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Neoclassical Navier–Stokes Equations Considering the Gyftopoulos–Beretta Exposition of Thermodynamics

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Abstract: The seminal Navier–Stokes equations were stated even before the creation of the foundations of thermodynamics and its first and second laws. There is a widespread opinion in the literature on thermodynamic cycles that the Navier–Stokes equations cannot be taken as a thermodynamically correct model of a local “working fluid”, which would be able to describe the conversion of “heating” into “working” (Carnot’s type cycles) and vice versa (Afanasjeva’s type cycles). Also, it is overall doubtful that “cycle work is converted into cycle heat” or vice versa. The underlying reason for this situation is that the Navier–Stokes equations come from a time when thermodynamic concepts such as “internal energy” were still poorly understood. Therefore, this paper presents a new exposition of thermodynamically consistent Navier–Stokes equations. Following that line of reasoning—and following Gyftopoulos and Beretta’s exposition of thermodynamics—we introduce the basic concepts of thermodynamics such as “heating” and “working” fluxes. We also develop the Gyftopoulos and Beretta approach from 0D into 3D continuum thermodynamics. The central role within our approach is played by “internal energy” and “energy conversion by fluxes.” Therefore, the main problem of exposition relates to the internal energy treated here as a form of “energy storage.” Within that context, different forms of energy are discussed. In the end, the balance of energy is presented as a sum of internal, kinetic, potential, chemical, electrical, magnetic, and radiation energies in the system. These are compensated by total energy flux composed of working, heating, chemical, electrical, magnetic, and radiation fluxes at the system boundaries. Therefore, the law of energy conservation can be considered to be the most important and superior to any other law of nature. This article develops and presents in detail the neoclassical set of Navier–Stokes equations forming a thermodynamically consistent model. This is followed by a comparison with the definition of entropy (for equilibrium and non-equilibrium states) within the context of available energy as proposed in the Gyftopoulos and Beretta monograph. The article also discusses new possibilities emerging from this “continual” Gyftopoulos–Beretta exposition with special emphasis on those relating to extended irreversible thermodynamics or Van’s “universal second law”.

Keywords: energy; energy conversion; energy storage; energy interactions; balance of energy; energy flux; entropy flux; volume flux; mass flux; neoclassical Navier–Stokes; available energy; irreversibility; Gyftopoulos–Beretta exposition

1. Introduction—The Gyftopoulos–Beretta Exposition of Thermodynamics

For more than three decades, a scientist at the Massachusetts Institute of Technology has developed a novel exposition of the foundations of thermodynamics that applies to all systems and

both equilibrium thermodynamic and non-equilibrium thermodynamic states. The main results have twice been published in Gyftopoulos' and Beretta's monograph [1].

In the new Gyftopoulos–Beretta exposition, a starting point is a weight process that always leads to the measure of the change in elevation of a weight between two positions that is a purely mechanical effect. This concept is reminiscent of the pioneers' efforts to measure any effects like temperature via a simple visual observation. We note that in contrast to other expositions, this concept does not involve the concepts of energy, temperature, heat, and work (all of which are defined later).

The new exposition needs quite new mathematics and a new flexible system of notations. Let us recall three main expressions of the Gyftopoulos–Beretta exposition [1] (pp. 38, 103, 108). If A is a system under consideration in two states A_1 , A_2 , and R is a reference thermal reservoir, then:

$$\text{Balance of energy : } E_2 - E_1 = E^{\leftarrow}, \quad (1)$$

$$\text{Definition of entropy : } S_1 = S_0 + \frac{1}{c_R} [(E_1 - E_0) - (\Omega_1^R - \Omega_0^R)], \quad (2)$$

$$\text{Balance of entropy : } S_2 - S_1 = S^{\leftarrow} + S_{irr}. \quad (3)$$

In Equation (1), E^{\leftarrow} denotes the net energy transferred to the system A from all the other interacting systems during the process that changes the state of A from A_1 to A_2 . The precise interpretation of mathematical Equation (1) does not allow us to express the implicit fact that energy gained by the system must be accounted for by the energy transferred across the boundary of the system E^{\leftarrow} since energy *per se* can neither be created and destroyed. The idea of energy transfer relates to the fluxes of energy \mathcal{F}_E transferred in time Δt_{1-2} as follows: $\mathcal{F}_E \Delta t_{1-2} = E^{\leftarrow}$. Beretta and Gyftopoulos underline [2] that any amount of energy can be transferred to a system, *e.g.*, by doing electrical work on it, but the availability of this energy depends on how the final state is reached. Usually, we define the “adiabatic availability” [1] (Chapter 5) to be the available energy if the final state is reached without irreversibility. However, if the final state is reached with irreversibility, then this capacity will be smaller than the energy transferred, and may even be equal to zero. Importantly, the available energy of system A is derived from the adiabatic availability in case A interacts with a reservoir operating at constant thermodynamic conditions and at a permanently stable equilibrium state.

Equation (2) shows two properties: energy E and available energy Ω^R determine the property of the system A that is unfortunately called by the traditional name: “entropy” and denoted by Clausius' “ S .” A better name for the property defined by Equation (2) would be: “thermal entropy.” However, Gyftopoulos and Beretta do not make explicit reference to “thermal entropy” because the definition of entropy is related tout-court to a constant parameter of the reservoir R . In their textbook [1] temperature, chemical potential, and pressure are defined using the same definition of entropy characterized by the constant parameter. In this regard, Palazzo, mentioned in this manuscript [3] at the outset of Section 3, proposed a generalized definition of entropy in which thermal entropy, chemical entropy, and mechanical entropy components depend on temperature, potential, and pressure, respectively, as constant parameters of the reservoir.

The Gyftopoulos–Beretta positive constant c_R in Equation (2) depends only on the reservoir, which means that the dimension of S depends on the dimensions of both energies E , Ω^R and on c_R . The constant c_R , without physical meaning, has been introduced firstly in: [4]. Strictly speaking, the energy and the available energy for a reference reservoir with the addition of some constant determine a third property named “entropy”.

In Equation (3), the entropy defined by Equation (2) is balanced, suggesting that the entropy gained by system A can be accounted for by the entropy transferred across the boundary of the system and by the entropy created inside the system. It is an independent assumption of nonequilibrium thermodynamics that $S_{irr} > 0$ (see, for instance: [5–9]). This is usually interpreted as that the entropy created by irreversibility can be only produced *ex nihilo* and never destroyed. We emphasize that this assumption is treated to be a primary postulate in non-equilibrium thermodynamics. It is a

unique example in the whole nature of a half-conservation law with fundamental consequences, especially for cosmology [10].

However, it must be underlined that the role of the balance of entropy (Equation (3)) in the Gyftopoulos–Beretta explanation is quite opposite to the role in classical non-equilibrium thermodynamics based on Onsager, Prigogine, Klutenberg, and Voita postulates. In non-equilibrium thermodynamics, the entropy production, due to the Eckart procedure [11] (or the Coleman–Noll procedure in rational thermodynamics), plays a dominant position, whereas, in the Gyftopoulos–Beretta exposition, the balance of energy and the dissipated energy are in the foreground.

This paper offers several new arguments for the unconventional order of thermodynamics exposition where entropy is defined before the heat and specific volume are defined before work. Our motivation is to augment the complete original line of MIT-reasoning based on the approach and logical sequence of exposition of Gyftopoulos and Beretta (firstly in [1,12–14]) and other authors (Zanchini [15,16], von Spakovski [17,18], and Palazzo [3,19]). Wide surveys of this topic are published [1,12–15,19]. We also apply the Gyftopoulos–Beretta exposition to the fluid mechanics described by Navier–Stokes equations.

When developing the new exposition of thermodynamics, we completely removed two meaningless words “work” (mechanical, chemical, electric, *etc.*) and “heat” from any considerations [20]. Chemical work means work of chemical origin; similarly, thermal work means work of thermal origin. Instead, work interaction (mechanical) should be considered in addition to heat interaction (thermal) and mass interaction (chemical). Work and heat are not properties of a system. Accordingly, the symbols δQ and δW , which have been used in traditional Clausius’ exposition of thermodynamics to denote infinitesimal amounts of work and heat, do not refer to changes in property values. Therefore, it is wrong to say that there is heat storage and work storage. Nor are heat and work contained or stored within a system. Being interactions, their magnitudes depend upon the arbitrary selection of boundaries between systems and reservoirs.

In our exposition of thermodynamics, we prefer to use the notion of “heating” and “working”, which underline processes occurring on the system boundaries. Especially, when we consider “the working fluid” in a 3-dimensional statement, both “heating” and “working” take a simple visualization. Instead of an expression “heat flow-in to a body, we use more convenient “the internal energy of a body increase due to its heating”. Additionally, having a proper definition of “internal energy” we are sure that the Callen structure of thermostatics can be easily adopted [21] and the consistent interrelations with statistical mechanics can be established [22].

From a general viewpoint, our aim is a proper adaptation of the Gyftopoulos–Beretta approach to three-dimensional, local representation of the laws of thermodynamics, staying on the ground of continuum physics. We show that reasoning based on global time and space formulation can be adapted to a local formulation within the framework of continuum thermodynamics with some consequences for the co-called irreversible thermodynamics [6] and extended non-equilibrium thermodynamics [7,8].

The paper is organized as follows. Summaries of the Gyftopoulos–Beretta exposition and its commentaries are presented in Sections 1 and 2. The classical Navier–Stokes equations are shortly given in Section 3. A brief discussion of the novel role of energy storage and energy interactions via corresponding fluxes is presented in Sections 4–9. The exposition of the balance of energy is given in Section 10. The role of state variables (intensive and extensive) is discussed in Section 11. Proper forms of balances of the extensive state variables are stated in Section 12, both for the global and local (3D) formulation. Section 13 discusses the balance of entropy without “heat”, and Section 14 proposes the constitution of entropy and volume fluxes. An example of volume balance for solid working continua is presented in Section 15. In Section 16, we discuss the form of energy balance proper for a calculus of the amount of converting and dissipating energy.

In Sections 17–22, the neoclassical Navier–Stokes equations are formulated as the main consequences of the Gyftopoulos–Beretta exposition of thermodynamics. A brief discussion of the novel role of the Gyftopoulos–Beretta exposition via corresponding fluxes is shown in Sections 23

and 24. In Sections 25–28, in the light of the new developments, comments about the entropy and the second law are presented. Concluding remarks are given in Section 29.

2. Logical Loops

Zanchini and Beretta [15,16], when speaking on main conceptual loops of thermodynamics, underline the first logical circularity following from a special statement of the first law for a cycle that possesses a historical form of energy balance without resorting to the term “energy”:

$$\begin{aligned} Q &= JW \text{ (Kelvin's heat units of energy),} \\ W &= AQ \text{ (Clausius' work units of energy),} \\ a_1 W &= a_2 Q \text{ (Rankine's universal units of energy; } a_1 = a_2 = 1). \end{aligned} \quad (4)$$

Traditionally, the energy equivalence A has been used on the European continent up to circa 1920, J on the British Islands, and the Rankine universal constant was introduced by Gibbs and used mainly in the USA. Numerous dimensions of energy have led to an ambiguous paradigm with the existence of “different forms of energy” and many various units of energy. This leads to the next logical circuit that negates an axiom of energy additivity. Recall, the different units of energy are usually dedicated to independent phenomena and come from the names of their inventors—these can be summarized as: chemical— μL (mole–Lavoisier), mechanical— mN (metro–Newton), electrical— eV (electrono–Volt), magnetical— mK (magneto–Kelvin), thermal— cR (caloro–Rankine), electro-magnetic— pM (photonno–Maxwell). Nowadays only two SI units are commonly used, namely: $mN = 1 \text{ joule}$ and $eV = 1.6022 \times 10^{-19} \text{ joule}$.

In such various basic forms of the first law of thermodynamics, the notions “work” and “heat” appear as *deus ex machine* without the concept of “energy” E . The explanation of the mutual convertibility of heat and work is a typical mistake of the traditional European school of thermodynamics because without the notion of “internal energy” one cannot introduce the concept of “convertibility of forms of energy.” However, the first appropriate explanation was introduced by Sadi Carnot [23], which we further explain. In the traditional statement, expressed by Equation (4), we also see a reminiscence of the conceptual dichotomy between a hypothesis concerning the nature of heat and the principle simply expressing convertibility of heat to work.

In the Gyftopoulos–Beretta approach, the energy of a system is a primal property of substance and fields, and it is always a sum of internal \mathcal{U} , kinetic \mathcal{K} , and potential energy Φ :

$$E = a_3 \mathcal{U} + a_4 \mathcal{K} - a_5 \Phi. \quad (5)$$

The kinetic and potential energies in Equation (5) are external and account for the system as a whole while internal energy is determined by interparticle kinetic and potential energies. In the universal system of units, the equivalence coefficients are equal to one: $a_3 = a_4 = a_5 = 1$, which means that Joule’s pioneering efforts to measure the energy equivalence as $J = \mathcal{U}/\mathcal{K}$ were baseless.

Another key notion in the Gyftopoulos–Beretta approach is the “conversion of energy.” If our system A undergoes a process from state 1 to state 2: $A_1 \rightarrow A_2$ then $\mathcal{U}_1, \mathcal{K}_1, \Phi_1$ change their values to $\mathcal{U}_2, \mathcal{K}_2, \Phi_2$ and this mysterious process is called energy conversion. There is no such thing as the conversion of heat into work and vice versa because both the work and the heat are only a convenient manner of expressing the net amount of energy conversion during a single process where the net change of E disappears.

Explaining the notion of “energy interaction” is more difficult. Gyftopoulos and Beretta [1,13,14] before defining different systems A, B, \dots have defined a natural reservoir (thermal, mechanical, chemical, electric, etc.) denoted R_T, R_M, R_{Ch} , and R_E , respectively [15]. We note that chemical energy represents a component of internal energy in addition to thermal energy. Energy is stored in a reservoir R due to its deriving mechanism for action when system A and Carnot-like reservoirs are in contact

through their boundary and a proper physical phenomenon takes place between A and R that can be restored from R and flow into the system.

Gyftopoulos and Beretta [1] denote the energy interaction for all possible energy flows by symbols: either E^{\rightarrow} or E^{\leftarrow} , depending on whether it is the in-flow or the out-flow of energy. Denoting all interactions by one common letter is a fundamental step for their paradigm of thinking especially because in everyday language there exist a single meaningful equivalence for E^{\leftarrow} transferred in time Δt , i.e., it is power \mathcal{P} (watt = joule per second), which is understood as a rate of energy consumption by any technical device. We say that devices have more or less power, therefore the balance of energy (Equation (1)), being the main manifestation of the first law of thermodynamics, is also interpreted as the rate of generation (or consumption) of energy, i.e., power: $\frac{d}{dt}E = \mathcal{P}$. The most convenient and familiar unit of power is the watt. This does not mean that this is a rate of making heat or work because power is a more basic concept than heat and work. Therefore, heat and work should be only treated as power multiplied by time (for this line of reasoning the unit is kWh, however, the established SI system unit is joule: This statement is confirmed by economics that states, “we buy power, but we pay for energy.” Truly speaking, we are correct only in converting kilowatt-hours to joules: 1 kWh = 3.6 MJ not vice versa—it is a basic amount of energy for payment.

Unfortunately, the word “power” does not indicate a place where the exchange of energy takes place. Therefore, instead of letter \mathcal{P} , we propose to introduce another letter \mathcal{F} that denotes the flux of net energy supplied to system A from all interacting systems and reservoirs. The energy gained by A must be accounted for energy transferred across a boundary of the system because energy can neither be generated *ex nihilo* nor destroyed in A :

$$E_2^A - E_1^A = \left(\iint_{\partial A} \vec{\mathcal{F}}_e \cdot \vec{n} dS \right) \Delta t_{1-2} = \mathcal{F}_E \Delta t_{1-2} = E^{\leftarrow}. \quad (6)$$

Here, $\vec{\mathcal{F}}_e$ is the vector of the total flux of energy transferred across the boundary of the system (∂A) oriented by the unit vector \vec{n} . Only the normal component of energy flux is important—it defines the net flux of energy \mathcal{F}_E that mathematically cannot be differentiated by the \leftarrow or \rightarrow arrow. Regardless of the nature of the phenomenon studied (described by quaternions, spinors, tensors, multinions, etc.), the flux of energy is always a vector.

3. The Classical Navier–Stokes Equations

The science of thermodynamics is (or should be) the practice of asking questions. At least it is prudent to look back from time to time to check one’s basis. Explanations that were found long ago may be valid or irrelevant once the context has been understood better. Both Claude-Louis Navier and Gabriel Stokes were only familiar with the notion of Newtonian work and they probably believed that conservation of kinetic and potential energy $E_{kin} + E_{pot} = 0$ is correct because this is the form of energy conservation law known to them. Both researchers were unfamiliar with the notion of “internal energy”, and therefore their model of fluid, nowadays called “the Navier–Stokes” cannot, even on the conceptual level, realize a conversion of work into heat and vice versa. Therefore, some aspects of Navier’s and Stokes’ views on energy conservation and energy dissipation cannot be correct in a modern light. We note that that full framework of classical physics became known only after 1850 when the first and second laws of thermodynamics were discovered. Therefore, we see a need for a new exposition of those classical models of simple fluids.

Therein lies the motivation for Sections 17–22: It answers questions about the set of governing equations called the Navier–Stokes equations describing the motion of a working fluid and fulfills the first and second law of thermodynamics. From a formal mathematical viewpoint, the Navier–Stokes equations consist of only the equation of mass continuity and the balance of momentum. It is well known that the momentum balance equation, as proposed by Cauchy, is equivalent to a special case of energy balance called kinetic energy. However, within a soft continuum (deformable solid/fluid)

framework, in the balance of kinetic energy, some unexpected sources of energy are seen and related to viscous or turbulent stresses. Therefore, the balance of kinetic energy is not exactly closed, and some kind of internal, artificial, source of energy should be considered. This leads to the need to complete the energy balance or add it to another balance. By the appearance of the dissipative source of energy, the kinetic energy balance becomes incomplete and cannot be treated as fulfilling the first law. This internal source of energy is sometimes called “dissipation of kinetic energy” and we usually ask: “how to transform this dissipated energy further?”

Therefore, it is obvious that the balance of kinetic energy of a continuum cannot be treated as a complete balance of energy, and we need to add this form of energy into the whole balance of energy that we usually postulate to be: “the first law of thermodynamics.” Thus, we obtain a full conversion of kinetic energy partially into “energy storage” (reversible) and partially into another form of “energy degradation” (irreversible). Thus, it is difficult to determine whether the balance of momentum fulfills the first law of thermodynamics.

The relation between momentum and kinetic energy balance is an important moment since in both the pioneering papers by Claude-Louis Navier [24] and Gabriel Stokes [25] there is an explicit recoiling to this relation. It also means that the paradigm on “kinetic energy conservation” has been taken into account at a “moment of birthday.” However, we want to say that this paradigm is not sufficient and must be replaced by a more fundamental paradigm as follows from the first law of thermodynamics.

Returning in our motivations up to the original arguments by Navier, one can easily find that his Lagrangian variation $\delta\mathcal{L}$, being his starting point, is possible to be rebuilt as a “balance of kinetic energy of fluid continuum” [24] (pp. 395–411):

$$0 = \delta\mathcal{L} = \iiint_V dx dy dz [\delta\mathcal{W}_{ext} + \delta\mathcal{W}_{rev} + \delta\mathcal{W}_{d'Alem} + \delta\mathcal{W}_{visc}] + \iint ds \delta\mathcal{W}_s. \quad (7)$$

Note that, it has a part $\delta\mathcal{W}_{vis}$ which can be interpreted as the “kinetic energy degradation” and the d'Alembert principle is applied. Taking next the variation of kinetic energy Lagrangian to be

$$\delta\mathcal{W}_{ext} = \vec{f}_{body} \cdot \delta\vec{x}, \quad (8)$$

$$\delta\mathcal{W}_{rev} = p \operatorname{div}(\delta\vec{x}), \quad (9)$$

$$\delta\mathcal{W}_{d'Alem} = \rho \vec{a} \cdot \delta\vec{x}, \quad (10)$$

$$\delta\mathcal{W}_s = v \vec{v} \cdot \delta\vec{v} dt, \quad (11)$$

$$\delta\mathcal{W}_{visc} = \mu [\operatorname{grad} \vec{v} + \operatorname{grad}^T \vec{v}] \cdot (\delta \operatorname{grad} \vec{v}) dt + \mu [\operatorname{tr}(\operatorname{grad} \vec{v})] [\operatorname{tr} \delta(\operatorname{grad} \vec{v})] dt. \quad (12)$$

Navier, making integration by parts, got not only a local form of momentum balance but also a proper “slip” boundary condition as

$$\iiint_V dx dy dz \{-\vec{f}_{body} + \operatorname{div}(p \vec{I}) + \rho \vec{a} - \operatorname{div}[2\mu(\vec{d} + \frac{1}{3} \operatorname{tr} \vec{d} \vec{I})]\} \cdot \delta\vec{x} + \iint ds \{-v \vec{v} + [2\mu(\vec{d} + \frac{1}{3} \operatorname{tr} \vec{d} \vec{I})] \vec{n}\} \cdot \delta\vec{x} = 0. \quad (13)$$

Next, taking into account the continuity of flow for the case of liquid as an incompressibility condition: $\operatorname{tr} \vec{d} = 0$ Navier got the local equations of momentum balance [24] (p. 414):

$$\rho \vec{a} + \operatorname{div}(p \vec{I}) = \vec{f}_{body} + \operatorname{div}(2\mu \vec{d}) \quad (14)$$

in the domain of fluid and the slip boundary conditions:

$$v \vec{v} = 2\mu \vec{d} \cdot \vec{n}. \quad (15)$$

In the above, a variation of placement is related to a variation of velocity: $\vec{x} = \delta \vec{v} dt$, the Euler tensor of the rate of deformation is defined by $2\vec{d} = \text{grad} \vec{v} + \text{grad}^T \vec{v}$. Note that Navier could introduce the concept of bulk viscosity: μ and the surface viscosity: ν , respectively. Strictly speaking, the letters μ , ν are taken from Stokes' paper [25]. Navier used ε , E notations for internal (bulk) viscosity and for external (surface) viscosity, respectively [24].

In the text above, we used modern notations, ρ represents the fluid density, \vec{a} means the d'Alembert–Euler acceleration vector [10], \vec{f}_{body} is the body force (Newtonian *vis impressa*), p denotes the Euler thermodynamic pressure, \vec{n} represents the unit vector normal to the fluid surface and \vec{I} means the Gibbs' idemfactor. We currently call this form of momentum balance a “non-conservative” one, which means that the mass continuity equation is incorporated into the balance.

The same form of balance of momentum of Stokes was repeated but without using variational arguments. His Equation (12) [25] is the balance of momentum also in the “non-conservative” form, but looking on his interpretation of material time derivative, we find that Stokes was close to introducing “the flux of convective momentum” $\vec{\tau}^c = \rho \vec{v} \otimes \vec{v}$, and the “conservative form of balance of momentum”.

In the oldest literature, kinetic energy was called *Vis Viva* what means: “living force.” Therefore we can find the statement: “conservation of living force” especially in the papers by Leonardo da Vinci, G.W. Leibniz, Johann Bernoulli, Jean Le Rond d'Alembert, Leonard Euler, Samuel Koenig, Thomas Young, Lazar Carnot. Reassuming, within the period 1500–1850 first and second law of thermodynamics were used as [10,26]: *the principle of conservation of living forces* and *the principle of impossibility of perpetual motion*.

The text above suggests that the balance of momentum is consistent only with the balance of kinetic energy of continua, but is far from the fulfillment of the first law of thermodynamics. We write in detail in Section 16 about this “partial” fulfillment of the kinetic energy balance. Thus, we are sure “that one needs special proof that the Navier–Stokes equations comply with the first law of thermodynamics”.

Therefore, our motivation in Sections 17–22 is as follows: to extend the set of governing equations that in the literature have been named: “the Navier–Stokes equations”, which contains nothing more than a balance of momentum and mass continuity. This set of equations describes only a part of the energetic relations that occurs within the working fluid. We assume that there is common agreement that every given set of governing equations should fulfil the laws of thermodynamics. Our aim in Sections 17–22 is to check whether “the Navier–Stokes equation” fulfills the laws of thermodynamics. We use Gyftopoulos–Beretta's exposition of thermodynamics as a logical tool.

4. Energy as a Fundamental Concept

Energy is the oldest concept on the Earth—even older than astronomy and mathematics. Its main goal is to describe natural phenomena in terms of “peripatetical motion” and its “entelechy.” Those two notions of Aristotelian thermodynamics became the starting concept for Lavoisier and Carnot and others with respect to equilibrium thermodynamic developments 25 centuries later [27,28]. Thermodynamics has the same aims but is expressed in modern technical language: It describes all known (or yet unknown) phenomena in terms of energy and its possibility of conversion.

From the viewpoint of bases of our civilization, it is important that there is the concept that unifies our understanding of experience. The popular use of the word “energy” refers to capacity of certain material bodies to perform work or other useful tasks. This capacity to work represents other quantities that scientists call “available energy.” In distinguish to “energy”, the concept of “available energy” is related to both first and second law of thermodynamics. In other words, the concept of energy is the essence only the first law, and, to date, cannot be involved as a postulate coming from other principles of science including even Quantum Field Theory where “energy” is always before “action” [18].

According to Aristotle, every peripatetic motion (i.e., chemical, atomic, nuclear, thermal, mechanical, etc.) is of two kinds: active or potential. In modern language, this classification

can be approximately stated as a motion of matter and a motion of fields. The main property of these motions, being the first, the main, scalar invariant, is energy—the very abstract notion based on our anthropological view of nature [27,28]. Mathematically we have the following energy additivity:

$$E = E_{matter} + E_{fields}. \quad (16)$$

“Energy” has no definition: It is a primary concept without any complicated definition based on true or wrong understanding of the such terms as “matter”, “system”, “state”, “property”, “heat”, “work”, etc. No doubt, energy is a crucial concept of our civilization. Note the incorrect definitions of energy commonly used in electronic encyclopedias that says: “Energy it is the capacity of matter to perform work.” This deals rather with the “available energy” concept. Energy concept does not need previous usage “work” and “heat” words. “Energy” is also a fundamental concept in philosophy where it frequently has a clear theological association and is an indestructible entity, created, sustained, and destructed only by Creator’s power [27].

Energy stored in matter can refer to the unit of mass and therefore we speak of “mass-specific energy”. However, the energy of fields can only refer to a volume of space (actually partially occupied by some mass). The Aristotelian concept of “energy conversion” is based on phenomenological observations of transforming some amount of energy from matter to fields or vice versa. We no longer use Aristotle’s definition, and by energy conversion, we also define all possible transformations between E_{matter} and E_{fields} . Concerning energy of fields—two fields are always present in our description of Nature: the infinite fields of gravitation and electromagnetism.

5. Internal Energy

Energy stored in matter is a kind of “actual energy” of peripatetic motions. Nowadays, Aristotle’s peripatetic motion can be interpreted as a motion in a quantum mechanical sense. Some of these motions transfer a property called “momentum” and some are “momentum-less.” Therefore, matter–energy is considered as a sum of internal and kinetic energy:

$$E_{matter} = \mathcal{U} + \mathcal{K}. \quad (17)$$

In our treatment, internal energy \mathcal{U} represents stored kinetic energy of momentum-less peripatetic motion. William Thomson (1856) proposed calling this kind of “actual energy” *vis calida*. Finally, the Victorian interpretation of internal energy as a “hidden kinetic energy” was abandoned since the concept of internal energy should be unifying all the various branches of physics without the necessity of entailing reduction of these branches to mechanics [29].

However, internal energy represents the combination of stored interparticle kinetic energy and stored interparticle potential energy. In real systems, this “internal” potential energy is associated with interatomic chemical bonds and Van der Waals interactions among molecules; this duality should be considered to extend the validity of fundamental concepts. Therefore, this duality is presented in the Neoclassical Boundary Conditions (Section 21). Moreover, in quantum physics, the Schrödinger equation is based on the same duality since the Hamiltonian operator results from the sum of a kinetic component and a potential component and affects the wavefunction.

To be historically correct, we recall that the notion of internal energy was used from 1788 to 1850 many times but inexplicitly or under another name. One popular name used frequently by Poisson and de Saint Venant was “stored energy.” Therefore, by using “stored energy” we return with our line of reasoning back to time yet before Sadi Carnot when heat was stored as heat within a “working fluid”, and work was stored separately as a work. Sadi Carnot said that heat and work can be stored within a working fluid only in a form of “internal energy” as noted by him as \mathcal{U} . Therefore, in our opinion, the notion of “stored energy” is more pioneering and deeper than the notion of “internal energy.” Additionally, the first law of thermodynamics emerges from the technical needs of balancing changes

of “stored energy” and not from the balance of the whole form of energy *per se*. Equation (57) shows the explicit form of “stored energy” in detail.

Our understanding of “internal energy” is closely based on Josiah Willard Gibbs’ concept of introducing such a quantity into the thermodynamic framework. In 1872, it was such an amazing idea that other distinguished researcher James Clerk Maxwell made a gypsum model of internal energy for water in three phases. This demonstrated internal energy as something real. Section 11 presents an “operational” understanding of this notion.

6. Kinetic Energy \mathcal{K}

The Rankine concept of internal energy can be treated to some extent as an analytical representation of Aristotle’s division of the motion *entelechy* into the potential and the active parts. Rankine (1855) mentioned during his development of the “kinetic energy” concept: $\frac{1}{2} m \vec{v} \cdot \vec{v}$ [30]. He treated all perceptible physical worlds of matter as a manifestation of active motion. This motion can be divided into balanced internal motion, measured quantitatively by internal energy, and external energy of motion, which is only a qualitative component of *vis viva* called the “kinetic energy”. Because both the internal and kinetic energies are of the same nature, these can be calculated using the same units, without employing any of Joule’s energy equivalents.

Rankine was in some opposition to Joule whose goal was to find the equivalent as a ratio of internal energy to the kinetic energy ($J_{\text{Joule}} = \mathcal{U}/\mathcal{K}$). Joule’s approach was also innovative but only in relation to the concept of Sadi Carnot who was preferring the equivalent of work in the form $J_{\text{Carnot}} = W_{\text{cycle}}/Q_{\text{cycle}}$.

7. Potential Energy

The concept of the energetic potential $E_{\text{pot}} = \Phi$ was introduced by Laplace in 1797 to describe the gravitational force (*vis moltara* later *vis latente*) acting between two material bodies (action at distance). This means that Laplace assumed that each of the material bodies coming from nature’s source of gravitational potential possesses the spatial memory of this source to finally be described by energy induced by the source Φ . In other words, the Laplace concept described the action of the anticipated gravitational field by the potential (later called potential energy) [28].

In some sense, the gravitational energy Φ cannot be treated as a substantial property since it is localized in space. The field nature of gravitational force is obvious in the general relativity where the first law of thermodynamics cannot be separated from the set of governing equations. Recall the main features of the General Relativity governing equations that have the following structure:

- Kinetic relations: $G_{\alpha\beta}$ = function of metric potential $g_{\alpha\beta}$ and scalar potential ϕ ; $\alpha, \beta = 0, 1, 2, 3$
- Constitutive equations: $S_{\alpha\beta} + T_{\alpha\beta} + W_{\alpha\beta}$ = function of $G_{\alpha\beta}$
- Balance equations: $\partial_\beta (T_{\alpha\beta} + S_{\alpha\beta} + W_{\alpha\beta} + G_{\alpha\beta}) = J_\alpha$ and $\partial_\alpha J_\alpha = 0$.

Here $G_{\alpha\beta}$, $T_{\alpha\beta}$, $S_{\alpha\beta}$, and $W_{\alpha\beta}$ are, respectively, the Abraham gravitational energy tensors, the Nordström energy-momentum tensor of matter, the Minkowski energy-momentum tensor of electromagnetic fields, and the Nordström thermal energy tensor. Additionally, J_α is a net density flux.

The Laplace concept had a huge advantage over Newton’s gravity model: This concept does not need adjustments in the form of an additional postulate of the existence of “eternal light.” Recall that Newton’s model had a serious drawback. His concept did not describe the permanence of the firmament (*Stellae Fixae*) to explain why the stars do not fall into one another, Newton postulated additional unknown i.e., the pressure of light “eternal light”, which repelled the stars from each other. Today the role of the eternal light in cosmology meets the “dark energy” notion also postulated *ex nihilo* [28]. Under earthly conditions, the Laplace potential is described accurately enough by the distance of the body from the Earth surface enlarged by Earth’s radius (position vector). Upon extending the Gibbs–Rankine concept of state variables also onto the potential energy Φ , it can be concluded that the

position vector \vec{x} plays the role of the primary state variables, and the gravitational acceleration \vec{b} is a dual state variable: $\vec{b} = -\partial\Phi/\partial\vec{x}$.

8. Energy of Radiation

There is also additional internal energy (radiation energy) that was not associated with the substance of the working medium and that is distributed in space. In 1865, Maxwell proposed that this non-substantial energy of the electromagnetic field ε_{em} can be expressed by the primary state variables as electric field \vec{E} and magnetic field \vec{H} . Maxwell also identified the dual state variables of radiation energy i.e., the electric displacement vector $\vec{D} = \partial e_{em}/\partial\vec{E}$ and the magnetic displacement vector $\vec{B} = \partial e_{em}/\partial\vec{H}$. Here, e_{em} is the only energy space density (Jm^{-3}). This concept allowed Planck (1905) [10] to formulate the energetically consistent theory of radiative heat transfer.

9. Mathematical Denotation of the Fundamental Concepts

It is necessary to assign mathematical objects to the physical concepts of energy. In the literature, dozens of different signs for the same quantities exist, and it is reasonable to employ the system of denotations proposed in the papers of pioneers—mostly Rankine, Gibbs, Duhem, Natanson, and Kestin [30–33]. The method of description is based on the foundations of rational thermodynamics given by Keenan, Hatsopoulos, Gyftopoulos [4], Truesdell [34], Germain [10], Gyftopoulos [35,36] and, contemporarily, by Beretta [37,38], Feidt [39–41], Müller and Ruggeri [7], Sieniutycz [6], Kjelstrup and Bedeaux [9], Jou, Casas-Vázquez and Lebon [8], Badur [10,20,28], and others.

Let us mark the finite elementary volume by the sign, and the volume of system A by letter V . System A interacts with the external environment by the processes acting at the system boundary ∂V . The internal, kinetic, and potential energy can be denoted by \mathcal{U} , \mathcal{K} , and Φ respectively, and the energy of radiation by ε_{em} . Beside the integral quantities, there are some quantities related to the unit of mass, as:

$$\text{Internal energy } \mathcal{U} = \iiint_V \rho \varepsilon dV = \iiint_{V_0} \rho_0 \varepsilon dV, \quad (18)$$

$$\text{Kinetic energy } \mathcal{K} = \iiint_V \frac{1}{2} \rho \vec{v} \cdot \vec{v} dV = \iiint_{V_0} \frac{1}{2} \rho_0 \vec{v} \cdot \vec{v} dV, \quad (19)$$

$$\text{Potential energy } \Phi = \iiint_V \rho \phi dV = \iiint_{V_0} \rho_0 \phi dV. \quad (20)$$

Two kinds of volumes of the system can be distinguished: the referential volume V_0 , non-deformed, using in the Lagrange description, and the actual volume V related to the Euler description. Therefore, V_0 relates to arbitrary 3D description, ρ is density, ϕ is specific potential energy, and ε is the specific internal energy.

Let us denote the mass density in its initial state and its actual state by ρ_0 and ρ , respectively. Following Gibbs, mass-specific internal energy (J/kg) related to the unit mass can be denoted by ε . The quantities $\rho\varepsilon$ and $\rho_0\varepsilon$ are volumetric energy densities related to actual and initial volumes, respectively.

The fourth kind of energy that undergoes balancing is the energy of radiation:

$$\varepsilon_{em} = \iiint_{\infty} e_{em} dV. \quad (21)$$

Here, e_{em} (J/m^3) is a volumetric density of the energy of the electromagnetic field postulated by Maxwell (1874). This means that the field quantity cannot be related to the mass of a substance, but only to the volume where the radiation is acting. We assume, in line with the Rankine concept, that the energy fluxes are additive. This allows us to formulate the total energy flux as the sum of particular processes:

$$\mathcal{F}_E = \mathcal{F}_{work} + \mathcal{F}_{heat} + \mathcal{F}_{chem} + \mathcal{F}_{elec} + \mathcal{F}_{mag} + \dots, \quad (22)$$

working, heating, chemical, electric, and magnetic energy fluxes, respectively. Gaggioli first proposed to design the various energy fluxes by one common letter [42]. However, Gaggioli proposed a single letter “ I_E ” that has a rather weak connotation with 3D formulation; therefore we propose the letter “ \mathcal{F} ”. Precisely, he has proposed $I_E = pI_V$ for volume energy flux and $I_E = TI_\theta$ for thermal energy flux (we propose \vec{h}_V and \vec{h}_S denotations, respectively).

We note that Gaggioli introduced an entropy flux density concept (our \vec{h}_S) in a quite different manner than Eckart (1940) because it involved a 3D formulation. For Gaggioli, the \vec{h}_S should be a rate of some thermal charge transfer and temperature θ in $\theta\vec{h}_S$ plays a role of the energy scale multiplier quite similar to pressure in I_V (our \vec{h}_V). The \mathcal{F}_{heat} relates to the heat transfer rate traditionally denoted by \dot{Q} , in watts (W), whereas $\vec{\mathcal{F}}_{heat}$ relates to the heat flux commonly expressed as a vector \vec{q} (W/m²) by the integration of the flux over the surface of the system. The mathematical set presented in Equation (22) can be treated as a universal one—there is a place for new yet unknown processes. There is no radiative flux described by the Pointing vector (1899) because it is indirectly related to the system’s substantial boundary. If the substantial boundary ∂V is oriented outside by the normal unit vector \vec{n} , then one can write the energy flux as a normal component of the total energy vector:

$$\vec{\mathcal{F}}_E = \iint_{\partial V} (\vec{\mathcal{F}}_{work} + \vec{\mathcal{F}}_{heat} + \vec{\mathcal{F}}_{chem} + \vec{\mathcal{F}}_{elec} + \vec{\mathcal{F}}_{mag} + \dots) \cdot \vec{n} \, dA. \quad (23)$$

Two first energy fluxes are very well known in the literature: $\vec{\mathcal{F}}_{work}$ is a mechanical energy flux of Umov (1874) and Volterra (1899), and $\vec{\mathcal{F}}_{heat}$ is a heat energy flux of Rankine (1851) and Stokes (1851).

The essence of the proper definition for the various fluxes is to find a correct relationship of the energy flux to the other fluxes including momentum, angular momentum, mass, volume, entropy, electricity. If a specific internal energy ε is expressed by the primary variables of the state, and there are some spatial and time gradients of the variables of state, then the fluxes of mechanical energy and heat can be expressed by a relatively simple combination of the momentum flux tensor \vec{t} the volume flux vector \vec{h}_V and entropy flux vector \vec{h}_S :

$$\vec{\mathcal{F}}_{work} = \vec{t} \vec{v} + p \vec{h}_V + \vec{\mathcal{F}}_{work}^{int}, \quad (24)$$

$$\vec{\mathcal{F}}_{heat} = \theta \vec{h}_S + \vec{\mathcal{F}}_{heat}^{int}. \quad (25)$$

Here, \vec{v} is the velocity vector of the substance, p is the pressure, and θ is the absolute temperature. Furthermore, some energy fluxes: $\vec{\mathcal{F}}_{work}^{int}$, $\vec{\mathcal{F}}_{heat}^{int}$ appear in the above definitions—these are called “the interstitial working” and “the interstitial heating” vectors and are related with the gradient or higher-order models of working continua presented also in the article [43]. Prof. Cimmelli’s last paper [43] is devoted to the problem of thermodynamic consistency of main mathematical models in non-equilibrium and extended thermodynamics.

In the case of field energy, there is the pointing radiation energy flux defined as $\vec{\mathcal{F}}_{em} = \vec{E} \times \vec{H}$. The chemical flux of energy is usually defined as [6]: $\vec{\mathcal{F}}_{chem} = \mu \vec{h}_\mu$, however, the electric energy flux is [44] (pp. 70–72): $\vec{\mathcal{F}}_{elec} = z \vec{i}$, where $z = c_e z_e$, is a general electric potential and $\vec{i} = q \vec{E}$ —electric current. Resuming, the energy flux vectors are strictly related to the model of continua and should be rather postulated as some additional “consistency relations”.

10. Balance of Energy

Among the different forms of energy balance, only one mathematically expresses the first law of thermodynamics. This universal law of energy conservation can be anticipated as follows. Based on human experience, we assume that there is an objective universal law that states that the change of the energy storage of system A occurs at the expense of processes (fluxes), or mathematically:

$$\frac{d}{dt}(\mathcal{U} + \mathcal{K} - \Phi + \mathcal{E}_{em}) = \iint_{\partial V} \vec{\mathcal{F}}_e \cdot \vec{n} \, dA + \iint_{\infty} \vec{\mathcal{F}}_{em} \cdot \vec{n} \, dA + \mathcal{S}_e. \quad (26)$$

Here, the energy source or sink \mathcal{S}_e , which usually is to be zero, appears only formally. It is a measure of the degree of non-conservation of energy because we assume that the fundamental property of our universe is the indestructibility of energy. While the first law is undoubtedly one of best known pillars of classical science, its typical formulations are frequently folklore-minded and not mathematically unique. This situation is especially unfortunate in that there is no one meaning of energy notion that unifies the entire domain of applicability from quantum theory of elementary strings to the universe cosmology. This work removes the energy balance from the first position even before the first law of thermodynamics giving it a new status of “all-pervading law of the conservation of energy” (William Thomson’s words). Why are there so many schools of reasoning based on different mathematical formalism and different traditions in derivation? One probably cannot find one clear-cut derivation of the first law, and thus we must still rule-out some pertinent pre-suppositions on our reasoning and our logic.

This energy balance equation can be integrated for the phenomenon occurring between time t_{in} and t_{out} (time scale associated with human activity). Therefore, we also assume that time is related to a scale of human activity. Due to the assumption of reversibility concerning the total energy storage, the integral on the left-hand side of Equation (26) depends only on the initial and final states of the storage. Provided that the processes are summed exactly, Equation (26) finally transforms into:

$$(\mathcal{U} + \mathcal{K} - \Phi + \mathcal{E}_{em})|_{t_{out}} - (\mathcal{U} + \mathcal{K} - \Phi + \mathcal{E}_{em})|_{t_{in}} = \int_{t_{in}}^{t_{out}} (\mathcal{F}_E + \mathcal{F}_{em}) \, dt. \quad (27)$$

This is a formulation known as an integral in time and space form of the primary energy conservation law Equation (26). Gyftopoulos and Beretta write this to be: $E_2 - E_1 = E^{\leftarrow}$ [1,14].

A special integral form of Equation (27) can be obtained for the phenomenon occurring periodically in closed cycles. In this case, the summed energy changes in a single cycle are equal to zero, and the balance can be simplified to the closed integrals of fluxes that compensate each other. If the considered phenomenon only consists of heating and working interactions, then their line integrals are called the cycle heat and cycle work, and Equation (27) can be written as:

$$\mathcal{F}_{work}^{cycle} + \mathcal{F}_{heat}^{cycle} \equiv W + Q = 0, \quad (28)$$

which can be read as follows: “After a single, complete cycle of transformations the internal, kinetic and potential energies stored in the working medium take again their initial value, and the cycle work is equal to the cycle heat.” Therefore, we assume closed system in Equation (28). For instance, with the use of the classical Navier–Stokes model of the working fluid, the integral process functions like W , Q can be computed in terms of the 3D model as:

$$\mathcal{F}_{work}^{cycle} = \oint (\iint_{\partial V} \vec{\mathcal{F}}_{work} \cdot \vec{n} \, dA) dt = \oint (\iint_{\partial V} \vec{t} \cdot \vec{v} \cdot \vec{n} \, dA) dt, \quad (29)$$

$$\mathcal{F}_{heat}^{cycle} = \oint (\iint_{\partial V} \vec{\mathcal{F}}_{heat} \cdot \vec{n} \, dA) dt = \oint (\iint_{\partial V} \theta \vec{h}_S \cdot \vec{n} \, dA) dt. \quad (30)$$

Here, in Equations (27) and (28), it is assumed that $S_e = 0$, but strictly speaking, only the law of energy conservation (First Law of Thermodynamics) should decide the existence of the internal energy source S_e . Here we observe an anthropocentric, not objective hypotheses dealing with energy sources.

11. Expressions for the Internal Energy—Variables of State

New notions were introduced by Rankine together with the concept of the internal energy: the thermodynamic variables of state, which can estimate the change of internal energy. Two kinds of properties were attributed to every form of energy—a primary one, which is extensive, mass-dependent, say $x_{(k)}$, and a secondary one, say $a_{(k)}$, which is dual, intensive, and mass-independent. The variables $a_{(k)}$ cannot be arbitrarily defined; they must be measurable via modern measurement techniques based on fine-scale crossing effects.

The first state variable was called a *mataphoric* function, and the second one was called a *methamorphic* function (Rankine, 1855) [30]. The first example of the variables of state for gases were: volume V and entropy S (extensive variables). These are complementary to the thermodynamic pressure p and temperature θ (intensive variables). More variables appear when the solid body is considered, namely: the tensor of deformation density v_{ij} , the tensor of specific entropy η_{ij} , and complementary to them, the tensor of stresses (pressure) p_{ij} and the tensor of temperature θ_{ij} .

The variables of state in Rankine's proposal were a practical way to calculate the amount and the change of internal energy. The primary and extensive variables of state do not reflect the individualism of internal motion. They are anthropocentric and convenient for average measurements over the internal motion. Unfortunately, the internal energy conversion so clearly imagined by Rankine's "vortex atom", when analyzed in terms of variables of the state, no longer has a simple representation. It hard to imagine graphically an exemplary conversion as for the case when the internal energy remains constant, but the specific volume decreases at the expense of the specific entropy increase [28]. The internal energy concept expressed by primary variables of state was finally formulated by Gibbs (1873) who defined the relationship between primary and dual variables of state to be:

$$a_{(k)} = \frac{\partial \varepsilon}{\partial x_{(k)}}, \quad (k) = v, \eta, c_i, \varphi, \vec{E}, \vec{H}, \quad (31)$$

This equation is one of the most fortunate in the thermodynamic foundations. It allows one to relate the set of governing equations describing the arbitrary process with the law of energy conservation. In other words, governing equations that describe a physical process include heat conduction in a solid body that may be erroneously formulated in the sense that they can lead to the violation of the law of energy conservation. Therefore, it is necessary to know the Gibbs constitutive relations (Equation (31)) to transform the governing equations, such as the Schrödinger or the Maxwell equation, into the energetic relationship. Simultaneously, the well-defined partial energy fluxes for working and heating processes of all kinds are also needed.

Gibbs realized that for the internal energy changes occurring due to changes of the primary variables of state, it is important to determine the total internal changes expressed by changes of both primary and dual variables of state, mathematically:

$$d\varepsilon = \sum_{k=1}^n a_{(k)} dx_{(k)}. \quad (32)$$

which have the exemplary form [45,46]:

$$\text{for fluids: } d\varepsilon = p dv + \theta d\eta + \mu dc + \dots \quad (33)$$

$$\text{for solids: } d\varepsilon = p_{ij} dv_{ij} + \theta_{ij} d\eta_{ij} + \mu_{ij} dc_{ij} + \dots \quad (34)$$

Here increment d means any kind of substantial differentiation in time (d/dt), proper for type tensor, quaternion, spinor, etc. [46]. For instance, in the case of vectorial or tensorial type of internal state variables, the proper time rate is the Zaremba-Jaumann type of derivatives [46]. For the solid bodies that accumulate both volumetric and shape changes, there are specific deformations, specific entropy, specific concentration, etc. Strictly speaking, this literal form of the Gibbs equation for solids has recently been introduced by B. Stuke [45]. If our system A undergoes small time changes, then the local Gibbs Equation (32) can be adopted to small increments of global variables, e.g., $d\mathcal{U} = pdV + TdS$.

12. Balance of Extensive Variables $X_{(k)}$

The fundamental question of thermodynamics is the problem of how extensive state variables (global: $X_{(k)} = \iiint_A \rho x_{(k)} dA$ or local) evolve under physical processes, e.g., how volume and entropy change during simple isoenergetic processes in steam. Starting from the original line of reasoning (Carnot, Rankine, Reech, Clausius, and Gibbs [10,23,30])—and extending the Hatsopoulos, Keenan, and Gyftopoulos [4] (also Gyftopoulos and Beretta approach [1,12–14])—we propose to write following evolution equations:

$$d_{(k)}X_{(k)} = \frac{\delta_{(k)}\mathcal{F}_{(k)}}{a_{(k)}} + \mathcal{N}_{(k)}, \quad k = 1, 2, 3, \dots \quad (35)$$

In case of simple conversion, where: $k = 1, 2$, $X_{(1)} \equiv V$; $X_{(2)} \equiv S$; $a_{(1)} = p$; $a_{(2)} = T$; $\mathcal{F}_{(1)} = \mathcal{W}$; $\mathcal{F}_{(2)} = \mathcal{Q}$, Equation (35) reduces to the volume and entropy evolution equations respectively:

$$dV = \frac{\delta\mathcal{W}}{p} + \mathcal{N}_V dt, \quad (36)$$

$$dS = \frac{\delta\mathcal{Q}}{T} + \mathcal{N}_Q dt. \quad (37)$$

Here some “fluxes” of volume and entropy appear. Unfortunately, they are defined, according to original Rankine–Clausius reasoning through corresponding fluxes of energy. We are now removing this erroneous concept. Therefore, looking for more primary quantities of these particular definitions, one can define the local volume flux \vec{h}_V and local entropy flux \vec{h}_S as:

$$\frac{\delta\mathcal{W}}{p} = \left[\iint_{A_w} \vec{h}_V \cdot \vec{n} dA \right] dt, \quad (38)$$

$$\frac{\delta\mathcal{Q}}{T} = \left[\iint_{A_Q} \vec{h}_S \cdot \vec{n} dA \right] dt. \quad (39)$$

In Equations (36)–(39), according to Clausius’ pioneering assumption, some uncompensated energy transformations $\mathcal{N}_{(k)}$; $\mathcal{N}_V = \iiint_V \rho n_V dV$; $\mathcal{N}_Q = \iiint_V \rho n_Q dV$ are present. However, in Beretta’s recent statement of the volume balance ($V_2^A - V_1^A = V^{A \leftarrow R}$ [37]) the uncompensated transformation of volume \mathcal{N}_V does not appear. Similarly, Beretta [38] postulates, like our Equation (35), the balance of other extensive state variables such as chemical amounts $c_{(k)}$ in a form: $c_{(k)2}^A - c_{(k)1}^A = c_{(k)}^{A \leftarrow R}$; $k = 1, 2, 3 \dots$ balance of constituent (k), where irreversibility sources also are removed. The uncompensated heat transformation \mathcal{N}_S was introduced by Clausius in 1854, yet before his definition of “disgregation” (1862) and “entropy” (1865) [47]. However, the uncompensated work transformation \mathcal{N}_V was introduced by Duhem in the preface to the book [48].

Next, dividing Equations (36) and (37) formally by the dt increment and using the mass conservation balance, we can write that: $dV/dt = \iiint \rho \frac{d}{dt} v dV$ and $dS/dt = \iiint \rho \frac{d}{dt} \eta dV$. In practice, the specific

densities n_V, n_Q are treated as the source of irreversible generation of state variables. Remembering that $V = \iiint \rho v dV$ and $S = \iiint \rho \eta dV$, in local statement, the Equations (36) and (37) take a final form:

$$\rho \frac{d}{dt} v = \operatorname{div} \vec{h}_V + \rho n_V, \quad (40)$$

$$\rho \frac{d}{dt} \eta = \operatorname{div} \vec{h}_S + \rho n_Q. \quad (41)$$

Here, η represents the specific entropy and v defines the specific thermodynamic volume, which, for this case, is not a simple inverse of density, ρ , in line with Brenner's approach [49].

13. Do We Need a Generalized Balance of Entropy?

Equations (37) and (41) are not the first in the literature. Such a generalized balance of entropy between states 1 and 2 was written by Gyftopoulos and Beretta as [1] (p. 106) and [2,14]: $S_2 - S_1 = S^{\leftarrow} + S_{irr}$. This states that the entropy changes of a system ($S_2 - S_1$) must be at least equal to the entropy received from the surrounding S^{\leftarrow} . Also, entropy cannot be destroyed and may be greater than entropy received if an amount S_{irr} is created inside of the system by irreversibility. Mathematically, it is a half-conservation law: entropy can be only created and never destroyed. The important innovation of the Gyftopoulos–Beretta statement is that the flux S^{\leftarrow} does not denote the flux of heat energy divided by an integrating factor—consequently S^{\leftarrow} is a much more general notion than E^{\leftarrow}/T .

However, the temperature is not the only (thermal) integrating factor; indeed, chemical potential and pressure represent integrating factors, and a generalized integrating factor can be defined to generalize the formulation of entropy. Based on the Gyftopoulos and Beretta definition of entropy, additional constant parameters characterizing the reservoir become $c_R = \mu_R$ and $c_R = P_R$ were introduced by Palazzo in his article [3].

Nevertheless, the question of how to define an energy flux corresponding to fluxes \vec{h}_V and \vec{h}_S remains open. Let us recall that in the extended non-equilibrium thermodynamics (see [10,12]), this is a crucial point for the correct formulation of the set of governing equations. Gyftopoulos and Beretta [1] (pp. 177, Equation (12.25)) (also [13,14]) define the vector \vec{h}_S in terms of Q^{\leftarrow}/T_Q —heat interaction between the system and the surrounding reservoir. This is extremely important for T_Q and the almost common value of the initial temperature T_1^A and T_1^R . Only this kind of energy interaction can be called “heat” and therefore should be distinguished from the classical heat “ δQ .” In our opinion, this rigorous continuation of Sadi Carnot's line of reasoning leads to a definition of only a kind of “confinement heat” and it is far from common understating of “heat flow vector” that exists not only for special temperatures $T_A = T_Q = T_R$. This statement leads to a new question of what kind of “heat” flows from system A to B when both systems have the same temperature T_Q .

Finally, using these assumptions, Gyftopoulos and Beretta define the balance of entropy to be [1] (p. 179, Equation (12.27)):

$$S_2 - S_1 = \frac{Q^{\leftarrow}}{T_Q} + S_{irr}, \quad (42)$$

This equation only deals with the process $A_1 \rightarrow A_2$ where heat Q^{\leftarrow} is the energy interaction at common temperature T_Q . In other words, for a heat-only-process, the net amount of energy E^{\leftarrow} exchanged by the system, denoted by Q^{\leftarrow} and divided by the common interaction temperature T_Q , describes the net entropy exchanged with the surrounding.

This special energy exchange via “heat-only-process” cannot be realized in the classical Carnot cycle where energy interaction by working is present in each of the four particular processes. Rankine was probably the first to think in this way when he wrote the “principle of equal entropy fluxes” as follows in 1851:

$$\frac{Q_{(hot)}^{\leftarrow}}{\theta_{hot} + \kappa} + \frac{Q_{(cold)}^{\rightarrow}}{\theta_{cold} + \kappa} = 0. \quad (43)$$

This expression is a prototype for numerous different relations between entropy flux and thermal energy flux [9]. In the present paper we continue the tradition of the absolute temperature denotation. The letter “ T ” is used for the Kelvin scale, and “ θ ” is used for Rankine scale. Equation (43) shows the small constant temperature κ , postulated by Rankine, looks like a cosmos background temperature: $\kappa = 2.1 \text{ }^\circ\text{R}$.

14. Constitution of the Entropy and Volume Flux

What is the role of the entropy and volume balance (Equations (36) and (37) or Equations (40) and (41))? Should entropy S and volume V be treated as equilibrium or non-equilibrium quantities? Why are these balances traditionally omitted within the local formulations of thermodynamics? For instance, does the well-known Navier–Stokes equations, without a local balance of volume in Equation (40) and local balance of entropy in Equation (41), stay thermodynamically correct and consistent?

Therefore, keeping the original Sadi Carnot line of reasoning, where the balance of volume is explicitly used for calculations, and, additionally, the balance of entropy is the main postulate expressed as a “law of caloric conservation”. Thus, we may assume that state variables S and V of working continuum change both under conversion and external sources of the process described by a proper set of equations. From a thermodynamic point of view, no details of momentum transport are important but the “evolution” of main extensive state variables. Thus, solving the balances of Equations (40) and (41) are only possible if fluxes of appropriate quantities (i.e., \vec{h}_V and \vec{h}_S) are defined by some constitutive relations.

Both vectors \vec{h}_V and \vec{h}_S must also have a contribution to the energy flux vector. Considering Equations (36)–(39) into account, we can define additional mechanical volumetric $\vec{\mathcal{F}}_m$ and thermal $\vec{\mathcal{F}}_q$ energy flux as:

$$\vec{\mathcal{F}}_m = p\vec{h}_V, \quad (44)$$

$$\vec{\mathcal{F}}_q = \theta\vec{h}_S. \quad (45)$$

Variables of state p and θ should be here treated as some Lagrangian multipliers [10]. Proposed here the volume flux of energy \vec{h}_V is consistent with a model of diffuse volume transport recently developed by H. Brenner [49]. He defines the volume flux by a kind of volume velocity $\vec{h}_V = \vec{v}_v$ that is fundamentally different from the mass velocity \vec{v} introduced 260 years ago by Euler. Brenner underlines the thermodynamic role of \vec{v}_v velocity calling it the “the work velocity.” Surprisingly, such extended fluid kinematics with two fluid velocities is independently postulated by the General Equation for Non-Equilibrium Reversible-Irreversible Coupling (GENERIC)—field theoretical treatment of continuum physics, discovered in a pioneering paper by Grmela and Öttinger [50].

15. Balance of a Volume Tensor

The balance of thermodynamic volume Equation (40) cannot be directly treated as another form of mass balance since $v \neq \rho^{-1}$. Equation (40) should be interpreted as a balance of state variable for mechanical-type of contribution to the internal energy. In a solid working continuum, the role of thermodynamic volume fulfilled by an elastic tensor of deformation or, more generally, the symmetric volume tensor $\vec{v} = v_{ij}\vec{e}_i \otimes \vec{e}_j$. Then, instead of Equation (40) we now postulate tensorial evolution equation:

$$\rho \frac{d}{dt} \vec{v} = \text{div } \mathbb{h}_V + \rho \vec{n}_V. \quad (46)$$

Physical interpretations of the volume flux $\mathbb{h}_V = h_{ijk}\vec{e}_i \otimes \vec{e}_j \otimes \vec{e}_k$ is rather complex: In the literature, it appears in the case of so-called weekly non-local plasticity [20]. However, the irreversible generation of volume tensor \vec{n}_V is present in many irreversible solid phenomena (creep deformation tensor, slip and plastic deformation tensor, etc.) For instance, the heat engines used in aeronautics are

based on zirconia solids as a working continuum with the austenite-martensite phase transition as the main form of energy storage [51]. Even after a few thousand cycles, this working continuum degrades so much due to the occurrence of irreversible plastic deformation induced by a cyclic phase transition.

16. Partial Balance of Kinetic Energy

As recognized by Coriolis (1842) and Umov (1878), we balance the kinetic energy of a simple continuum by using the balance of momentum (Newtonian equation of motion). The scalar property of energy will be related with momentum only if we do scalar multiplication of momentum balance by the specific momentum \vec{v} :

$$\vec{v} \cdot \left[\rho \frac{d}{dt} \vec{v} = \text{div} \overset{\leftrightarrow}{t} + \rho \vec{b} \right]. \quad (47)$$

Assuming that the tensor of momentum flux for this simple (non-gradient) working fluid is defined as an additive contribution of spherical pressure tensor and the viscous laminar fluid: $\overset{\leftrightarrow}{t} = -\pi \overset{\leftrightarrow}{I} + \overset{\leftrightarrow}{\tau}$, we can also split the contribution of energy into recoverable and dissipative parts:

$$\rho \vec{v} \cdot \frac{d}{dt} \vec{v} = \rho \frac{d}{dt} \kappa = \rho \vec{v} \cdot \vec{b} + \rho \pi \frac{d}{dt} \rho^{-1} + \text{tr}(\overset{\leftrightarrow}{\tau} \overset{\leftrightarrow}{d}) - \text{div}(-\pi \vec{v} + \overset{\leftrightarrow}{\tau} \vec{v}). \quad (48)$$

The above equation we read as: the rate of change of kinetic energy depends on the gain of generation $\rho \vec{v} \cdot \vec{b}$ proportional to the rate of gravitational energy, the amount of energy conversion $\rho \pi \frac{d}{dt} \rho^{-1}$, part of energy dissipation $\text{tr}(\overset{\leftrightarrow}{\tau} \overset{\leftrightarrow}{d})$ (where $\overset{\leftrightarrow}{d}$ is symmetric part of the velocity gradient), and the exchange of energy by a part of the mechanical flux $\vec{\mathcal{F}}_{work} = -\pi \vec{v} + p \vec{h}_V + \overset{\leftrightarrow}{\tau} \vec{v}$, where p is thermodynamic pressure and π represents co-pressure due to Brenner's concept of internal volume evolution [52,53]. This equation means that only in a partial balance of energy can we explicitly observe the three manners of energy transformations: expansion, conversion, and dissipation.

We have two contradict schools in the definition of tensor of momentum flux. The first one comes from Cauchy (1822) who defined it as a "generalized tension": $\overset{\leftrightarrow}{t}$. The second one is from the British school and comes from Stokes (1845), who defined this tensor to be "a generalized pressure": $\overset{\leftrightarrow}{p}$. Of course, $\overset{\leftrightarrow}{t} = -\overset{\leftrightarrow}{p}$. Above, the pressure p means mechanical total pressure which is measurable via a barometer.

17. Neoclassical Navier–Stokes Energy Equations

Let us consider now an example of the Gyftopoulos–Beretta exposition of thermodynamics strictly adopted to the classical Navier–Stokes–Fourier equations. It leads to a neoclassical Navier–Stokes model of working fluid. Below we present a thermodynamically consistent statement of simple visco-elastic, "heat" conducting, fluid mathematical model, i.e., a model of fluid in which constitutive relations are expressed only by the intensive state variables: velocity \vec{v} (specific density of momentum), specific volume v and specific entropy: η . Specific internal energy is a function of state variables: $\varepsilon = \varepsilon(v, \eta)$. Moreover, a material which is not required to possess a potential ε , e.g., thermo-elastic Duhamel–Neumann or Cauchy elastic material, cannot be proven directly not to be a perpetuum mobile of the first kind. Let us first consider the primary energy balance in the form of global equality:

$$\frac{d}{dt} (\mathcal{U} + \mathcal{K} - \Phi) = \iint_{\partial V} (\vec{\mathcal{F}}_{work} + \vec{\mathcal{F}}_{heat}) \cdot \vec{n} dA. \quad (49)$$

Here, for our system A (e.g., a simply connected body \mathcal{B}), with a total volume V and a boundary surface ∂V , oriented externally by the normal vector \vec{n} , we denote the internal energy by: $\mathcal{U} = \iiint_V \rho \varepsilon dV$; kinetic energy by: $\mathcal{K} = \iiint_V \rho \kappa dV$; the potential energy of body forces by: $\Phi = \iiint_V \rho \phi dV$. Equation (49) reads that the total change of stored energy of a body \mathcal{B} is compensated

by energy being supplied (extracted) through the mechanical energy flux: $\vec{\mathcal{F}}_{work} = \overleftrightarrow{t} \vec{v} + p \vec{h}_V$ and the thermal energy flux: $\vec{\mathcal{F}}_{heat} = \vec{h}_S \theta$. Definitions for these fluxes are fundamental for the primal statement of energy balance in the Carnot sense—they contain the total, and not only reversible, momentum flux \overleftrightarrow{t} and total, not only diffusive, flux of entropy \vec{h}_S .

Looking on flux of energy in Equations (24) and (25), yet another fundamental question appears: It is somehow stranger splitting of energy fluxes into reversible and irreversible parts: $\vec{\mathcal{F}}_{work} = \vec{\mathcal{F}}_{work}^{\rightarrow rev} + \vec{\mathcal{F}}_{work}^{\rightarrow irr}$; $\vec{\mathcal{F}}_{heat} = \vec{\mathcal{F}}_{heat}^{\rightarrow rev} + \vec{\mathcal{F}}_{heat}^{\rightarrow irr}$. From Equation (49) it follows that such splitting is possible in the case of mechanical flux of energy. However, nothing is known on splitting of thermal energy flux. Only one case where $\vec{\mathcal{F}}_{heat}^{\rightarrow rev}$ appeared in the literature is the model is Green–Naghdi theory of heat superconducting [6]. Unfortunately, it means that for the classical Navier–Stokes–Fourier model entropy based on reversible flux of thermal energy cannot be defined.

Even though the mechanical and thermal energy fluxes are applied on disjoint side surfaces $\partial V = A_{heat} \cup A_{work}$, there is no mathematical obstacle whatsoever to employ Stokes' theorem on the divergence. Assuming, that: $\frac{d}{dt} \rho + \rho \operatorname{div} \vec{v} = 0$, or, in other words, the satisfaction of mass balance, Equation (49) may be rewritten:

$$\iiint_V [(\varepsilon + \kappa - \phi)(\dot{\rho} + \rho \operatorname{div} \vec{v}) + \rho(\dot{\varepsilon} + \dot{\kappa} - \dot{\phi}) - \operatorname{div}(\overleftrightarrow{t} \vec{v} + \vec{h}_V p + \vec{h}_S \theta)] dV = 0. \quad (50)$$

This equation is always true, whether the set of governing equations (that is, equations for mass, momentum, volume, and entropy balances) is satisfied or not. It will now be shown that, presuming the fields and variables of state satisfy conditions imposed by governing equations, the equation of energy receives a very important form allowing for further restrictions to describe fields. This means that even though the solutions may satisfy conservation equations for mass, momentum, volume, and entropy, they need not satisfy conservation equations for energy. Consequently, this generates energy *ex nihilo*.

18. Volume Flux Splitting

In Equation (50), according to Brenner's concept of volume balance [52], we introduce the following splitting of the volume flux:

$$\vec{h}_V = \vec{v} + \vec{h}'_V, \quad (51)$$

which is consistent with the postulate that the volume flux is identical with the volume velocity: $\vec{h}_V = \vec{v}_v = \vec{v} + \alpha_B \operatorname{grad} p$ [52]. The volume velocity, \vec{v}_v , is fundamentally different from the mass velocity \vec{v} . Therefore, \vec{h}'_V is introduced and represents pressure gradient, $\vec{g}'_V = \operatorname{grad} p$, multiplied by the Brenner coefficient, α_B .

Material derivatives of kinetic and potential energy are $\dot{\kappa} = \dot{\vec{v}} \cdot \vec{v}$ and $\dot{\phi} = -\frac{\partial \phi}{\partial \vec{x}} \cdot \dot{\vec{x}} = -\vec{b} \cdot \vec{v}$, respectively. The following identities also occur: $\operatorname{div}(\overleftrightarrow{t} \vec{v}) = \operatorname{div} \overleftrightarrow{t} \cdot \vec{v} + \overleftrightarrow{t} \cdot \operatorname{grad} \vec{v}$ and $\operatorname{div}(\vec{h}_S \theta) = \theta \operatorname{div} \vec{h}_S + \vec{h}_S \cdot \operatorname{grad} \theta$. According to the well-accepted tradition, the velocity gradient will be denoted by $\overleftrightarrow{l} = \operatorname{grad} \vec{v}$ and decomposed into a symmetric and anti-symmetric part $\overleftrightarrow{l} = \overleftrightarrow{d} + \overleftrightarrow{w}$. A temperature gradient will be denoted by $\vec{g}_S = \operatorname{grad} \theta$ and pressure gradient by $\vec{g}'_V = \operatorname{grad} p$.



19. The First Law of Thermodynamics for the Navier–Stokes Fluid

Through the addition and subtraction of $\pm\theta(\rho\dot{\eta} - \rho n_S)$ and $\pm p(\rho\dot{v} - \rho n_V)$, the integral of Equation (50) becomes:

$$\begin{aligned} & \iiint_V \{ \rho \dot{\varepsilon} - (\operatorname{div} \vec{t} + \rho \vec{b} - \rho \dot{\vec{v}}) \cdot \vec{v} - (\operatorname{div} \vec{h}_S + \rho n_S - \rho \dot{\eta}) \theta - \\ & (\operatorname{div} \vec{h}_V + \rho n_V - \rho \dot{v}) p - (\varepsilon + \kappa - \phi) (\dot{\rho} + \rho \operatorname{div} \vec{v}) \\ & \theta (\rho \dot{\eta} - \rho n_S) + p (\rho \dot{v} - \rho n_V) - \vec{h}_S \cdot \vec{g}_S - \vec{h}_V \cdot \vec{g}_V - \vec{t} \cdot \vec{l} \} dV = 0. \end{aligned} \quad (52)$$

Recall that the thermodynamical volume v is not a simple inverse of density ρ ; another thermodynamic argument for balance of volume has recently been undertaken by Brenner [49]. Once the fields ρ , \vec{t} , \vec{v} , \vec{h}_S , η , \vec{h}_V , v , satisfy balance equations of mass, momentum, moment of momentum $\vec{t} = \vec{t}^T$ as well as volume and entropy, remembering that $\vec{t} \cdot \vec{l} = \vec{t} \cdot \vec{d}$; $\vec{t} = \vec{t} - p \vec{I}$ energy Equation (52) finally reduces to:

$$\iiint_V \{ \rho \dot{\varepsilon} - \theta (\rho \dot{\eta} - \rho n_S) - p (\rho \dot{v} - \rho n_V) - \vec{h}_S \cdot \vec{g}_S - \vec{h}_V \cdot \vec{g}_V - \vec{t} \cdot \vec{d} \} dV = 0. \quad (53)$$

The scalar quantity $\vec{t} \cdot \vec{d}$ in this case has a generalized form—it is a product of total momentum flux and total rate of deformation, e.g., $(\vec{t} + \vec{t}^{\leftrightarrow e} + \vec{t}^{\leftrightarrow vis} + \vec{t}^{\leftrightarrow e} + \vec{t}^{\leftrightarrow pl} + \vec{t}^{\leftrightarrow cr} + \dots)$. Similarly, the temperature field and entropy flux may be split into reversible and irreversible components: $\theta \vec{h}_S = (\theta^{rev} + \theta^{ir}) (\vec{h}_S^{\rightarrow rev} + \vec{h}_S^{\rightarrow irr})$ because they originate from total fluxes of other balanced quantities.

Even if a thermo-elastic fluid is expressed via scalar state variables v and η —which is much simpler than for solids, the mechanism of internal energy storage is more complex because of a multiplicative, not additive, contribution to $\varepsilon = \varepsilon(\eta, v)$. The material time (not the spatial one) rate of internal energy is: $\dot{\varepsilon} = \frac{\partial \varepsilon}{\partial \eta} \dot{\eta} + \frac{\partial \varepsilon}{\partial v} \dot{v}$. Therefore, by taking the material derivative of the internal energy, we obtain:

$$\iiint_V \{ \rho \left(\frac{\partial \varepsilon}{\partial v} - p \right) \dot{v} + \rho \left(\frac{\partial \varepsilon}{\partial \eta} - \theta \right) \dot{\eta} + \rho \theta n_S + \rho p n_V - \vec{h}_S \cdot \vec{g}_S - \vec{h}_V \cdot \vec{g}_V - \vec{t} \cdot \vec{d} \} dV = 0. \quad (54)$$

The working fluid will be thermo-elastic in the Carnot sense (completely reversible) if and only if thermodynamic pressure and thermodynamic temperature are connected with internal energy by equations of state:

$$p = \frac{\partial \varepsilon}{\partial v}, \quad (55)$$

$$\theta = \frac{\partial \varepsilon}{\partial \eta}. \quad (56)$$

These two constitutive relations are fundamental for proving that balance of total energy can be fulfilled in any processes governed by the balance of mass, momentum, moment of momentum, volume, and entropy.

Additionally, internal energy may not be an arbitrary function of intensive variables of state. In accordance with the Principle of Energy Conversion, it has to satisfy a supplementary condition. The actual state must be acquirable with interchangeable cycle combinations; this may be expressed mathematically with the first equation of thermodynamics postulated independently by Carnot (but not explicitly), Clapeyron (1836), and Clausius (1850): $\frac{\partial}{\partial v} \left(\frac{\partial \varepsilon}{\partial \eta} \right) = \frac{\partial}{\partial \eta} \left(\frac{\partial \varepsilon}{\partial v} \right)$. This equation has been extended by Kirchhoff (1858) to chemical state variables and Gibbs (1878) to electrical state variables. Finally, Maxwell (1871) written it to be: $\varepsilon_{,\alpha\beta} = \varepsilon_{,\beta\alpha}$.

In the case of an ideal gas, internal energy depends on two constitutive coefficients— c_v and c_p —the specific heat at constant volume and constant pressure, respectively. From this pair; c_v , c_p , one can obtain yet another pair—Carnot: (1824) $R = c_p - c_v$ and Poisson (1831): $\gamma = \frac{c_p}{c_v}$ [23,54]:

$$\varepsilon(\eta, v) = \varepsilon_0 \frac{1}{\gamma - 1} \left(\frac{v}{v_0} \right)^{1/(\gamma-1)} \exp\left(\frac{\eta}{c_v}\right), \quad (57)$$

This leads to well-established constitutive equations:

$$p = p_0 \left(\frac{v}{v_0} \right)^{-\gamma} \exp\left(\frac{\eta}{c_v}\right), \quad (58)$$

$$\theta = \theta_0 \frac{1}{\gamma - 1} \left(\frac{v}{v_0} \right)^{1-\gamma}. \quad (59)$$

Finally, the remaining part of the balance of energy is:

$$\mathcal{S}_e = \iiint_V \{ \rho \theta n_S + \rho p n_V - \vec{h}_S \cdot \vec{g}_S - \vec{h}'_V \cdot \vec{g}_V - \vec{t}' \cdot \vec{d} \} dV = 0. \quad (60)$$

This shows that the dissipative contribution to energy balance should be self-equilibrated because energy dissipation does not mean creation *ex nihilo*. Equation (43) can be also interpreted as an “inner dissipative conversion of energy.” Thus, in some sense Equation (43) could be treated to be the definitions of irreversible contributions n_V and n_S . If these contributions were non-negative, i.e., $n_V \geq 0$, $n_S \geq 0$, the remaining parts would be non-negative $\vec{h}_S \cdot \vec{g}_S \geq 0$; $\vec{h}'_V \cdot \vec{g}_V \geq 0$; $\vec{t}' \cdot \vec{d} \geq 0$ as well.

The condition of self-equilibrated dissipation of Equation (60) can be fulfilled also if we define n_V and n_S as a form of specific dissipation potential ω . In fluids, the momentum flux tensor \vec{t}' becomes an additive composition of spherical and shape viscous contributions, i.e., $\vec{t}' = -(\pi - p)\vec{I} + \vec{\tau}$. In general, the viscous part is traceless: $\text{tr}(\vec{\tau}) = 0$, and the volume-like viscous part is a spherical one: $-(\pi - p)\vec{I}$. Thus, the expression $\vec{t}' \cdot \vec{d}$ in Equation (60) turns into $(\pi - p) \text{div} \vec{v} + \vec{\tau} \cdot \vec{d}$, and

$$\theta \rho n_S + \rho p n_V = \vec{h}'_V \cdot \vec{g}_V + \vec{h}_S \cdot \vec{g}_S + (\pi - p) \text{div} \vec{v} + \vec{\tau} \cdot \vec{d}. \quad (61)$$

However, the viscous work and heat diffusion properties depend on the following dissipative potential:

$$\omega(\vec{g}_V, \vec{g}_S, \vec{d}) = \frac{1}{2} k_\eta \vec{g}_S \cdot \vec{g}_S + \frac{1}{2} \alpha_B \vec{g}_V \cdot \vec{g}_V + \mu \vec{d} \cdot \vec{d} + \left(\frac{2}{3} \mu - \lambda' \right) (\text{tr} \vec{d})^2, \quad (62)$$

where k_η is an entropy diffusion coefficient connected with the Fourier conductivity coefficient k simply as: $k_\eta = \theta k$; μ and λ' are the Stokes shape and volumetric viscosity coefficients, respectively; and α_B is the Brenner coefficient.

20. Neoclassical Constitutive Equation

Having made use of Equation (61) and the definitions of diffusive fluxes: $\vec{\tau} = \frac{\partial \omega}{\partial \vec{d}}$; $\vec{h}_S = \frac{\partial \omega}{\partial \vec{g}_S}$; $\vec{h}'_V = \frac{\partial \omega}{\partial \vec{g}_V}$; $\pi - p = \frac{\partial \omega}{\partial \text{tr} \vec{d}}$; we finally obtain the well-established constitutive equations:

$$\vec{h}_S = k_\eta \vec{g}_S, \quad (63)$$

$$\vec{h}'_V = \alpha_B \vec{g}_V, \quad (64)$$

$$\vec{\tau} = 2\mu\vec{d} + \frac{2}{3}\mu(\text{tr}\vec{d})\vec{I}, \tag{65}$$

$$\pi - p = \lambda' \text{tr}\vec{d}. \tag{66}$$

Additionally, several restrictions are imposed on constitutive coefficients including the Petit inequalities $c_p > c_v > 0$; the Lamè–Kowalski inequality $k_\eta > 0$; and the Duhem inequalities $\mu > 0$, $2\mu + 3\lambda' > 0$ [26]. From the positivity of dissipation functional, the positivity of the Brenner coefficient $\alpha_B \geq 0$ follows.

21. Neoclassical Boundary Conditions

Some consistency of boundary conditions for the neoclassical Navier–Stokes equation can simply be recognized if we compare the internal and external (at the boundary) physical coefficients appearing in the model. Starting from Navier’s [24] and Stokes’ [25] boundary condition, even this consistency can be extended on reversible properties of the model, i.e., the internal (Euler) and the external (Stokes) pressures p and p_S , respectively. Table 1 compares these properties. Better consistency of the above model of fluid bounded via proper boundary conditions suggests that the model needs three coefficients of internal friction (λ', μ, μ_2) and three coefficients of the external friction ($f_{SS'}, \nu, f_k$), respectively. Therefore, we can define a relation ratio between the internal and external friction with a dimension-less coefficient λ_{vis} and two lengths of velocity slip: l_{1v} and l_{2v} (Table 1). Having measured the internal property of friction, one can connect the external properties of friction at the Stokes boundary layer by appropriate closures written for λ_{vis} , l_{1v} , and l_{2v} , respectively [55–58].

Table 1. Comparison of a concise model of internal and external friction according to Newton’s postulate. The model (*) of a viscous bulk pressure has been proposed by Natanson [31,57].

Friction Phenomena	Internal (Bulk)	External (Boundary)	Characteristic Ratio
Elastic pressure	p (N/m ²)	p_S (N/m ²)	$\lambda_{press} = p/p_S$
Frictional pressure	$p_{vis} = \lambda' J$ (*) (Pa)	$f_{SS'}$ (%)	$\lambda_{vis} = k_{vis}/f_{SS'}N$
Linear slip velocity	μ (Ns/m ²)	ν (Ns/m ³)	$l_{1v} = \mu_1/\nu$
Square slip velocity	μ_2 (Ns ² /m ²)	f_k (Ns ² /m ³)	$l_{2v} = \mu_2/f_k$

An important phenomenon for boundary conditions is surface mobility called transpiration (Table 2), which should be added to the proper definition of surface friction [59].

Table 2. Five kinds of motions connected with a surface mobility of a particle immersed in a rest fluid. Here: $c_{v\theta}$ —the thermo-mobility coefficient, c_{vN} —the concentration-mobility coefficient, $c_{v\varphi}$ —electro-mobility coefficient, c_{vp} —the pressure-mobility coefficient, c_{vx} —the phase mobility coefficient [56].

Phenomena	Driving Potential	Coefficient	Resulting Velocity
Thermophoresis	Temperature θ	Thermo-mobility $c_{v\theta}$	$\vec{v}_{wall} = c_{v\theta}\text{grad}_s\theta$
Diffusion-phoresis	Concentration N	Concentration-mobility c_{vN}	$\vec{v}_{wall} = c_{vN}\text{grad}_sN$
Electrophoresis	Electric potential φ	Electro-mobility $c_{v\varphi}$	$\vec{v}_{wall} = c_{v\varphi}\text{grad}_s\varphi$
Pressure-phoresis	Pressure p	Pressure-mobility c_{vp}	$\vec{v}_{wall} = c_{vp}\text{grad}_sp$
Phase-phoresis	Order parameter x	Phase-mobility c_{vx}	$\vec{v}_{wall} = c_{vx}\text{grad}_sx$

Note that another mobility force, other than the difference of pressure or difference of temperature, was discovered by Graham in 1849 who found a new kind of transpiration called “atomisis”. This is currently called “diffusional transpiration” or “diffusionphoresis” [60,61]. It is quite a different kind of flow from the classical transpiration flow induced by the difference of the normal surface pressures, i.e., “pressure transpiration.” The diffusion transpiration deals with a flow of gas mixture via a long

capillary pipe where there is another interaction of any gas with a surface, which leads to the mixture separation. Here, a coefficient of diffusion mobility c_{vN} is the most important. Another type of induced motion stems from the difference of an electric potential φ on a surface—this phenomenon is called “electrophoresis” and was discovered by von Smoluchowski in 1916 [62,63] and governed by an electro-mobility coefficient $c_{v\varphi}$. Yet another mobility mechanism is connected with the phase transition change [64,65] and the surface gradient of the phase order parameter x . Let us note that all of the mobilities: pressure, thermal, diffusional, phase, and electrical define only an external mobility force in the Stokes layer [66,67].

In the special case when gas is at rest, we can observe the motion of the particle-induced by different surface inequalities—this kind of motion is called “*phoretic motion*” in the literature [68,69]. In general, any nano-particle immersed in the fluid can simultaneously undergo five kinds of motions [70,71].

22. Conclusions from Neoclassical Navier–Stokes Equation

Summarizing the consequences of the Gyftopoulos–Beretta thermodynamics exposition, this mathematical model of the continuum has several consequences. The first is that the neoclassical Navier–Stokes relationship has a thermodynamic consistency, which means that unknown fields assigned from a proper set of governing equations must additionally fulfill the condition of not creating energy from nothing Equation (60).

The second consequence is that energy conversion is impossible if state variables are defined by constitutive equations other than Equations (55) and (56). For a multiplicative form of specific energy, like Equation (57), the energy conversion is possible without additional assumptions. However, for an additive expression of internal energy, like in thermo-elastic solids, or thermo-electric fluids, convertibility is expected only by additional crossing term in constitutive relations.

The third consequence is the condition of self-equilibrated dissipation that follows from the condition of $S_e = 0$ and the frequently postulated in the literature principle of mutual “inner conversion” of dissipative energy. Therefore, numerous inequalities (like Drucker–Prager inequality for granular solids) used in the literature have their sources in the first, not in the second, law of thermodynamics. Finally, it means that the classical Clausius–Duhem inequalities have no deeper foundations and should now be treated as a historic improper composition of Clausius’ global entropy inequality with Duhem’s local energy inequality [58].

The fourth consequence is a new role of the vector of entropy flux for which we have proposed an independent constitutive Equation (63). It is a helpful solution because the question of interrelation between thermal energy flux and entropy flux is now eliminated.

23. Further Possibilities of the Gyftopoulos–Beretta Expositions

The above considerations show that the Gyftopoulos–Beretta exposition offers a new, logical, and powerful tool of reasoning. However, it also leads to other questions: Can this exposition also be useful for other models of continua such as a non-simple second-order continuum, weakly nonlocal in the time continuum, etc.? It remains unclear whether the neoclassical Navier–Stokes expression is only a single example of application and whether there are any chances for other expressions.

We note that a novelty of the Gyftopoulos–Beretta exposition is within an unusual role of first and second laws that now have a position of “supervisor” and cannot be involved in “the governing equations” as a quasi-balance equation that determines the unknown field. We remember that from a mathematical viewpoint, both the first and second laws are “scalar laws” in the domain of energy and entropy. Therefore, it is incorrect to claim that one can compute a vector of velocities from the kinetic energy balance. Strictly speaking, the first and second laws have no place during calculations based on “the governing equations.” That is, they become important only after calculations and can be used only for checking the correctness of a model.

Our results showed that it is possible to adopt the Gyftopoulos–Beretta exposition for a continuum media like a Navier–Stokes fluid. We are now enforcing this exposition to the case of turbulent fluid,

where, as we suppose [64], the classical model of Osborne Reynolds needs some thermodynamic reconsiderations. For instance, if one takes a so-called $k - \varepsilon$ model as a well-known phenomenological model of turbulent momentum evolution, then the question becomes, “Which role for two scalar evolution equations k and ε is proper?” What role of these two equations should be stated within the framework of the first law and which should be stated within the framework of a second law. Thankfully, the Gyftopoulos–Beretta exposition gives clear tools and logical arguments.

Badur and Nastalek [72] previously used the Gyftopoulos–Beretta exposition to identify the thermodynamic consistency of a weakly-nonlocal force in the space of an elastic continuum with a first-order microstructure. The Gyftopoulos–Beretta exposition is also proper for solids, and it was shown that first-order gradients of strains lead to an explicit definition of unknown fluxes: the “interstitial working” and the “interstitial heating” fluxes. Therefore, having the results of [72] in mind, we added, *ex chatetra*, those fluxes into the general definition of fluxes (see Equations (24) and (25)).

However, we are also familiar with other expositions of the law of thermodynamics. Therefore, we emphasize that there are numerous ways to approach this issue. Even if they are equivalent, they give us a variety of approaches. The variety of approaches have value *per se*. Therefore, we agree that “the classical thermodynamics in its modern formulation is a perfectly logical theory that is completely self-consistent.” However, we also agree that this “academic perfection” of thermodynamics is undergoing heavy efforts while building a very new model of continua.

One typical example of when this “perfection” was shaken is Ingo Müller’s problem that he discovered when preparing for his Ph.D. dissertation in 1968. Briefly, while looking for a new formulation of an extended, non-Fourieran flow of heat, he discovered that the relation between the flux of energy and flux of entropy is not trivial, and the classical solution proposed by Eckart [11] is not sufficient. However, searching for a new, “extended” relation between both fluxes, Müller has remained under the strong influence of the Eckart–Truesdell manner of exposition of rational thermodynamics [7].

This key problem is still open within the frame of extended irreversible thermodynamics [7,8]. However, the Müller problem does not occur within the frame of the Gyftopoulos–Beretta exposition at this stage of constructing a model and its “set of governing equations.” Therefore, we have a crucial question: Whether a relation between the flux of heat and flux of entropy is a new constitutive relation?

For instance, let us consider “weakly nonlocal (in time and space) irreversible thermodynamics” as proposed by Peter Ván [73]. This paper expressed non-Fourieran transport of heat within the frame of “generalized currents” versus “generalized fluxes” standing on the ground of Onsager’s exposition of thermodynamics. The goal of that work was the same: to check whether the Guyer–Krumhansl governing equation fulfills the laws of thermodynamics. He wrote: “one cannot include higher-order gradients in the governing equations at an arbitrary place; all equations are compatible with basic physical principles especially the second law of thermodynamics.” We principally agree with this fundamental statement, but only if its form of realization can be in some sense arbitrary. For instance, the Onsager exposition starts from the second law looking for a proper reformulation of fluxes and currents; however, the Gyftopoulos–Beretta exposition otherwise starts from a separate physical phenomenon and finishes upon checking the fulfillment of the second law.

Trying to keep the line of reasoning according to the Onsager exposition, Peter Ván [73] proposed two original solutions being a “last resort”: The first is a special dependence of entropy from the heat flux (in the current notation):

$$\eta(\varepsilon, \vec{\mathcal{F}}_{heat}) = \eta_0(\varepsilon) - \frac{1}{2} \vec{\mathcal{F}}_{heat} \overleftrightarrow{m} \cdot \vec{\mathcal{F}}_{heat}, \quad (67)$$

and the second is a very special relationship between the flux of entropy and the flux of heat:

$$\vec{h}_s(\varepsilon, \vec{\mathcal{F}}_{heat}) = \overleftrightarrow{B}(\varepsilon, \vec{\mathcal{F}}_{heat}) \vec{\mathcal{F}}_{heat}, \quad (68)$$



Here, \vec{m} is a so-called tensor of thermodynamic inductivities that is usually taken as a constant. The tensor \vec{B} is called the current intensity factor that plays the role of an additional “internal variables.” Therefore, we need further constitutive equations on \vec{B} . One can find that this proposal is elegant and very logical but is very far from the physical motivations by Guyer and Krumhansl. The physical motivation of Guyer and Krumhansl was to describe a novel mode of heat transport in crystals at very low temperatures. Even Peter Ván himself is not completely satisfied with his solution because he wrote: “However, all of these derivations contain several *ad hoc* assumptions . . . moreover, the derivation mentioned above does not have the heuristic power of irreversible thermodynamics, therefore the generalization of their assumptions in the case of more difficult situations can be very ponderous if not impossible.” We agree that the new constitutive postulate of Ván looks a little artificial, but every new solution (at the beginning) has too much “novelty.” In one case, it is “the Onsager exposition” and in the other case, it is “the Gyftopoulos–Berreta” exposition. However, we have a common aim—to show how the Guyer and Krumhansl equation fulfills the second law of thermodynamics.

Yet another interesting question is undertaken in the paper by Peter Ván [73]. It is a problem of the fulfilment of the second law by an additional equation describing the evolution of phase transition far from equilibrium. The literature has shown examples of such an equation including the Ginsburg–Landau equation or the Chan–Hilliard equation. The proposal of Ván is extraordinary and unusual, and he proposed to check the fulfillment of the second law of thermodynamics by creating a new constitutive relation:

$$\vec{h}_s(a, \vec{h}_a, \vec{\xi}) = \Gamma \vec{h}_a + \vec{A} \vec{\xi} \quad (69)$$

This relationship connects the vector of the flux of entropy with the vector of the current \vec{h}_s of phase transition, amount a , and some additional internal variable $\vec{\xi}$. Even if the coefficients Γ and \vec{A} are completely unknown, we cannot prove that the Chan–Hilliard governing equation fulfills the second law. However, we do get the impression that these *ad hoc* assumptions are physically superfluous and are postulated only for further developing the classical Onsagerian method. The literature suggests that the Onsager exposition of thermodynamics has bounds and limitations of usefulness. However, we now believe that the Gyftopoulos–Beretta exposition is, in this case, is more fruitful and promising than other expositions of the first and second law of thermodynamics.

Moving on to other possibilities, we mention the paper by Ván and Papenflous [74]. The authors start from an essential critic of their *ad hoc* solutions represented by previous “heat flux–entropy flux” relations like those in Equation (68) and Equation (69). They write: “The classical form of the Clausius–Duhem inequality does not allow higher than first-grade elasticity and plasticity without any further ado.” This statement is equivalent to a statement that: The Eckart–Truesdell manner of exposition of rational thermodynamics has too strong limitations, and we are pressed to find a new way of exposition. Ván and Papenflous proposed a rather new approach that does not contradict the second law and leads to original constitutive relations of higher-grade finite strain elasticity and viscoelasticity that are compatible with rigorous thermodynamic methods and requirements. Their method is based on two basic assumptions: (a) the entropy flux is a constitutive quantity and (b) for higher-ordered weakly nonlocal state spaces, the gradient of the balances and other kinematic constraints result in further constraints on the entropy inequality. Instead of using the Coleman–Noll procedure, this work uses the more efficient Liu–Müller one to find a quite general and concise form of constitutive equations for the entropy flux. We repeat: This system is more general and concise than *ad hoc* Equations (68) and (69). We emphasize that, in this point, the Ván–Papenflous exposition of thermodynamic coincidences with the Gyftopoulos–Beretta one, which means that the entropy flux is defined by proper constitutive equations and it cannot be a function of heat flux.

24. Application the Gyftopoulos–Beretta Exposition to the Quantum Heat Engines

Let us return to briefly discuss the role of the electromagnetic flux vector: $\vec{\mathcal{F}}_{em}$ which takes part in the general form of the first law of thermodynamics expressed by Equation (26). This vector can be a fundamental form of energy flow within a so-called quantum heat engine. The main difference with the classical flux of energy is that electromagnetic flux possesses a discrete spectrum of energy, for instance $\vec{\mathcal{F}}_{em} = \vec{n}\hbar\omega\vec{k}$, which is interpreted as a flow of n (hot or cold) phonons with frequency. Such fluxes can be found in masers and lasers. As, in the 1959 year, Scovil and Schultz-DuBois showed that the quantum engine is an analog to the Carnot thermal engine [75]. Therefore, this conversion cycle has been called the “Scovil–Schultz–DuBois cycle” (SSD-cycle) [76]. Furthermore, M.O. Scully et al. have prolongedated this principle even into the photovoltaic quantum heat engines (QHE) [77]. However, one can expect, that in this case, the internal energy of working substance (an electron, ions) should be a function of discrete variables, like photon frequencies and an “entropy element” proposed originally by Max Planck.

The balance of energy says that the change of internal energy of working medium is possible only by “heating” and “working” fluxes impressed on the boundary of the control volume. Therefore, “work(ing)” and “heat(ing)” are not quite straightforward to separate. Additionally, in the case of lasers and photocells quantum heat engines (QHE), the thermodynamic picture is more composed, since we must put into the play the electromagnetic fluxes of energy (see Equation (26)).

Generally, as follows from SSD-cycle [75–77] we have two radiative heat fluxes $\vec{\mathcal{F}}_{heat}^{\rightarrow hot}$ and $\vec{\mathcal{F}}_{heat}^{\rightarrow cold}$ coming from the hot and cold reservoirs. Both fluxes $\vec{\mathcal{F}}_{heat}^{\rightarrow hot}, \vec{\mathcal{F}}_{heat}^{\rightarrow cold}$ are acting continuously in a radiative zone of infrared frequencies. These fluxes exchange the energy across the proper filters, which convert a continuous spectrum into a discrete one. The filters play a role in thermal baths known from the quantum thermodynamics. It means that within a hot filter in temperature T_h we have a transition: $\vec{\mathcal{F}}_{heat}^{\rightarrow hot} \rightarrow \vec{\mathcal{F}}_{e-m}^{\rightarrow hot}$. Similarly, in the cold bath in temperature T_c we have $\vec{\mathcal{F}}_{heat}^{\rightarrow cold} \rightarrow \vec{\mathcal{F}}_{e-m}^{\rightarrow cold}$. Now the fluxes are defined to be:

$$\vec{\mathcal{F}}_{e-m}^{\rightarrow hot} = \dot{n}_h v_h \hbar \vec{k}_h, \tag{70}$$

$$\vec{\mathcal{F}}_{e-m}^{\rightarrow cold} = \dot{n}_c v_c \hbar \vec{k}_c. \tag{71}$$

where \dot{n} means the number of photons per second. In general, these fluxes can be responsible for changing the internal energy U of working medium (electron, or ion) but only in a discrete, quantum manner. The system under consideration also contains the third flux of energy:

$$\vec{\mathcal{F}}_{e-m}^{\rightarrow laser} = \dot{n}_l v_{laser} \hbar \vec{k}_l, \tag{72}$$

This is called “signal mode”, which acts similarly as “a piston in typical heat engines” [77]. Therefore, it is rightly called “quantized photonic work(ing)”.

The SSD-cycle contains only three transitions (the Carnot-cycle four)—the first, most important is called “pumping” realized via hot phonons, the second is “inverse to cold” (idler transition) and the last is the laser signal with the frequency ν_{laser} . Since after a one full CCD-cycle the internal energy U of the working medium return to the same value, one can write the balance of energy as:

$$\oint \left[\frac{d}{dt} U = \iint_{\partial V} (\vec{\mathcal{F}}_{e-m}^{\rightarrow hot} - \vec{\mathcal{F}}_{e-m}^{\rightarrow cold} - \vec{\mathcal{F}}_{e-m}^{\rightarrow laser}) \cdot \vec{n} dA \right] dt \tag{73}$$

and after introducing $\oint \left[\frac{d}{dt} U \right] dt = 0, n_h = \oint \dot{n}_h dt; n_c = \oint \dot{n}_c dt; n_l = \oint \dot{n}_l dt; n_h/n_c > 1$, we got:

$$0 = n_h \hbar \nu_h - n_c \hbar \nu_c - n_l \hbar \nu_{laser}. \tag{74}$$

This balance of energy during one cycle was postulated by Scovil and Schultz–DuBois in 1959 [75]. The flux $\vec{\mathcal{F}}_{e-m}^{\rightarrow laser}$ has a discrete, coherent, quantum nature. Power realized by this flux is:

$$\mathcal{P}_{laser} = \mathcal{A} \hbar \nu_{laser} \dot{n}_l = \iint_{\partial V} \vec{\mathcal{F}}_{e-m}^{\rightarrow laser} \cdot \vec{n} dA, \quad (75)$$

where \mathcal{A} a function of decay rates, or in the case of the noise-induced coherence, the function of probabilities of spontaneous emission. This sketch indicates the possibility of “separation of work and heat”. The case of photocell QHE is more complex but it is possible to solve.

25. Entropy as a Primary Concept

The prevailing belief in the literature is that entropy is a statistical measure of disorder, and that a spontaneous entropy increase is associated with irreversibility. If thermodynamics is a general science encompassing all the disciplines of our knowledge starting from the theory of elementary particles and ending on cosmology, then this definition of entropy cannot be further accepted. Therefore, Gyftopoulos and Beretta suppose that entropy is an inherent property of any system in any state and that its analytical expression must conform to some criteria [1,14,37,38].

In the Gyftopoulos–Beretta exposition, the key assumption concerns the nature of entropy. Entropy is a property in the same sense as energy, momentum, and electric charge. In principle, entropy is a measurable property because being defined in terms of energy and available energy, its measure can be determined upon a simple mechanical measurement of the changes in elevation of weights.

Entropy, defined by Equation (3), is not restricted to equilibrium states: it is defined for both equilibrium and non-equilibrium states because energy and available energy are defined for all states. Finally, the entropy definition does not involve the concepts of heat and temperature that have not yet been defined. However, Lieb and Yngvason recently developed a formulation of thermodynamics [78] in which they try to remove problems with the definition of entropy in a mathematically rigorous way in terms of adiabatic accessibility.

26. The Second Law of Thermodynamics

In every-day teaching and using of thermodynamics, we think about laws of thermodynamics in a simplified manner: the first law dealing with the quantity of energy and the second law dealing with the quality of energy, or with the available energy. The necessity of dividing the science of energy into two laws came from Leonardo da Vinci’s research, who distinguished “impossibility of eternal motor” and “impossibility of eternal motion” from “*perpetuum mobile*”, nowadays known to be *perpetuum mobile of the first and the second kind*, respectively [24,25,79]. Available energy has previously been prescribed by several authors (for some different expressions see: [4,5,37]) under different names: motivity (1856), available-work (1856), availability (1871), energy-utilisable (1887), exergy (1961), essergy (1956), etc.)

Lazare Carnot proposed a mathematical expression for the second law of thermodynamics as a loss of available work during mechanical action of a dual system, composed from a water wheel and its inverse. Such a system fulfills the law of creating energy from nothing but after every cycle, it loses some mechanical energy, available at the beginning of this cycling process. The loss of the available energy from cycle to cycle in the case of a physical rigid body (pendulum) was written by L. Carnot (1803) as:

$$\mathcal{K}_2 - \mathcal{K}_1 < 0, \quad (76)$$

$$\text{or } \Phi_2 - \Phi_1 < 0 \quad (77)$$

for the system consisting of a water wheel and its reverse. The first inequality is interpreted in the literature as a loss of kinetic energy between two states: $t_2 > t_1$, which eventually leads to damping of any pendulum’s oscillations. However, the second inequality of Equation (77) means that the water

level in the source tank cannot reach the same level as it had in the sink tank at the beginning of the process. Lazare Carnot's restriction Equations (76) and (77) within the framework of mechanical engines are nowadays known as the "*mechanical perpetuum mobile of the second kind*" [10,58].

27. The Second Law of Thermodynamics in the Language of "Energy Notion"

This line of reasoning was very fruitful. Because of the various sorts of available energy, various statements of the second law were formulated in the literature, known as: thermal (1824), chemical (1878), electrical (1804), and *perpetuum mobile of the second kind* [23,36–41]. The most promising was Sadi Carnot's statement about the loss of available thermal-like energy in a dual system consisting of two ideal cycles (heat engine cycle and heat pump cycle). Based on this approach to the issue of "losses", Clausius (1856) and Kelvin (1856) formulated the seminal verbal expressions of the second law that correctly corresponds only to thermal engines, especially for thermomechanical form. Recall that two classical verbal statements of the second law negate the existence of thermal *perpetuum mobile of the second kind*. It is worth noting that both are expressions on the integral level of cycles, that cannot be simply transformed into 3D expression. One is the Clausius statement that refers to the direction of heat transfer, expressing the never violated fact that heat cannot flow from a cold to a hot thermal reservoir by itself, without any work transferred to the system. The second one is the Kelvin–Planck statement that expresses the never violated fact that it is impossible to obtain work in a real cycle process using only a single thermal reservoir. Sometime in the literature, the Kelvin–Planck statement is erroneously interpreted as divides with 100% efficiency are impossible. Such a misleading situation probably is due to an unclear interpretation of the Carnot cycle by Kelvin and Planck, therefore, Gyftopoulos and Beretta [1] proposed in their book to remove this statement from considerations and presented it as an example of logical difficulties. But in our opinion, an additional argument against Kelvin and Planck's statement should be formulated on the ground of classical thermodynamics. Some basis is presented in monography by Pauli [80].

Therefore, one should agree with numerous authors that the second law must be formulated from the very beginning, both, in the general context as well in a correct mathematical formulation.

Whereas according to the first law, energy is conserved, the available energy according to the second law is easily lost. The loss of availability is commonly observed, e.g., when energy is transferred from one system to another, when mixing or a chemical reaction of two constituencies takes place. Physically, the loss of available energy appears due to irreversibility that occurs during energy transformations.

In their pioneering textbook "Principles of General Thermodynamics" [81], Hatsopoulos and Keenan have proposed a new verbal statement of the second law that is exposed in two steps—the first one postulate the existence of a stable equilibrium state for each set of energy values and the second one that "starting from any state of a system, it is always possible to reach a stable equilibrium using a reversible weight process". However, according to the statement of Gyftopoulos and Beretta, the concept of uniqueness has to be added to the concept of the existence of stable equilibrium in the postulate of second law.

28. Gyftopoulos–Beretta Exposition of the Second Law in Terms of the Concept of Energy

Gyftopoulos and Beretta in their exposition took Hatsopoulos–Keenan [81] second law's formulation as a starting point for various reinterpretations of basic notions, essential to understanding and explaining many phenomena [12–14]. They underline that the statement of second law is "an indispensable premise of the exposition of thermodynamics. Its validity is essential to most basic results, such as the existence of entropy as a property of any state, be it stable equilibrium or not" [13]. Continuing the efforts of Keenan and Hatsopoulos, Gyftopoulos and Beretta proposed a formulation that develops the basic concept without ambiguities and logical inconsistencies. They introduce a carefully worded and unambiguous statement of the second law in terms of the concepts of energy, stable equilibrium and reversible weight process. It should be emphasized that Gyftopoulos–Beretta's

second law statement implies the existence of stable equilibrium states but does not require that all states are stable equilibrium. It is important because the vast majority of states are non-equilibrium.

From the Gyftopoulos–Beretta exposition follows numerous facts. For instance, they have shown that the entropy balance “the change in entropy equals the entropy supplied by heat interaction plus the entropy generated spontaneously by irreversibility within the system” should be just a very special consequence of two laws of thermodynamics and for this reason cannot be called “the second law” [13]. It corresponds to Prigogine appraisal, as was proposed in books [79,82].

Gyftopoulos and Beretta [13] underline that their exposition of thermodynamics is based on the non-statistical statement of the first and the second laws. Their disagreement with statistical thermodynamics of Maxwell and Boltzmann and their criticism of the statistical character of the disorder (like, for instance: “the second law is due to properties of a large number”, or “origins of the second law is statistical” or “second law follows from our inability to keep track of a large number of molecules”, or “increasing entropy must be statistical in character”, or “Boltzmann discovered the deepest relation between the second law of thermodynamics and probability theory”, etc.) follows from two premises: (1) thermodynamic ideas that entropy is a property of matter and not of the mind, and (2) the quantum thermodynamics idea that nothing moves in equilibrium. Nowadays, we treat the statistical thermodynamics of Maxwell, Boltzmann, and Gibbs only as a kind of restricted scientific tools.

Strictly speaking, Gyftopoulos–Beretta’s approach to the second law is based on an exact introduction of a notion of adiabatic availability, which, like energy and available energy, is a property defined for all states of any system, whether they are steady, unsteady, equilibrium, non-equilibrium, stable or unstable states [1]: (Chapter 5). The property called “adiabatic availability”, denoted by symbol Ψ , equals the energy transferred to a weight in the course of a reversible weight process that interconnect state A_1 with state A_{S1} with the same values of state variables as state A_1 [13]. However, the adiabatic availability of a complex system consisting of a system A in state A_1 and a given thermal reservoir R fixed once and for all is called “available energy” for reservoir R and is denoted by the symbol Ω_1^R . Both adiabatic availability and available energy have been defined in terms of mechanical processes that do not change amounts of constituents and variables of the system A . It means that the adiabatic availability is the maximum energy that can be extracted from a system in a given state to perform useful tasks without vary amounts of constituents and variables. Gyftopoulos and Beretta note that there is also mechanical processes that end in states of A with assigned values of constituents and variables different from those of the initial state. That yields to the “generalized adiabatic availability” and “generalized available energy”.

The second law can be expressed in terms of both adiabatic availability and available energy. We note that neither of these two properties is necessarily conserved in the weight process. Neither of them can be created from nothing but is partly or totally destroyed in any process that is irreversible. Mathematically it is formulated:

$$\Psi_2 - \Psi_1 < 0, \quad (78)$$

$$\text{and } \Omega_2^R - \Omega_1^R < 0 \quad (79)$$

It means that both adiabatic availability as well as available energy are destroyed in a real process between A_1 and A_2 .

Although energy is conserved, the amount of energy that can be transferred to a weight in a weight process, the available energy is not conserved. Popularly speaking: the “quantity of energy” is conserved, but the “quality of energy” decreases in a real process.

Summarizing, Gyftopoulos–Beretta second law’s formulation is not only modern exposition but, first of all, it brings us closer to unify our knowledge about nature. Recently Beretta [83] has found that all six most popular thermodynamic frameworks have in their fundamentals the same first and second laws. Nevertheless, regardless of the wide acceptance of the Gyftopoulos–Beretta second law, its reexamination on the ground of three-dimensional continuum physics is still open. As of

today, the most applied approach to the second law has been proposed and examined by Bejan in his “Entropy generation through heat and fluid flow” [84]. However, in the light of results of Sections 17–22, remembering that irreversibility comes both from n_S and n_V , we propose yet another useful 3D form of the second law: “Irreversibility generated through heat and fluid flow”. Here, the irreversibility generation should be understood as $\mathcal{I} = (\Omega_1^R - \Omega_2^R)dt_{1-2}$, and Equation (79) as $\mathcal{I} > 0$.

Let us finally discuss other formulations of the second law. The oldest comes from da Vinci’s works: “Perpetual motion is impossible”.

It is nothing else but a misunderstanding of the Aristotelian principle of eternal entelechy [27]. This statement is not a practical one because in modern science we have lost the Aristotelian meaning of the concept of peripatetic “motion”. In modern classical thermodynamics, the Clausius formulation of the second law: “The entropy of the Universe strives to attain a maximum value”, is still popular. This expression of the fundamental law is nowadays incorrect, even wrong, therefore a huge part of us prefer to use Duhem’s statement: “In every conversion of energy, a part of available energy is degraded”, that has common roots with Maxwell’s “principle of degradation of energy”. Additionally, Rankine’s statement sounds: “The entropy of Universe is constant”.

Quite recently Peter Ván [85], standing on his long experiences and achievements, proposed a new statement of the second law: “Thermodynamic equilibrium of simple materials is stable under neutral conditions”. The idea that the second law is connected with material stability, as Ván says, comes from “ancient” observations of sources of chaos. If chaos is, according to the statement of Prigogine and Stengers [82], some primary source of irreversibility in nature, then material stability is an important indicator of the direction of time. It is reasonable to believe, says Ván, that dissipation leads to the stability of isolated simple materials. The Ván statement of the second law should be at this moment considered as a guiding idea, a challenge, a starting point of a program for research of exact conditions [85]. We agree that this idea needs some new exposition of thermodynamics, that the traditional one, like Eckart–Truesdell exposition, is too narrow, too particular.

However, we believe that the Gyftopoulos–Beretta exposition is capacious enough and sufficient in general, because the second law in this treatment is taken as primary, independent law of the whole physics, without any auxiliary conditions, without any overriding laws. If the universality of the first and the second laws of thermodynamics is the *basic mystery* of thermodynamics [85], then some facts coming from traditional conditions, like the classical non-relativistic concept of material objectivity, should agree with the laws of thermodynamics, not vice versa. In other words, partial arguments stemming from relativistic physics, quantum thermodynamics, statistical physics cannot forbid any form of laws of thermodynamics. But we agree with Peter Ván that these supra-disciplinary aspects of thermodynamics, its *mysterious universality*, still indicate a perennial need for a reevaluation of our classical exposition.

29. Conclusions and Perspectives

In this presentation, we emphasized that one of the aims of Gyftopoulos–Beretta’s exposition of thermodynamics should be to find a general framework connecting several branches of science that apply the first law of thermodynamics on different scales and at various levels. Our interest was to extend the Gyftopoulos–Beretta exposition into a thermodynamics continuum domain. This program has been partially carried out for viscous-conducting working fluid, and its result is called the neoclassical Navier–Stokes set of local 3D governing equations.

The main difference between classical and neoclassical sets of governing equations is that both primary variables of state appear as two uncompensated energies in a neoclassical statement: specific volume and specific entropy possess independent balances in the form of Equations (40) and (41); the uncompensated heat transformation of Clausius and uncompensated work transformation by Duhem are seen.

The neoclassical statement offers value for constitutive relations. The first is an entropy flux, and the second is a volume flux vector (see Equations (63) and (64)). In addition, connections between

the heating and working fluxes as well as with the entropy, volume, and momentum fluxes are not simple (Equations (24) and (25)); they can be extended to the cases where Cimmelli's interstitial heating and interstitial working vectors appear. In addition, the Brenner splitting of volumetric flux (Equation (51)) has been validated within the Gyftopoulos–Beretta exposition of thermodynamics.

In a neoclassical approach, the balance of energy (Equation (52)) plays a special role where any set of governing equations can be checked to determine whether or not it fulfills the first and the second laws of thermodynamics. It means that we express both laws of thermodynamics in the language of energy, then the well-known irreversible thermodynamics notion of “rate of entropy generation” does not appear in our statement.

Finally, if the classical Navier–Stokes set of governing equations contains only the mass and momentum balance and the Fourier equation of heat flow, then the set of governing equations in the neoclassical statement contains a set: mass continuity equation, specific volume evolution Equation (40), specific entropy evolution Equation (41), and momentum Equation (47). The moment of momentum balance is fulfilled identically.

“Work” and “working” touch not only mechanical effects but also magnetic, electrical, chemical, etc., because we say, for instance. “electrical work” and so on. Therefore, the balance of energy, like Equation (23), contains not only mechanical but other fluxes, among them the electromagnetic as a special “working flux” in a case of lasers and photocells. It is some mystery of thermodynamics that there is only one “heating flux” and many of “working fluxes”—“work” is probably more anthropomorphic than “heat”. If the mechanical flux of energy $\vec{\mathcal{F}}_{work}$ is well known in the literature, then, concerning $\vec{\mathcal{F}}_{heat}$ there are many controversies [see Equations (67)–(69)]. We think that our proposal for defining $\vec{\mathcal{F}}_{heat}$ only in terms of the entropy flux is, at least, correct, and fruitful.

Our balance of energy says that the change of internal energy of working medium is possible only by “heating” and “working” fluxes impressed on the boundary of the control volume.

Finally, we want to underline that the notions “heat” and “work”, well known from primary schools, within the frame of unified thermodynamics which contains even the quantum thermodynamics, cannot be further treated as the “basic objects”. In our approach “work” and “heat” are secondary, these appear as a resulting quantity only if the “heating” and “working” fluxes are previously known.

Compressible, viscous, conducting working medium (like steam–water vapor), being a local in space and time, the concept of “work” and “heat” is further incommensurate, therefore it is the need for use: “heating” (realized in 3D by flux $\vec{\mathcal{F}}_{heat}$) and “working” (realized in 3D by flux $\vec{\mathcal{F}}_{work}$).

It is especially interesting to apply this model of fluid to cosmology. The primary concepts also require a new examination. We are hopeful that a similar study will be applied to other continuum models such as the elasto-plastic material with destruction.

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