Recent examples of such mathematical methods applied to obtain restrictions on constitutive equations using these theories can be found in [42] for RT and in [43] for EIT. The main difference between EIT and RT is that in EIT the dissipative fluxes, such as the heat flux and stress tensor, are considered as unknown fields ruled by their own balance equations, while in RT such fluxes are assigned using suitable constitutive equations.

Both theories are capable of describing parabolic and hyperbolic phenomena. For instance, the celebrated Maxwell–Cattaneo equation for the evolution of the heat flux [44] can be obtained in RT by postulating a time rate constitutive equation for the heat flux [45], while in EIT it represents a particular form of the balance law for the latter quantity [46]. In the parabolic case, compatibility with the principle of causality is achieved in the generalized sense proposed by Fichera [22].

The other two theories mentioned in Section 1, namely, Classical Irreversible Thermodynamics and Rational Extended Thermodynamics, exploit the entropy principle in order to achieve other additional tasks.

In Classical Irreversible Thermodynamics (CIT), which is weakly nonlocal, the Onsager procedure for exploiting the entropy principle is applied to obtain evolution equations for additional internal variables which describe inelastic properties of the materials [2,11,12]. For the sake of completeness, we illustrate such a procedure below.

Suppose that the state space \mathcal{Z} is spanned by ν scalar internal variables a_β , $\beta = 1, \dots, \nu$, i.e.,

$$\mathcal{Z} = \{a_\beta\}. \tag{76}$$

The evolution equations for a_β can be written as

$$\dot{a}_\beta = f_\beta(a_\beta), \tag{77}$$

with f_β constitutive quantities. Then, the local balance of entropy on the state space takes the form

$$\rho \frac{\partial s}{\partial a_\beta} \dot{a}_\beta + \frac{\partial J_k}{\partial a_\beta} a_{\beta,k} \geq 0. \tag{78}$$

In CIT, both the ν quantities $\rho \frac{\partial s}{\partial a_\beta}$ and the 3ν quantities $a_{\beta,k}$ are referred to as generalized thermodynamic forces, the ν time derivatives \dot{a}_β are called thermodynamic rates, and the 3ν elements $\frac{\partial J_k}{\partial a_\beta}$ are the generalized thermodynamic fluxes [11,12]. It can be easily seen that the above inequality can be put in the form

$$\mathbf{x} \cdot \mathbf{y} + \mathbf{X} : \mathbf{Y} \geq 0, \tag{79}$$

where \mathbf{x} and \mathbf{y} are vectors of \mathbb{R}^ν for which the components are the ν thermodynamic forces $\rho \frac{\partial s}{\partial a_\beta}$ and the ν thermodynamic rates \dot{a}_β , respectively, while \mathbf{X} and \mathbf{Y} are second-order tensors for which the components are the 3ν thermodynamic forces $a_{\beta,k}$ and the 3ν thermodynamic fluxes $\frac{\partial J_k}{\partial a_\beta}$, respectively. The following theorem constitutes a milestone of Onsager linear thermodynamics [11,12].

Theorem 8. *For isotropic systems, the linear relations*

$$\mathbf{x} = \mathbf{L}\mathbf{y} + \mathbf{M}\mathbf{Y}, \tag{80}$$

$$\mathbf{X} = \mathbf{N}\mathbf{y} + \mathbf{P}\mathbf{Y}, \tag{81}$$

with \mathbf{L} , \mathbf{M} , \mathbf{N} , and \mathbf{P} being positive definite tensors on the state space, are sufficient to ensure that the unilateral differential constraint (79) is fulfilled along arbitrary thermodynamic processes.

Thus, in the particular case $\mathbf{M} = \mathbf{0}$, the relation (80) yields the evolutionary Equation (77) as $\mathbf{y} = \mathbf{L}^{-1}\mathbf{x}$.

In Rational Extended Thermodynamics (RET), the entropy principle is instead exploited in order to write the system of balance laws in a symmetric form. In fact, one of the fundamental postulates of RT is that the state space is local [2,16]. As such, the system of balance laws can be regarded as a particular case of the quasi-linear first order system (3), having the form

$$\frac{\partial F_0(\mathbf{u})}{\partial t} + \frac{\partial F_k(\mathbf{u})}{\partial x_k} = f(\mathbf{u}), \quad k = 1, 2, 3, \tag{82}$$

wherein \mathbf{u} is a vector of the state space and the fields $F_0(\mathbf{u})$, $F_k(\mathbf{u})$, and $f(\mathbf{u})$ are constitutive quantities [2,16]. If such a system is compatible with a supplementary inequality of the type

$$\frac{\partial h_0(\mathbf{u})}{\partial t} + \frac{\partial h_k(\mathbf{u})}{\partial x_k} \leq 0, \quad k = 1, 2, 3, \tag{83}$$

with $h_0 = -\rho s$ and $h_k = -J_k - \rho s v_k$, which represents the local form of second law of thermodynamics, then the following theorem can be proved [2,16].

Theorem 9. *The constitutive equations for $F_0(\mathbf{u})$, $F_k(\mathbf{u})$, and $f(\mathbf{u})$ are compatible with the entropy inequality (83) if, and only if, there exist four potential functions h'_0 and h'_k (generators) and a privileged field \mathbf{u}' (main field) such that*

$$F_0 = \frac{\partial h'_0}{\partial \mathbf{u}'}, \tag{84}$$

$$F_k = \frac{\partial h'_k}{\partial \mathbf{u}'}, \tag{85}$$

$$h'_k = \mathbf{u}' \cdot \frac{\partial h'_k}{\partial \mathbf{u}'} - h_k, \tag{86}$$

$$\mathbf{u}' \cdot \mathbf{f} \leq 0. \tag{87}$$

Moreover, if h_0 is a convex function of \mathbf{u} , then the system of field equations is symmetric, and the Cauchy problem is well-posed for initial data in a Sobolev space $W^{p,2}$ with $p \geq 4$.

For the sake of illustration, in Table 2 we show the tasks achieved by the exploitation of the entropy principle in all the mentioned thermodynamic theories.

Table 2. Tasks achieved by exploitation of the entropy principle in the different thermodynamic theories.

The Entropy Principle Is Exploited in Order to Obtain:	Constitutive Equations Which Guarantee That Second Law Is Satisfied Whatever Is the Solution of the Balance Laws	The System of Balance Laws in a Symmetric Form	Evolution Equations for Dissipative Fluxes and/or Internal Variables
Classical Irreversible Thermodynamics (CIT)	Yes—Refs. [11,12]	No	Yes—Refs. [11,12]
Rational Thermodynamics (RT)	Yes—Refs. [3,13]	No	No
Extended Irreversible Thermodynamics (EIT)	Yes—Refs. [14,15]	No	No
Rational Extended Thermodynamics (RET)	Yes—Refs. [16,17]	Yes—Refs. [16,17]	No

From Theorem 9, it follows that in RET the entropy principle restricts the form of the functions $F_0(\mathbf{u})$, $F_\alpha(\mathbf{u})$, and $f(\mathbf{u})$, while, from Theorem 8 it can be inferred that in CIT the relation $\mathbf{y} = \mathbf{L}^{-1}\mathbf{x}$ in practice yields the constitutive functions f_α . Moreover, in the stationary case ($\mathbf{y} = \mathbf{0}$), the relations

$$\mathbf{x} = \mathbf{M}\mathbf{Y}, \tag{88}$$

$$\mathbf{X} = \mathbf{P}\mathbf{Y}, \tag{89}$$

following from Equations (80) and (81), yield thermodynamic restrictions on the form of s and J_k analogous to those obtained by the classical Coleman–Noll procedure [3].

The considerations above suggest that the correct interpretation of the entropy principle plays a central role in any thermodynamic theory, and that it is important to investigate whether the hypothesis that the consequences of such a principle depend on the regularity

of the solutions of the system of balance laws is a necessary consequence of a physical law or whether it can be avoided under a more general formulation of the principle. Herein, we proved that the entropy principle restricts the constitutive equations in the presence of discontinuity surfaces, and does not restrict the thermodynamic processes. This achievement constitutes the main result of the present paper, which allows us to regard within a unitary frame the approaches to second law of all the thermodynamic theories.

For the sake of illustration, in Table 3 we show the different interpretations of the constraints imposed by the second law of thermodynamics. We underline that the present theory does not provide any new results regarding the propagation of shockwaves in particular cases, as this is not within its scope. Rather, the present theory provides new and more precise results regarding the interpretation of the entropy principle in the presence of shockwave propagation. Such results must be regarded as an application of Theorem 2 proved in Section 4.

Table 3. Different Interpretations of the constraints imposed by the second law of thermodynamics.

Interpretation of the Consequences of Second Law of Thermodynamics	Restriction on the Constitutive Equations	Selection of the Thermodynamic Processes
Regular solutions of balance laws	Ref. [3] -Ref. [1] -Ref. [5] -Ref. [47]	
Weak solutions of balance laws	Present paper	Ref. [47]

Our future investigations will be concerned with extended procedures of exploitation of the second law of thermodynamics which seem to be appropriate when the constitutive equations depend on both the unknown fields and on their higher-order gradients. The generalized procedures consider both the basic balance laws and their gradients as constraints for the entropy inequality until reaching the order of the gradients entering the constitutive equations [48,49]. Their application has provided satisfactory results in the study of materials with nonlocal constitutive equations, such as nanosystems [15,50] and Korteweg fluids [36], as well as in the thermodynamic analysis of Ginzburg–Landau phase transitions [51] and Cahn–Hilliard phase diffusion [52]. A first extension of the Muschik and Ehrentraut theorem to these methodologies has been obtained in [9]. In our future research we intend to revisit that result within the geometric framework developed in [5] and generalized here.

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