

On a Carnot working continuum with non-equilibrium state parameters

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Abstract We explain that a full description of how the non-equilibrium state of the system evolves in time requires the consideration and solution of its general equation of motion. In the case of the Carnot medium, as a general equation of motion, there must be taken two balances of: non-equilibrium specific volume and non-equilibrium specific entropy. Instead of taking the classical approach where the balance of entropy is postponed to more advanced and theoretical treatments, we focus on the analysis of two, most general, volume and entropy fluxes. These fluxes of motion are universal features of thermodynamics. It has been shown that the Carnot working continuum mathematical model is captured by the two general non-mathematical statements valid for all systems that we call the first law and the second law of thermodynamics.

Keywords: Non-equilibrium state parameters; Carnot cycle; Balance of entropy

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1 Introduction

In 1823 Sadi Carnot introduced [1] the concept of a four-part thermodynamic cycle, dealing with an ideal gas as a working fluid. The name “working fluid” came from the fact that the Carnot cycle is aimed to convert a “flux of heating energy” into the “flux of working energy”. On the level of a whole cycle, by integrating the heating and working fluxes Carnot was able to obtain two basic notions: “cycle heat” and “cycle work” which, helpfully, were known from engineering practice as “heat” and “work”.

Sadi Carnot has borrowed the concept of conversion from his father “General Mechanic”. Such a situation that the son takes something from his father is normal in our Western civilization. Probably it was in 1818 year in Warsaw, where General Lazar Carnot stayed as a French Revolution emigrant. During the visit of Sadi Carnot, as historians inform us, both – father and son – had an occasion to see the demonstration of a Watt steam engine. Probably then, Lazar Carnot asked: on what principle the steam engines are acting?

It is obvious that Lazar Carnot was a tremendous pattern for young Sadi Carnot. At that time, on the whole European Continent, Lazar Carnot was recognized as: “French Newton”. He proposed [2] quite a new concept of mechanics, with the laws of motion that have followed from the Aristotelian principle of least action. Lazar Carnot extending Aristotelian notions of “energea” and “entelehy” was able to introduce the concept of “energy conversion”. The main example of energy conversion, developed by Lazar, was the conversion of “potential energy” into “the actual energy” which takes place in mill wheels, with river water as “the working medium”. Lazar has introduced the concept of two energy magazines: higher and lower, in the form of water reservoirs. Lazar’s working medium possesses two state parameters: “gravitational head” and “flow speed”. Unfortunately, the son was a disappointment since in Sadi’s concept of working fluid these state parameters are unimportant – the “gravitational head” is constant and “flow speed” is equal to zero. Sadi was impressed to find some analogy.

In the year 1823, Sadi changed the configuration of Lazare’s cycle – in his case, both energy magazines were mobile but the working fluid was fixed in a geometrical domain of the engine cylinder. It has led to the case where Lazare’s state parameters: “gravitational head” and “flow speed” were nonessential. And it opened the need for a new state parameter of working fluid. Sadi Carnot has decided to introduce two complementary state parameters: “specific volume” and “specific caloric” (nowadays: spe-

cific entropy). In his description of a cycle, Sadi Carnot decided to introduce two yet unknown laws of physics into consideration. These are:

- a law of conservation of specific volume (say v) and
- a law of conservation of specific entropy (say s).

These laws were expressed in words as: at the cycle end, after four arbitrary transformations of state parameters, working fluid is in the same thermodynamical state as at the beginning, and it is ready to make a new cycle. Let us note that the balance of energy, which can be treated to be the mathematical statement of the First Principle of Thermodynamics does not appear in the Carnot model of working medium. The balance of energy in the Carnot working medium was used in a special place and in a special role (see [1] footnote 9) – only for making calculations of the equality of cycle work and cycle heat: $W_{\text{cycle}} = H_{\text{cycle}}$. It means that in Said Carnot's statement, the first principle of thermodynamics plays a special distinguished role; it is not part of a system of governing equations, since it plays a role in final judgement.

Internal energy located within the whole working fluid is denoted by Sadi Carnot as U (see [1] footnote 5). Expressing the specific internal energy as $\varepsilon = U/m$, where m is a mass of the whole working fluid enclosed within the container volume Ω , taking into account that gravitation energy is constant and kinetic energy is zero, the energy balance of 1 kg of working fluid can be reduced to:

- a law of first principle of thermodynamics:

$$\varepsilon_{(\text{beginning of a cycle})} = \varepsilon_{(\text{end of a cycle})}$$

what means that the specific internal energy, being an internal magazine of energy, located within one kilogram of working fluid, after making four conversions, returns to its starting store. In other words, the Carnot mathematical model of working fluid is based only on two balances of state parameters. And in this model, principles of thermodynamics have a passive role and are fulfilled from the very beginning. In this paper, we like to extend this approach to a working fluid within the flow – extending a case of ideal equilibrium thermodynamics to real non-equilibrium thermodynamics.

2 Non-equilibrium thermodynamical statements

Every one of us knows that a real engine working fluid cannot be described by permanently stable and reversible behaviour. Unstable phenomena, like temperature and pressure changes, result from inherent fluctuations of the

respective state variables. Near global equilibrium, those fluctuations having a form of peripatetical motions, do not disturb the equilibrium. The natural trend toward equilibrium is distinguished by asymptotically vanishing dissipative contributions. In contrast, non-equilibrium states can amplify the fluctuations, and any local disturbances can even lead the whole system into an unstable or metastable state. This feature is an important indication of the qualitative difference between equilibrium and non-equilibrium states. Equilibrium states are needed for making the constitutive relation between equilibrium state parameters, but non-equilibrium state parameters take parts in every whole balance [4, 7, 16, 28].

Within the Carnot model, there is no irreversibility generated by any flow of fluxes: flux of volume, flux of entropy or flux of momentum. The change of state parameters during four transformations occurs immediately without any fluxes – the change is visualised by virtual volumetric contact of any small part of mass of working fluid with any virtual surface of the heat container (upper and lower) and a mobile surface of the working engine. It is, of course, an ideal thought by Carnot as “equilibrium change”. In our approach, we like to go further and to remove this strong condition, by assuming that during any change of state (i.e. heating or working fluxes on the load surfaces), there is a place for appearance of non-equilibrium state fluctuations. Even if, we resign from local action of fluxes, we can obtain some improvement of the Carnot model.

Let us also note that our approach has one important aim – we want to develop and to revalorize the science of the “finite-time thermodynamics” [8] from zero-dimensional and no-time formulation into a three-dimensional statement. There are many models of fluids in the literature, but from the Carnot point of view, those models (like the Navier–Stokes equation [3, 21]) are improper for 3D description of the Carnot cycle. It is important for thermodynamics that many different parts of this science have more precise relations and more unique fundamental stones.

Let us recall that in classical thermodynamics, in most of the existing models of working continua, the parameters of state such as: the specific entropy, the specific volume, temperature and pressure are introduced by assuming a kind of local equilibrium [6, 7, 14, 28, 33, 38], even if this assumption is quite dubious in far-from-equilibrium situations. In fact, it is known that in strict local equilibrium, there is no transport of mass, volume, entropy and momentum ($\mathbf{h}_m = \mathbf{h}_v = \mathbf{h}_s = \mathbf{t} \equiv 0$).

Thus, numerous extensions of thermodynamical ideas to far-from-equilibrium systems, that are summarised in Sieniutycz’s monograph [17, chap-

ter 4], from a formal point of view, can be selected into two groups. The first one consists of the models in which the concept of non-equilibrium state is entirely related to notions of non-equilibrium temperature and non-equilibrium pressure. On the contrary, the second one is related to models that are mainly based on the concept of non-equilibrium specific volume and non-equilibrium specific entropy. It must be noticed that there are no more consistent definitions of non-equilibrium state [25, 26]. In the literature [26, 27], one can find a variety of approaches to approximation of non-equilibrium thermodynamics. The one, most frequently used, is “linear irreversible thermodynamics”, which has in its basic assumptions, a resignation from a general balances of non-equilibrium entropy and non-equilibrium volume, and replaces these balances with a new type of balance based on a “concept of local non-equilibrium” [29].

Therefore, linear irreversible thermodynamics is advantageous to have a phenomenological approach to describe natural processes. This approach is a rational approximation of non-equilibrium thermodynamics proper to investigate physical, chemical, and biological 3D systems with irreversible processes, but not to describe the Carnot cycles. In the linear irreversible thermodynamics (LIT), the main formalism is coming from the increment of Carnot internal specific energy ε , nowadays known as the Gibbs equation. Nevertheless, it should be remembered that Sadi Carnot has introduced the notion of internal energy only for one need – for connecting together the balance of specific volume and balance of specific entropy, not for the possibility that combines the first and second laws of thermodynamics [7, 28, 29]. The Carnot internal energy increment together with the Gibbs relation have nothing in common with the second law of thermodynamics, as mistakenly assumed in Linear Irreversible Thermodynamics [28].

Yet, another fundamental difference between Carnot and linear irreversible thermodynamics (LIT) lies in the manner how both define and calculate the equilibrium temperature. For Carnot, temperature is a field related through the internal energy with the field of specific entropy; for LIT, temperature is calculated from the field of velocity: $\left\langle \frac{1}{2} \mathbf{v}^2 \right\rangle = \frac{3}{2} k_B T$, which means that molecular rotation and vibration are not accounted for.

In this article, we will analyse the possibility of formulation of a more consistent model of flowing working fluid with non-equilibrium state parameters s^* and v^* , respectively. The model under consideration would describe the relaxation $s^* \rightarrow s$, and $v^* \rightarrow v$ from a non-equilibrium state to the equilibrium state via n additional internal parameters ξ_α , $\alpha = 1, 2, 3, \dots, n$.

We assume that in Carnot fluid continuum, this property is also true when the fluid under consideration is inviscid and non-conductive. To avoid misunderstandings, it is worth mentioning that in the proposed model, the role played by the energy balance is similar to the classical role played by the entropy balance in LIT – it expresses the fact of still growing amount of dissipated energy. Our approach is based on the Beretta-Gyftopoulos exposition of thermodynamics in which such classical notions as “heat” and “work” are removed from considerations [6, 9, 38].

3 The accompanying state concept

If the framework of LIT is based on a concept of “a local equilibrium”, which leads to the correctness of the Gibbs equation and locally well-defined equilibrium internal energy, then in our approach to Carnot fluid continuum we put as a fundamental assumption the fact that every equilibrium state has its “accompanying state”. The concept of accompanying state was developed in the XX century by many thermodynamicists and finally proved by Josef Kestin [15, 18, 33].

Let us recall that yet in 1901 Władysław Natanson, in his pioneering paper [11], undertook the problem of non-equilibrium measure of specific volume (but in the case of solid body) and its relaxing approaching to the recoverable, equilibrium state. As Natanson showed, in some sense, the model after elimination of relaxing parameters leads to the Maxwell-like model of superposition of elastic and non-elastic components of continuum. This way of reasoning was extended by Mandelstam & Leontovich [12] into a more thermodynamical framework.

In 1958 Andrzej Szaniawski published a significant paper [13] concerning the non-equilibrium entropy within viscous and conductive fluid. Trying to give an answer to the question “what is to be understood by entropy in a non-equilibrium state”, Szaniawski introduced a concept of space non-equilibrium parameters which possess the accompanying equilibrium state and the accompanying reversible process. Following this concept, he considered a state of continuum in which non-equilibrium specific volume v^* and non-equilibrium specific entropy s^{ast} are distinguished from reversible, equilibrium specific entropy s and equilibrium specific volume v . Numerous examples of non-equilibrium phenomena were described in the papers by Kestin and Bilicki [18] and Bilicki and Badur [19].

Physically, the phenomenon responsible for differences between $s^* - s$ and $v^* - v$ is explained by the field of internal parameters $\xi_\alpha = \xi_\alpha(\mathbf{x}t)$, $\alpha = 1, 2, 3, \dots, n$, depending on the position vector \mathbf{x} and time t . These parameters take part in the model, no matter whether the fluid under consideration is viscous or not, conductive or not. The dissipate phenomena attributed to $\xi_\alpha = \xi_\alpha(\mathbf{x}t)$ can be explained as the effect of a far-from-equilibrium state, necessary in the places where experimentalists have withdrawn traditionally assumed local-equilibrium state. In the most simple case, the number of parameters is restricted and only two internal (scalar) parameters should be postulated: the first one – to describe the $s^* \rightarrow s$ relaxation and the second one to describe the $v^* \rightarrow v$ relaxation.

In Fig. 1, the non-equilibrium state is represented by s^* , v^* , ξ_α whereas a real state of process is described by a point (P^*), and any process by means of a curve l^* .

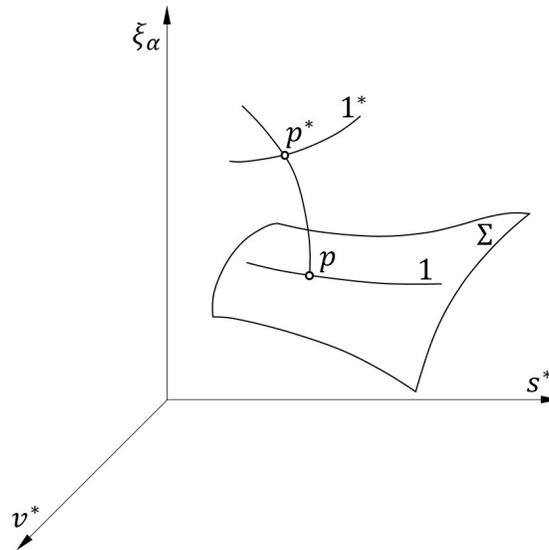


Figure 1: A space of non-equilibrium states with accompanying equilibrium state.

A set of states of equilibrium represents a surface called by Gibbs “*the primitive surface*” $\Sigma(s, v, 0) = 0$. For every state (P^*), one can find on a curve l of the accompanying reversible process, the point (P). It means that if $P^* \rightarrow P$, then $s^* \rightarrow s$, $v^* \rightarrow v$ and parameters $\xi_\alpha \rightarrow \bar{\xi}_\alpha(s, v)$ become independent and are functions of the equilibrium state parameters. In particular $\bar{\xi}_\alpha \equiv 0$.

Let us assume that the non-equilibrium state parameters are uniquely split additively into the following series:

$$s^*(v, s, \xi_\alpha) = s + \frac{1}{2}A_{\alpha\beta}(s, v)\xi_\alpha\xi_\beta, \quad (1)$$

$$v^*(v, s, \xi_\alpha) = v + \frac{1}{2}B_{\alpha\beta}(s, v)\xi_\alpha\xi_\beta, \quad (2)$$

where matrices $A_{\alpha\beta}$, $B_{\alpha\beta}$; $\alpha, \beta = 1, 2, 3 \dots, n$, should be symmetric and positively defined. Let us also assume that the specific internal energy is only a function of equilibrium state parameters s and v ; it means that the internal energy stored only elastic part of converted energy transported within working fluid. We omit here important Mandelstam's assumption [12] that a small amount of energy that is liberated during relaxation $P^* \rightarrow P$ can be recovered and, therefore, is stored in internal energy (i.e. $\varepsilon = \varepsilon(s, v, \xi_\alpha)$).

4 Balances of non-equilibrium entropy and non-equilibrium volume

Our line of reasoning assumes here that in the state of thermal equilibrium, working fluid is completely described by state parameters s and v , uniquely determining internal energy $\varepsilon = \varepsilon(s, v, \xi_\alpha)$. During a motion, which in general is not a state of equilibrium, a state of the inviscid non-conductive fluid must be represented by two non-equilibrium state parameters s^* and v^* , or according to Eqs. (1)–(2), through two equilibrium parameters s , v and n internal parameters ξ_α . The balances of changes of non-equilibrium entropy and non-equilibrium volume take the following form [8, 30, 38]:

$$\frac{d}{dt} \iiint_{\Omega} \rho s^* dV \geq \iint_{\partial\Omega_h} \mathbf{h}_s \cdot \mathbf{n} dA, \quad (3)$$

$$\frac{d}{dt} \iiint_{\Omega} \rho v^* dV \geq \iint_{\partial\Omega_h} \mathbf{h}_v \cdot \mathbf{n} dA. \quad (4)$$

In the above, the flux of entropy \mathbf{h}_s and flux of volume \mathbf{h}_v appear on a proper boundary surface oriented by unit normal vector \mathbf{n} . But traditionally in the Carnot, Clapeyron, Segiun, and Rankine style of presentation, instead of \mathbf{h}_v and \mathbf{h}_s fluxes, some corresponding energy fluxes are applied and used. Instead of \mathbf{h}_s we have the flux of heating energy $\mathcal{F}_h = T\mathbf{h}_s$ (sometimes

denoted as the vector: \mathbf{q}), and instead of \mathbf{h}_v we have the flux of working energy $\mathcal{F}_w = p\mathbf{h}_v$. But in general, the relation between fluxes is complicated especially in the case of continua with heating or working microstructure – then the additional interstitial working flux and interstitial heating flux are needed [20, 23, 27, 35]. The temperature T and pressure p appear in this relation not quite accidentally – they play the role of energy partners.

Rewriting Eqs. (3) and (4) in terms of the appropriate energy fluxes we obtain:

$$\frac{d}{dt} \iiint_{\Omega} \rho s^* dV \geq \iint_{\partial\Omega_h} \frac{\mathcal{F}_h \cdot \mathbf{n}}{T} dA, \quad (5)$$

$$\frac{d}{dt} \iiint_{\Omega} \rho v^* dV \geq \iint_{\partial\Omega_v} \frac{\mathcal{F}_w \cdot \mathbf{n}}{p} dA. \quad (6)$$

where \mathcal{F}_h and \mathcal{F}_w are the heating and working fluxes, respectively. If the surface integral in Eq. (5) is replaced and denoted by $\delta Q/T$ and the total entropy in the whole domain is denoted by S , then Eq. (5) takes a global form proposed originally by Clausius:

$$dS \geq \frac{\delta Q}{T}. \quad (7)$$

It follows from the above that the mathematical expression: $dS = dQ/T$ has no physical sense [see for instance 13, page 4]. The equation similar to Eq. (6) has been proposed by Gyftopoulos and Beretta [6], Beretta [38]. The Said Carnot concept of taking the balance of specific volume has turned an attention of Max Born in 1921 [31], and Peter Bridgeman [32]. The role of Eq. (6) within the framework of ideal fluids turned an attention of Eglit [34] and Badur & Banaszkiwicz [35].

It should be remembered that these fluxes are given on heating and moving surfaces through which working fluid transfers heat and work, respectively. However, T and p , in opposite to Clausius' approach, have a clear physical meaning of the thermodynamical temperature and thermodynamical pressure (corresponding to the polish word “prężność”). For a hyperelastic Carnot material, T and p are determined through the following state relation involving internal energy [17]:

$$T = \frac{\partial u}{\partial s} \Big|_{v=\text{const}}, \quad p = \frac{\partial u}{\partial v} \Big|_{s=\text{const}}. \quad (8)$$

It means, according to the Lazar Carnot concept of Aristotelian energy, that internal energy should be a function of “state parameters”: multiplicative or additive. Definitely standing against the additive concept of energy, developed early by Biot and Rumfold, Sadi Carnot has proposed a multiplicative form of the internal energy magazine, e.i. $\varepsilon \sim s \cdot v$; $s^2 \cdot v$ or $s \cdot \ln\left(\frac{v}{v_0}\right)$. Then balancing “working” with “heating” energy, he proposed the following state equation written in terms of energy as: $p(v - b) = R(\theta + 273)$, were b is an internal volume of gas molecules, θ is Celsius temperature and $R = N \cdot k_B$ is the internal contribution of elements of entropy (caloric), with k_B as a quantum of caloric (nowadays: the Boltzmann constant).

Introducing to inequalities (5)–(6) any always positive quantities, the so-called “uncompensated heat and uncompensated work transformations”: σ_s , σ_v , and with the help of the Reynolds transport theorem and the Gauss-Ostrogradski theorem for surface integral, we are able to change Eqs. (5) and (6) into the following equalities having a customary Cartesian form ($i = x, y, z$):

$$\iiint_{\Omega} \left[\frac{\partial}{\partial t} (\rho s^*) + \frac{\partial}{\partial x_i} (\rho s^* v_i) - \frac{\partial}{\partial x_i} \left(\frac{\mathcal{F}_{(h)i}}{T} \right) \right] dV = \iiint_{\Omega} \rho \sigma_s dV, \quad (9)$$

$$\iiint_{\Omega} \left[\frac{\partial}{\partial t} (\rho v^*) + \frac{\partial}{\partial x_i} (\rho v^* v_i) - \frac{\partial}{\partial x_i} \left(\frac{\mathcal{F}_{(w)i}}{p} \right) \right] dV = \iiint_{\Omega} \rho \sigma_v dV. \quad (10)$$

In the above: ρ – mass density, $\mathbf{v} = v_i \mathbf{e}_i$ is the substantial velocity of working fluid. At this point, we are able to introduce the second law of thermodynamics, in a novel form known also as the requirement that “uncompensated heat and work transformation” should be always positive [8], i.e.:

$$\sigma_s \geq 0, \quad \sigma_v \geq 0. \quad (11)$$

Of course, we agree also with a reader that the form of the second principle of thermodynamics is far from being complete, nevertheless, it is on the line of reasoning started by Aristotle and continued by Thomas of Aquine, Leonardo da Vinci and Lazare Carnot. Eq. (10) has been proposed by Mieczysław Mieczysławski [30].

Then, introducing by usual procedures the substantial time derivatives, one can obtain the field equations resulting from Eqs. (9) and (10). After multiplication of Eq. (9) by T and after multiplication of Eq. (10) by p we

obtain:

$$T\rho\sigma_s = Ts^* \left[\frac{\partial\rho}{\partial t} + \operatorname{div}(\rho\mathbf{v}) \right] + T\rho \left(\frac{ds^*}{dt} - \frac{ds}{dt} \right) + T\rho \frac{ds}{dt} - \operatorname{div}(\mathcal{F}_h) + \mathcal{F}_h \cdot \frac{\operatorname{grad} T}{T}, \quad (12)$$

$$p\rho\sigma_v = pv^* \left[\frac{\partial\rho}{\partial t} + \operatorname{div}(\rho\mathbf{v}) \right] + p\rho \left(\frac{dv^*}{dt} - \frac{dv}{dt} \right) + p\rho \frac{dv}{dt} - \operatorname{div}(\mathcal{F}_w) + \mathcal{F}_w \cdot \frac{\operatorname{grad} p}{p}. \quad (13)$$

5 Balance of linear momentum

The balance of momentum in any continuum is a simple continuation of Newton's approach, which is reducing the whole dynamics to the balance of translational momentum known as: $m\mathbf{a} = \mathbf{f}$. Within a dense continuum of particles, the form of Newton's equation is similar, only two elements are changed. The first one is the definition of acceleration vector, which is now: $= \frac{\partial}{\partial t}\mathbf{v} + (\operatorname{grad} \mathbf{v})\mathbf{v}$; this form was established by d'Alembert (in cylindrical coordinates) and by Euler (in arbitrary coordinates). The second one is redefinition of force – in continuum of particles, it is important to add for gravitational part some “particle interaction”: $\operatorname{div} \mathbf{t}$, where $\mathbf{t} = t_{ij}\mathbf{e}_i \otimes \mathbf{e}_j$ is the flux of momentum, which has been introduced by Cauchy, and sometimes called the Cauchy stress (tension) tensor. In fluid continuum, there is no reversible shear component, therefore, momentum flux must always be divided into two parts [3, 31]:

$$\mathbf{t} = -\pi\mathbf{I} + \boldsymbol{\tau}, \quad (14)$$

which are identified with elastic and viscous parts, respectively. Sometimes the viscous tensor is traceless $\operatorname{tr}(\boldsymbol{\tau}) = 0$, then splitting of elastic and viscous properties is complete. Thus, introducing the definition of acceleration into account, and turning the form of balance of momentum into “the conservative form”, one can obtain

$$\frac{\partial}{\partial t}(\rho\mathbf{v}) + \operatorname{div}(\rho\mathbf{v} \otimes \mathbf{v}) = \operatorname{div} \mathbf{t} + \rho\mathbf{b}, \quad (15)$$

where $\rho\mathbf{b}$ is a body force of general kind. By multiplication of Eq. (15) by velocity vector, we get the partial balance of kinetic energy κ . Or in

other words: the scalar property of energy will be related to the momentum only if we do scalar multiplication of momentum balance by the specific momentum \mathbf{v} :

$$\left[\rho \frac{d}{dt} \mathbf{v} = \operatorname{div} \mathbf{t} + \rho \mathbf{b} \right] \cdot \mathbf{v}. \quad (15a)$$

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

$$\rho \mathbf{v} \cdot \frac{d}{dt} \mathbf{v} = \rho \frac{d}{dt} \kappa = \rho \mathbf{v} \cdot \mathbf{b} + \rho \pi \frac{d}{dt} \rho^{-1} + \operatorname{tr}(\boldsymbol{\tau} \mathbf{d}) - \operatorname{div}(-\pi \mathbf{v} + \boldsymbol{\tau} \mathbf{v}). \quad (15b)$$

We read the above equation: the rate of change of kinetic energy depends on the gain of production $\rho \mathbf{v} \cdot \mathbf{b}$ taken from diminished gravitational energy, the amount of energy conversion $\rho \pi \frac{d}{dt} \rho^{-1}$, part of energy dissipation $\operatorname{tr}(\boldsymbol{\tau} \mathbf{d})$ [where $\mathbf{d} = 0.5(\operatorname{grad} \mathbf{v} + \operatorname{grad}^T \mathbf{v})$ is symmetric part of the velocity gradient], and the exchange of energy by a part of mechanical flux $\mathcal{F}_{\text{work}} = -\pi \mathbf{v} + p \mathbf{h}_v + \boldsymbol{\tau} \mathbf{v}$, where p is thermodynamic pressure and π represents co-mechanical pressure due to Gaggioli's concept of internal volume evolution [22]. It means that only in a partial balance of energy we can observe explicitly three manners of energy transformations: expansion, conversion and dissipation¹.

6 Equation of the balance of energy

6.1 Energy flux concept

Discovery of balance of energy which is consistent with the first principle of thermodynamics is not an easy thing. Every new exposition of thermodynamics needs quite new mathematics and a new flexible system of notations. This statement concerns the Carnot continuum too. The modern

¹Looking at the mechanical flux of energy in Eq. (15), yet another fundamental question appears – it is somehow strange splitting of energy fluxes into reversible and irreversible parts: $\vec{\mathcal{F}}_{\text{work}} = \vec{\mathcal{F}}_{\text{work}}^{\text{rev}} + \vec{\mathcal{F}}_{\text{work}}^{\text{irr}}$; $\vec{\mathcal{F}}_{\text{heat}} = \vec{\mathcal{F}}_{\text{heat}}^{\text{rev}} + \vec{\mathcal{F}}_{\text{heat}}^{\text{irr}}$. From Eq. (15) it follows that in the case of mechanical flux of energy such splitting is possible. However, nothing is known on splitting of thermal energy flux. The only case where $\vec{\mathcal{F}}_{\text{heat}}^{\text{rev}}$ appeared in the literature is the Green-Naghdi theory of heat superconducting [21, 22]. Unfortunately, it means that for the classical Navier-Stokes-Fourier model, the entropy based on the reversible flux of thermal energy cannot be defined.

candidate to an expression of energy balance is the Gyftopoulos-Beretta exposition [6, pp. 38, 103, 108]. They consider some abstract system A , which is a system taken in two states A_1, A_2 – in two times moments. Then the balance of energy is

$$E_2 - E_1 = E^{\leftarrow}. \quad (16)$$

In this balance: E^{\leftarrow} denotes the net energy transferred to system A from all the other interacting systems during the process that changes the state of A from A_1 to A_2 . Precisely interpreting the Gyftopoulos-Beretta exposition, we never express a violating 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* neither can be created nor destroyed.

Let us continue this idea – then, the energy transition needs to introduce a concept of energy flux, say: \mathcal{F}_E which is transferring energy in time $\Delta\tau_{1-2}$, as follows: $\mathcal{F}_E\Delta\tau_{1-2} = E^{\leftarrow}$. Beretta and Gyftopoulos have underlined that any amount of energy can be transferred to a system, for instance, by doing electrical work on it, but the availability of this energy depends on how the final state is reached. Usually one can define the “adiabatic availability” [6, Chapter 5] to be if the final state is reached without irreversibility – then the available energy is equal to transferred energy. However, if the final state is reached with irreversibility, this capacity will be smaller than the energy transferred, and may even be equal to zero. According to Kestin [15], it should be clarified that the available energy of a system A is derived from the adiabatic availability – it is a case when the system A interacts by reversible in-flow and out-flow with a reservoir. It practically means that the system A is operating at constant thermodynamic conditions and at a permanent stable equilibrium state.

Gyftopoulos and Beretta [6] denote the energy interaction for all possible energy flow by symbols: E^{\rightarrow} or E^{\leftarrow} depending on the in-flow or 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 exists a single meaningful equivalence for E^{\leftarrow} – it is power: \mathcal{P} [watt = joule per second], which is understood as a rate of energy consumption by any technical devices. We say that devices have more or less power, therefore the balance of energy – being the main manifestation of the first law of thermodynamics – is also interpreted as: the rate of production (or consumption) of energy is governed by power: $\frac{d}{dt}E = \mathcal{P}$. The most convenient and familiar unit of power is watt, which does not mean that this is a rate of making heat or work, since power is a more basic concept

than heat and work. Therefore, heat and work should only be treated as power multiplied by time (for this line of reasoning unit is kWh, however an established unit for the SI system is joule) – this statement is confirmed by the economy that says: “we buy power, but we pay for energy”².

Unfortunately, the word “power” does not indicate a place where the exchange of energy takes place. Therefore, instead of letter E^{\leftarrow} or \mathcal{P} , we propose to introduce another letter \mathcal{F} , which 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 as energy transferred across a boundary of the system, because energy neither can be generated *ex nihilo* nor destroyed in A :

$$E_2^A - E_1^A = \left(\iint_{\partial A} \mathcal{F}_e \cdot \mathbf{n} dS \right) \Delta\tau_{1-2} = \mathcal{F}_E \Delta\tau_{1-2} = E^{\leftarrow}, \quad (17)$$

where: \mathcal{F}_e is the local (3D) form vector of a total flux of energy transferred across the boundary of the system oriented by unit vector \mathbf{n} . Only the normal component of energy flux is important – it defines the net flux of energy \mathcal{F}_E , which mathematically cannot be differentiated by \leftarrow or \rightarrow arrow. It is worth noting that, independently of phenomena under account [described by quaternions, spinors, tensors, multinions, etc.], the flux of energy is always a vector [9, 10, 38].

6.2 Internal energy concept

Sadi Carnot discovered that if a material continuum underlines the heating flux \mathcal{F}_h acting on a continuum surface $\partial\Omega_h$ then “heat can be stored” in the whole continuum in the form of “internal energy”. It means that the operation of storage cannot be direct (one *joule* inflows and one *joule* is stored) and needs some conversion. 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 :

$$E = a_1\mathcal{U} + a_2\mathcal{K} + a_3\Phi. \quad (18)$$

If we adopt the Aristotelian sense of energy, it means that energy taken as a first invariant of general motion [mathematically expressed as a scalar] is

²Truly 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.

additive, not multiplicative. Additivity means that the matter and the fields are separable primary physical objects. This concept known as Aristotelian *hylomorphism* nowadays is interpreted as a primary assumption that the whole universe is created from three basic components: *matter*, *fields* and *quantum vacuum*. It is worth highlighting that kinetic and potential energies in Eq. (18) are external and account for the system, while internal energy is determined by inter-particle kinetic and potential energies. In the universal system of units, the equivalence coefficients are equal to one: $a_1 = a_2 = a_3 = 1$, what means that pioneering Joule's efforts to measure energy equivalence as $\mathcal{J} = \mathcal{U}/\mathcal{K}$ was baseless.

Another key notion in the Gyftopoulos-Beretta approach is "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. Does not exist conversion of heat into work and vice versa – work into heat, since both work and heat are only a comfortable manner of expressing the net amount of energy conversion during a single process, where a net change of E disappears.

Let us mark the finite elementary volume by the sign dV , and the whole volume of thermodynamic system A by letter Ω . The system A interacts with the external environment by the processes acting at the system boundary $\partial\Omega$. The internal, kinetic and potential energy can be denoted by U , K , and Φ , respectively, and besides the integral quantities, there are some quantities related to the unit of mass, such as:

$$\text{Internal energy} \quad \mathcal{U} = \iiint_{\Omega} \rho \varepsilon dV, \quad (19)$$

$$\text{Kinetic energy} \quad \mathcal{K} = \iiint_{\Omega} \frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} dV = \iiint_{\Omega} \rho \kappa dV, \quad (20)$$

$$\text{Potential energy} \quad \mathcal{\Phi} = \iiint_{\Omega} \rho \phi dV. \quad (21)$$

The actual volume Ω is related to the Euler description. Therefore, in arbitrary 3D description, ρ is density, ϕ is specific potential energy and ε represents specific internal energy. Following Gibbs, the specific internal energy [J/kg] related to the unit mass can be denoted by ε . The quantity $\rho\varepsilon$ is volumetric energy density related to actual volume.

Yet, the most restrictive assumption concerning internal energy should be taken into consideration. It must be a function of intensive state parameters. In our case, we have two intensive state parameters: v , s , thus, the

energy is stored in the Carnot continuum only as: $\varepsilon = \varepsilon(s, v)$. How much energy can be stored in one kilogram of mass? It will be reasonable to assume that there exists some limit value: $\varepsilon^{\text{crit}}$ that can never be exceeded. The first in the literature concise model of “critical energy”, known also as “energy hypothesis”, was established by Eugenio Beltrami (1885) and rediscovered by Tytus Huber (1904) and Włodzimierz Burzyński (1928) [5].

6.3 Splitting of the energy flux

Returning to energy total flux in Eq. (17), we next assume that the energy fluxes are additive. It allows us to formulate the total energy flux as the sum of processes:

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

where, respectively, appear: working, heating, chemical, electric and magnetic energy fluxes. It was R.A. Gaggioli who first proposed to denote various energy fluxes by one common letter [23] – a single letter “ I_E ”, which has a rather weak connotation with 3D formulation, therefore we propose to replace the Gaggioli notation with a more concise denotation by the letter “ \mathcal{F} ”. Precisely, Gaggioli has proposed $I_E = pI_V$ for volume energy flux and $I_E = TI_\theta$ for thermal energy flux (we propose: $\mathcal{F}_h = Th_s$ and $\mathcal{F}_w = p\mathbf{h}_v$, respectively).

Let us note that Professor Gaggioli introduced the entropy flux density concept (our \mathbf{h}_s) in a quite different manner than Eckart (1940) who proposed it in 3D formulation [23]. For Gaggioli, \mathbf{h}_s should be a rate of some “thermal charge” transfer. Up to now, no one is familiar with the notion of “thermal charge” – we are familiar only with an “entropy charge” discovered by Boltzmann as the constant $k_B = 1.38 \cdot 10^{-23}$ J/K. The introduction of k_B , called by Boltzmann “the entropy element”, is according to Ladislavus Natanson, the absolute beginning of the science of “Quantum Thermodynamics” [27]. Therefore, temperature T in Th_s plays a role of energy scale multiplayer, quite similar to pressure in I_V (our \mathbf{h}_v). It should also be added that, for example, F_{heat} means heat transferred rate, traditionally denoted by: \dot{Q} , in watts [W]. This total F_{heat} relates to heat flux surface density \mathcal{F}_h , commonly expressed as vector \mathbf{q} [W/m²], by integrating the flux over the surface of the system. Therefore, overwriting the dot in \dot{Q} is baseless.

The mathematical sum of scalars, presented in Eq. (22) can be treated as universal one – three dots mean that there is a place for new, yet unknown processes. There is a lack of radiative flux, described by the Pointing energy

vector (1899), because it is indirectly related to the system substantial boundary. If the substantial boundary $\partial\Omega$ is oriented outside by the normal unit vector \mathbf{n} , that allows us to write the energy flux as a normal component of the total energy vector:

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

Two first energy fluxes are very well known in literature: $\mathcal{F}_{\text{work}}$ is a mechanical energy flux of Umov (1874) and Volterra (1899), and $\mathcal{F}_{\text{heat}}$ is a heating energy flux of Rankine (1851) and Stokes (1851). Notice that, in practice, the radiation energy flux is localized on a surface, and approximated via the Stefan-Boltzmann radiation flux: $\mathcal{F}_{\text{rad}} = \mathcal{F}_{\text{rad}} \cdot \mathbf{n} = \sigma (T_{\text{surf}})^4 \text{ W/m}^2$, where $\sigma = 5.67 \cdot 10^{-8} \text{ W/m}^2\text{K}^4$ is the Stefan-Boltzmann constant. For instance, the radiation on the earth is: $\mathcal{F}_{\text{rad}} = 1418 \text{ W/m}^2$ (4 January, night) or $\mathcal{F}_{\text{rad}} = 1325 \text{ W/m}^2$ (4 June, day).

6.4 Where do energy fluxes come from?

The essence of the proper definition for the various fluxes is to find a correct relationship of the energy flux to the other fluxes, like: momentum, angular momentum, mass, volume, entropy, electricity, etc. If the 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 fluxes of the mechanical energy and heating energy can be expressed by a relatively simple combination of the momentum flux tensor \mathbf{t} the volume flux vector \mathbf{h}_v and entropy flux vector \mathbf{h}_s to be [21, 22, 35]:

$$\mathcal{F}_{\text{work}} = \mathbf{t}\mathbf{v} + p\mathbf{h}_v + \mathcal{F}_{\text{work}}^{\text{int}}, \quad \mathcal{F}_{\text{heat}} = T\mathbf{h}_s + \mathcal{F}_{\text{heat}}^{\text{int}}, \quad (24)$$

where \mathbf{v} is the velocity vector of the substance, p is the pressure and T is the absolute temperature. Additionally, some energy fluxes: $\mathcal{F}_{\text{work}}^{\text{int}}$, $\mathcal{F}_{\text{heat}}^{\text{int}}$ appear in the above definitions – these are called “the interstitial working” and “the interstitial heating” vectors, and are related to gradient or higher-order models of working continua, presented also in articles [21, 23, 24]. In the case of electrodynamical field energy, there exists the Poynting radiation energy flux defined as $\mathcal{F}_{\text{em}} = \mathbf{E} \times \mathbf{H}$. The chemical flux of energy is usually defined as [30]: $\mathcal{F}_{\text{chem}} = \mu\mathbf{h}_\mu$, however, the electric energy flux is [17, pp. 70–72]: $\mathcal{F}_{\text{elec}} = z\mathbf{i}$, where $z = c_e z_e$ is a general electric potential and $\mathbf{i} = q\mathbf{E}$ – electric current. To sum up, the energy flux vectors are strictly related to

the model of continua and should rather be postulated as some additional “consistency relations”.

In the present paper, we restrict our discussion only to two fluxes: $\mathcal{F}_{\text{heat}} \equiv \mathcal{F}_h = T\mathbf{h}_s$ and $\mathcal{F}_{\text{work}} \equiv \mathcal{F}_m + \mathcal{F}_w \equiv \mathbf{t}\mathbf{v} + p\mathbf{h}_v$.

6.5 Conservative and substantial form of balance

We now postulate a balance of total energy for an arbitrary material volume occupying a part Ω in the present configuration and rewrite it into the so-called *integrated form*:

$$\frac{d}{dt} \iiint_{\Omega} \rho(\varepsilon + \kappa + \phi) dV = \iint_{\partial\Omega} \mathcal{F}_e \cdot \mathbf{n} dA + \mathcal{S}_e. \quad (25)$$

The storages of energy ($\varepsilon + \kappa + \phi$) are defined above as in Eqs. (19)–(21); the flux of energy is equal to: $\mathcal{F}_e \equiv \mathcal{F}_m + \mathcal{F}_w + \mathcal{F}_h$ and the energy source is

$$\mathcal{S}_e = \iiint_{\Omega} (\rho T \sigma_s + \rho p \sigma_v) dV = \iiint_{\Omega} \rho \mathcal{s}_e dV. \quad (26)$$

Then, the local conservative form of Eq. (26) is

$$\begin{aligned} \frac{\partial}{\partial t} [\rho(\varepsilon + \kappa + \phi)] + \text{div} [\rho(\varepsilon + \kappa + \phi)\mathbf{v}] &= \text{div} (\mathcal{F}_m + \mathcal{F}_w + \mathcal{F}_h) \\ &+ (\rho T \sigma_s + \rho p \sigma_v). \end{aligned} \quad (27)$$

Since the Gibbs equation of evolution of internal energy is described in terms of the “objective” substantial time derivative, we rewrite Eq. (27) into a more consistent form

$$\begin{aligned} \iiint_{\Omega} [(\varepsilon + \kappa + \phi)(\dot{\rho} + \rho \text{div} \mathbf{v})] + \rho (\dot{\varepsilon} + \dot{\kappa} + \dot{\phi}) \\ = \text{div} (\mathcal{F}_m + \mathcal{F}_w + \mathcal{F}_h) + \rho \mathcal{s}_e] dV. \end{aligned} \quad (28)$$

Assuming that geometric continuity is always fulfilled: $\dot{\rho} + \rho \text{div} \mathbf{v} = 0$, it must be underlined that this equation is always true, regardless if the set of governing equations (that is, equations for mass, momentum, moment of momentum, volume and entropy balances) is satisfied or not. It will now be shown that, if the fields and variables of state satisfy conditions laid on by governing equations, the equation of energy receives a very important

form allowing for further restrictions to describe fields – it means that even though the solutions may satisfy conservation equations for mass, momentum, volume and entropy, they do not need to satisfy conservation equation for energy, and in consequence lead to generating energy *ex nihilo* [26, 32].

Therefore, we can formulate the strong form of the first principle of thermodynamics, which stands as

$$\text{Energy cannot be created ex nihilo: } \mathcal{S}_e = 0. \quad (29)$$

6.6 An energy justification procedure

Equation (28) represents a local (continuum) form of postulated by Gyftopoulos-Beretta form of energy balance given through Eq. (16). Now we want to present some “energy justification procedure” (EJP) whose aim is to evaluate the correctness of the set of governing equations and to give primary conditions for fulfilment of the first and second law of thermodynamics.

What is the physical meaning of Eq. (28)? To explain the role of energy as a “first invariant of the Aristotelian motion” let us remove from Eq. (28) the substantial objective rates $\dot{\phi}$ and $\dot{\kappa}$. Note that the evolution of potential energy is given as: $\dot{\phi} = \frac{d}{dt}\phi = \frac{\partial\phi}{\partial\mathbf{x}} \cdot \frac{d\mathbf{x}}{dt} = \mathbf{b} \cdot \dot{\mathbf{x}} = \mathbf{b} \cdot \mathbf{v}$, and the substantial derivative of kinetic energy $\rho \frac{d}{dt}\kappa = \rho \dot{\kappa} = \rho \mathbf{b} \cdot \mathbf{v} + (\text{div } \mathbf{t}) \cdot \mathbf{v} = \rho \mathbf{b} \cdot \mathbf{v} + \text{tr}(\mathbf{t} \mathbf{d}) - \text{div}(\mathbf{t} \mathbf{v})$ (15b) may be stated in a new form without the substantial derivative of ϕ and κ :

$$\iiint_{\Omega} [\rho \dot{\varepsilon} - (\text{div } \mathbf{t} + \rho \mathbf{b} - \rho \dot{\mathbf{v}}) \cdot \mathbf{v} - \text{tr}(\mathbf{t} \mathbf{d}) + \text{div}(\mathcal{F}_w + \mathcal{F}_h)] dV, \quad (30)$$

where the following identity occurs: $\text{div}(\mathbf{t} \mathbf{v}) = (\text{div } \mathbf{t}) \cdot \mathbf{v} + \text{tr}(\mathbf{t} \text{grad } \mathbf{v})$. According to the well-accepted tradition, the velocity gradient, which is $\mathbf{l} = \text{grad } \mathbf{v}$, can be decomposed into symmetric and anti-symmetric parts: $\mathbf{l} = \mathbf{d} + \mathbf{w}$. Since the moment of momentum of continua is fulfilled and the flux of momentum is symmetric $\mathbf{t} = \mathbf{t}^T$, then $\text{tr}(\mathbf{t} \text{grad } \mathbf{v}) = \text{tr}(\mathbf{t} \mathbf{d})$.

Taking the following identities: $\text{div}(\mathbf{h}_s T) = T \text{div } \mathbf{h}_s + \mathbf{h}_s \cdot \text{grad } T$ and $\text{div}(\mathbf{h}_v p) = p \text{div } \mathbf{h}_v + \mathbf{h}_v \cdot \text{grad } p$, with $\mathbf{g}_s = \text{grad } T$; $\mathbf{g}_v = \text{grad } p$, and next, through addition and subtraction of $\mp T(\rho \dot{s} - \rho \sigma_s)$ and $\mp p(\rho \dot{v} - \rho \sigma_v)$, the

integral equation (30) becomes:

$$\iiint_{\Omega} \left\{ \begin{array}{l} \rho \dot{\varepsilon} - (\text{div}] \mathbf{t} + \rho \mathbf{b} - \rho \dot{v}) \cdot \mathbf{v} - (\text{div} \mathbf{h}_s + \rho \sigma_s - \rho \dot{s}) T \\ - (\text{div} \mathbf{h}_v + \rho \sigma_v - \rho \dot{v}) p - (\varepsilon + \kappa + \phi) (\dot{\rho} + \rho \text{div} \mathbf{v}) \\ + T (\rho \dot{s} - \rho \sigma_s) + p (\rho \dot{v} - \rho \sigma_v) - \mathbf{h}_s \cdot \mathbf{g}_s \\ - \mathbf{h}_v \cdot \mathbf{g}_v - \text{tr}(\mathbf{t} \mathbf{d}) = 0 \end{array} \right\} dV. \quad (31)$$

Now us let introduce some assumption within the concept of volume balance – according to the physical statement that part of gas volume is occupied by the internal volume of molecules. Then, the following splitting of the volume flux is possible and motivated:

$$\mathbf{h}_v = \alpha \mathbf{v} + \mathbf{h}'_v, \quad (32)$$

where $\alpha \mathbf{v}$ can be called the “volume velocity” and

$$\alpha = \frac{p \text{div}(\mathbf{v})}{\|\mathbf{v}^2\| \|\text{grad} p\|} \quad (33)$$

is the so-called volume-slip coefficient. In Eq. (31), the parts, expressing the balance of mass, momentum, volume and entropy, respectively, are to be fulfilled identically if a set of governing equations is simultaneously solved. By introducing Eq. (32) and $\mathbf{t}' = -(\pi - p)\mathbf{I} + \tau$ into Eq. (31) we are able to reformulate of total momentum flux to be:

$$\iiint_{\Omega} \left[\rho \dot{\varepsilon} + T (\rho \dot{s} - \rho \sigma_s) + p (\rho \dot{v} - \rho \sigma_v) - \mathbf{h}_s \cdot \mathbf{g}_s - \mathbf{h}'_v \cdot \mathbf{g}_v - \text{tr}(\mathbf{t}' \mathbf{d}) \right] dV = 0. \quad (34)$$

Even if a thermo-elastic Carnot fluid is expressed via scalar state variables vs , which is a much simpler situation than in the Carnot solids [20], the mechanism of the internal energy storage is more complex, since one observes the multiplicative, not additive, contribution to $\varepsilon = \varepsilon(s, v)$. The material (objective) time rate of internal energy is: $\dot{\varepsilon} = \frac{\partial \varepsilon}{\partial s} \dot{s} + \frac{\partial \varepsilon}{\partial v} \dot{v}$. Therefore, by expressing the material derivative of the internal energy, we obtain:

$$\iiint_{\Omega} \left\{ \left\{ \rho \left(\frac{\partial \varepsilon}{\partial v} - p \right) \dot{v} + \rho \left(\frac{\partial \varepsilon}{\partial s} - T \right) \dot{s} + \rho T \sigma_s + \rho p \sigma_v - \mathbf{h}_s \cdot \mathbf{g}_s - \mathbf{h}'_v \cdot \mathbf{g}_v - \text{tr}(\mathbf{t}' \mathbf{d}) \right\} \right\} dV = 0. \quad (35)$$

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 state³:

$$p = \frac{\partial \varepsilon}{\partial v}, \quad T = \frac{\partial \varepsilon}{\partial s}. \quad (36)$$

These two constitutive relations are fundamental for proving that the balance of total energy can be fulfilled in any processes governed by the balance of mass, momentum, moment of momentum, volume and entropy. In the case of ideal gas, the internal energy depends on two constitutive coefficients – c_v and c_p – the specific heat at constant volume and pressure, respectively. From this pair; c_v , c_p , one can obtain another pair – Carnot’s (1824): $R = c_p - c_v$ and Poisson’s (1831): $\gamma = \frac{c_p}{c_v}$ [34, 35]:

Finally, after removing from Eq. (35) the reversible elastic state parameter definitions and after expressing the production of entropy and volume in terms of Eqs. (12)–(13), we obtain the remaining part of the balance of energy as

$$S_e = \iiint_{\Omega} \{\rho T \sigma_s + \rho p \sigma_v - \Phi\} dV = 0 \quad (37)$$

and the non-equilibrium sources expressed by Eqs. (12) and (13); few parts in the balance of energy can be excluded and the remaining part of that balance contains this energy that is dissipated. According to Rayleigh, we will call it a dissipated energy and denote it by Φ :

$$\begin{aligned} \Phi = & \rho p \left(\frac{dv^*}{dt} - \frac{dv}{dt} \right) + T \rho \left(\frac{ds^*}{dt} - \frac{ds}{dt} \right) + \mathbf{h}'_v \cdot \mathbf{g}_v + \mathbf{h}_s \cdot \mathbf{g}_s \\ & + \text{tr}(\boldsymbol{\tau} \mathbf{d}) + (\pi - p) \text{div} \mathbf{v}. \end{aligned} \quad (38)$$

Then, the requirement that the energy equation be identically satisfied leads to the inequality relating dissipative “forces” and “fluxes”. By setting

$$\frac{d}{dt} v^* = \frac{d}{dt} v + \frac{1}{2} \left(2B_{\alpha\beta} \xi_a \dot{\xi}_\beta + \frac{\partial B_{\alpha\beta}}{\partial s} \xi_\alpha \xi_\beta \dot{s} + \frac{\partial B_{\alpha\beta}}{\partial v} \xi_\alpha \xi_\beta \dot{v} \right), \quad (39)$$

³Additionally, the internal energy cannot be an arbitrary function of intensive variables of state. In accordance with the Principle of Energy Conversion, it has to satisfy a supplementary condition: it is required that the actual state 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): $\frac{\partial}{\partial v} \left(\frac{\partial \varepsilon}{\partial s} \right) = \frac{\partial}{\partial s} \left(\frac{\partial \varepsilon}{\partial v} \right)$. This equation has been extended by Kirchhoff (1858) to chemical state variables and Gibbs (1878) to electrical state variables. Finally, Maxwell (1871) wrote it to be: $\varepsilon_{,\alpha\beta} = \varepsilon_{,\beta\alpha}$.

$$\frac{d}{dt}s^* = \frac{d}{dt}s + \frac{1}{2} \left(2A_{\alpha\beta}\xi_\alpha\dot{\xi}_\beta + \frac{\partial A_{\alpha\beta}}{\partial s}\xi_\alpha\xi_\beta\dot{s} + \frac{\partial A_{\alpha\beta}}{\partial v}\xi_\alpha\xi_\beta\dot{v} \right), \quad (40)$$

and rejecting the infinitely small quantities of the third order, we finally obtain an expression for the dissipating energy:

$$\begin{aligned} \Phi = & \tau_{ij}d_{ij} + (\pi - p)(v_{i,i}) + \mathbf{F}_w \cdot \frac{\text{grad } p}{p} + \mathbf{F}_h \cdot \frac{\text{grad } T}{T} \\ & + (TA_{\alpha\beta} + pB_{\alpha\beta})\rho\xi_\alpha\dot{\xi}_\beta \geq 0. \end{aligned} \quad (41)$$

In the above formula for the case of inviscid, non-conductive fluid, the first three parts vanish identically, and dissipative phenomena reduce only to relaxation $s^* \rightarrow s$ and $v^* \rightarrow v$.

7 The neo-classical constitutive relations

Equation (40) resulting from the balance of energy will be regarded as an identity for every choice of the state parameters. It, in our approach, represents one global restriction concerning the form of constitutive equations.

It should be emphasised that so far no mention has been made of restrictions of constitutive equations, which usually in LIT arise from some form of the second law of thermodynamics understood as *entropy inequality* ($dS = d_iS + d_eS$ [28, 29]). In fact, the above inequality can be fulfilled by taking the energy dissipative potential:

$$\begin{aligned} \varpi(\mathbf{g}_s, \mathbf{g}_v, \dot{\xi}_\alpha, \mathbf{d}) = & \frac{1}{2}k_s\mathbf{g}_s\mathbf{g}_s + \frac{1}{2}k_v\mathbf{g}_v\mathbf{g}_v + \mu\text{tr}(\mathbf{d}\mathbf{d}) \\ & + \left(\frac{2}{3}\mu - \lambda'\right)(\text{tr}\mathbf{d})^2 + \frac{1}{2}N_{\alpha\beta}\dot{\xi}_\alpha\dot{\xi}_\beta + L_\alpha\dot{\xi}_\alpha\text{tr}(\mathbf{d}), \end{aligned} \quad (42)$$

which leads to linear Onsager-type constitutive relations:

$$\boldsymbol{\tau} = \frac{\partial\varpi}{\partial\mathbf{d}} = 2\mu\mathbf{d} + \frac{2}{3}\mu(\text{tr}\mathbf{d})\mathbf{I}, \quad (43)$$

$$\pi - p = \frac{\partial\varpi}{\partial\mathbf{d}} = \lambda'\text{tr}\mathbf{d} + L_\alpha\dot{\xi}_\alpha, \quad (44)$$

$$\mathbf{h}_s = \frac{\partial\varpi}{\partial\mathbf{g}_s} = k_s\mathbf{g}_s, \quad \mathbf{h}'_v = \frac{\partial\varpi}{\partial\mathbf{g}_v} = k_v\mathbf{g}_v, \quad (45)$$

$$\xi_\alpha = \frac{\partial\varpi}{\partial\dot{\xi}_\alpha} = N_{\alpha\beta}\dot{\xi}_\beta + L_\alpha(\text{tr}\mathbf{d}), \quad (46)$$

in which, according to the second Onsager postulate $N_{\alpha\beta} = N_{\beta\alpha}$, and the following conditions should be satisfied:

$$N_{\alpha\alpha} > 0, \quad 2\mu + \lambda' \geq 0, \quad (2\mu + \lambda')^2 \geq 0, \quad k_s \geq 0, \quad k_v \geq 0, \quad (47)$$

$$(2\mu + \lambda') N_{\alpha\alpha} - L_\alpha^2 \geq 0, \quad (48)$$

$$2[(2\mu + \lambda') N_{\alpha\alpha}]^{\frac{1}{2}} > 2|L_\alpha|, \quad \alpha = 1, 2, 3, \dots, n.$$

In the above constitutive relations: k_s means an entropy diffusion coefficient connected with the Fourier conductivity coefficient, k_v is the volume diffusion coefficient (say: the Brenner coefficient), μ and λ' are the Stokes shape and volumetric viscosity coefficients and $N_{\alpha\beta}$; L_α are nonequilibrium Maldenstam-Leontonovich diffusion coefficients. Let us note, in addition, that these coefficients must not be constant, but may depend on the parameters of the state of equilibrium.

8 The set of governing equations

Having for disposal the postulated balance of non-equilibrium state parameters in Eqs. (9) and (10), and knowing postulated relations between non-equilibrium and equilibrium state parameters (17) and (16), one can establish a final set of governing equations closed by the constitutive relations (43)–(46) and the caloric (recoverable, elastic) state relation (36). Let us note, that in a proposed final set of governing equations, the balance of energy (25) does not appear because it is identically fulfilled by the appropriate and consistent statement of the first and second law of thermodynamics.

The set of governing equations of the Carnot continuum with non-equilibrium state parameters is to be defined as follows:

a) *Balance of working fluid mass*

$$\frac{1}{\rho} = v + \left(1 + \frac{\pi - p}{p}\right) B_{\alpha\beta} \xi_\alpha \xi_\beta, \quad (49)$$

b) *Balance of working fluid momentum*

$$\frac{\partial}{\partial t} (\rho v_i) + \frac{\partial}{\partial x_j} (\rho v_i v_j + \pi \delta_{ij}) = \frac{\partial}{\partial x_j} \tau_{ij} + \rho b_i, \quad i, j = x, y, z, \quad (50)$$

c) *Balance of specific non-equilibrium entropy*

$$\frac{\partial}{\partial t} (\rho s^*) + \frac{\partial}{\partial x_j} (\rho s^* v_j) = \frac{\partial}{\partial x_j} h_{(s)j} + \rho \sigma_s, \quad (51)$$

d) *Balance of specific non-equilibrium volume*

$$\frac{\partial}{\partial t} (\rho v^*) + \frac{\partial}{\partial x_j} (\rho v^* v_j) = \frac{\partial}{\partial x_j} h_{(v)j} + \rho \sigma_v. \quad (52)$$

In the above, it is assumed that the continuity equation is fulfilled from the beginning, and the definition (49) is so exact that one may not use the mass continuity explicitly. Now, the constitutive relations are defined by Eqs. (43)–(46) and (36), respectively. Basic unknown fields are: *velocity* $\mathbf{v}(\mathbf{x}, t)$, *specific equilibrium volume* $v(\mathbf{x}, t)$, *specific equilibrium entropy* $s(\mathbf{x}, t)$ and the *non-equilibrium parameters* ξ_α . The number of governing equations and the number of unknowns is $1 + 3 + 1 + n = 5 + n$, no matter whether we describe viscous or inviscid fluid, conductive or non-conductive fluid. In this approach, temperature appears only as the thermodynamical temperature (36), therefore, putting thermal boundary conditions it must be remembered that a measurable temperature differs from the thermodynamical one.

For the above set of equations, the boundary conditions should be described as follows:

- a) *Known velocity vector at the boundary* $C_v: \mathbf{v}|_{C_v} = \mathbf{v}^0$,
- b) *Known value of measurable pressure at the boundary* $C_\pi: \pi|_{C_\pi} = \pi^0$,
- c) *Known value of thermodynamic temperature at the boundary* $C_T: T|_{C_T} = T^0$ and the thermodynamic pressure $p|_{C_T} = p^0$,
- d) *Known value of volume flux and entropy flux at the boundary* $C_h: \mathbf{h}_v \cdot \mathbf{n} = h_v^0$ and $\mathbf{h}_s \cdot \mathbf{n} = h_s^0$,
- e) *“Incipient point” for constitutive equation (46) for determination of a point and a moment of activation and passivation of this constitutive relation for the internal parameters.*

Boundary conditions a) and b) are related to the linear momentum equation, conditions c) and d) are related to the balance of entropy and balance of volume.

9 Further remarks on the concept of “non-equilibrium heat” and “non-equilibrium work”

The approach presented above is not the first solution to the problem. Other concepts, mainly based on the statement of non-equilibrium temperature and non-equilibrium pressure, are presented in the monographs of Kjelstrup and Bedeaux [7], Sieniutycz [17], Lebon *et al.* [28] and Ván [39]. However, within the ideal gas model and the timeless formulation close to the Carnot working continuum model, there are no original formulations that would lead directly to the foundations of finite-time thermodynamics [8].

In other words, within the framework of the approach known in the literature as the timeless approach, there is no clarity which of the models proposed in the literature is an important extension of Carnot’s reversible approach to the non-equilibrium case.

In addition to non-equilibrium temperature, non-equilibrium pressure, non-equilibrium entropy, and non-equilibrium temperature, there are also solutions in the literature with “non-equilibrium heat flux” and “non-equilibrium work flux”. Let us now discuss this last proposal from a timeless perspective. In this view, the first law of thermodynamics has the classical form of Clausius: $E = \delta Q - A\delta W$, where the Clausius equivalent today has a value of one: $A = 1$, and dE is an increment of internal energy, δQ is the heat gain and δW is increment of work. This corresponds to our $\frac{d}{dt}E = \mathcal{F}_{\text{heat}} + \mathcal{F}_{\text{work}}$.

In 1976, Kestin proposed to divide the heat flux into two parts: a non-equilibrium and an equilibrium one [33]. Using similar arguments, Gujrati in 2011 proposed dividing the work flux into two parts: equilibrium and non-equilibrium [41]. According to this concept, you can write (Fig. 2):

$$\delta Q = d_{\text{irr}}Q + d_{\text{eq}}Q, \quad \delta W = d_{\text{irr}}W + d_{\text{eq}}W. \quad (53)$$

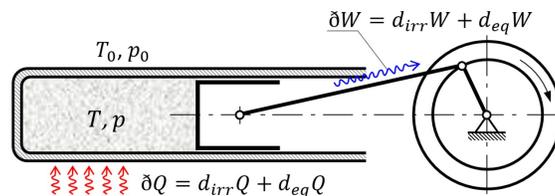


Figure 2: Separation of fluxes into equilibrium and non-equilibrium parts.

Integral values of state parameters are determined by equilibrium quantities: intensive S , V and extensive: T , p . According to Kestin, the reversible part of heating flux defines equilibrium entropy $dS = d_{\text{eq}}Q/T$ and according to Gujrati, the equilibrium part of the working flux defines the equilibrium volume $dV = d_{\text{eq}}W/p$. Using these definitions, we have the first law of thermodynamics in the form

$$\begin{aligned} dE &= \delta Q - A\delta W = d_{\text{irr}}Q + d_{\text{eq}}Q - (d_{\text{irr}}W + d_{\text{eq}}W) \\ &= TdS - pdV + (d_{\text{irr}}Q - d_{\text{irr}}W) = TdS - pdV. \end{aligned} \quad (54)$$

Gujrati notes that the non-equilibrium parts of work and heat fluxes must compensate for each other so that [41, Eq. (4)]

$$(d_{\text{irr}}Q - d_{\text{irr}}W) = 0. \quad (55)$$

This condition strongly limits the magnitude of the fluxes, and it is a reason that the first law of thermodynamics finally becomes equivalent to the Gibbs equation. It is an unacceptable paradoxical result. If we use an uncompensated heat $\mathcal{N}_{\text{heat}} = \oint d_{\text{irr}}S$ and an uncompensated work: $\mathcal{N}_{\text{work}} = \oint d_{\text{irr}}V$, then from Eq. (55) it follows that: $\mathcal{N}_{\text{heat}} = \mathcal{N}_{\text{work}}$.

Therefore, the approach presented in Section 4 is of a different kind; it assumes that uncompensated heat σ_s and uncompensated work σ_v are to be field sources, not surface ones. Similarly, energy fluxes are conceived, which act as surface quantities that cannot be divided into reversible and irreversible parts. For example, heat energy flux is a function of the temperature gradient $\mathbf{g}_s = \text{grad}T$. It can be divided when the temperature for instance is divisible: $T = T_{\text{eq}} + T_{\text{irr}}$. As you can see from the above, this approach spoils the concept of accompanying state and removes the possibility of developing 3D foundations for finite-time thermodynamics.

10 Concept of non-equilibrium energy

The concept of internal energy was finally introduced into thermodynamics by Gibbs in 1873. Internal energy has been defined as an invariant of motion expressed by state parameters. In the case of Carnot's working medium, these parameters were specific volume and specific entropy. Gibbs was the first to find the function $\varepsilon = \varepsilon(v, s)$ and to draw it as a surface in the space of state functions. Delighted by this fact, Maxwell made a plaster model of this surface in a wide range of values of state parameters, i.e.

for water, steam and ice. This surface was learned to be determined by experimentators – first for water and later for other gases and liquids.

It is difficult to imagine anything that would be a “non-equilibrium internal energy”. Nevertheless, as of recently, Gian Paolo Beretta, standing in the position of quantum thermodynamics, believes that it is possible to define non-equilibrium internal energy as a function of non-equilibrium, independent, state parameters: $\varepsilon^* = \varepsilon^*(\gamma_1, \gamma_2, \gamma_3, \dots)$ [38]. To ensure “full flexibility of formulation”, Beretta introduces a new law of thermodynamics, which he nominates to the position of the “fourth law of thermodynamics”.

In other words, Beretta states that this fourth principle is needed to introduce and motivate the concept of non-equilibrium internal energy. What is characteristic of Beretta’s formulation is that he does not consider specific entropy as a basic (non-eliminable) parameter of the state, but expresses it through the experimentally unknown function $s^* = s^*(\gamma_1, \gamma_2, \gamma_3, \dots)$. Contrary to the fundamental definition of Carnot, Reech, Rankine, Maxwell, the internal energy in Beretta’s view is not a direct function of specific entropy.

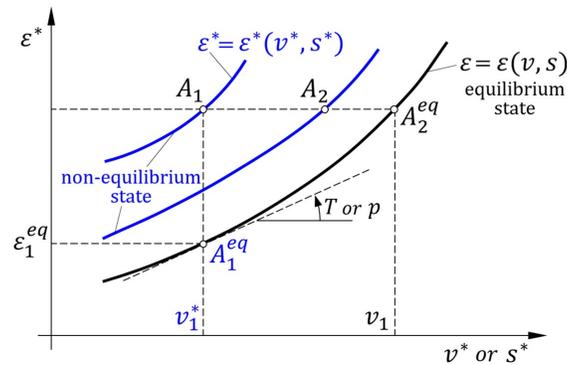


Figure 3: State representation of the non-equilibrium energy.

Note, that proposed by Beretta the evolution equations for non-equilibrium state parameters $\gamma_1, \gamma_2, \gamma_3, \dots$ have a form equivalent to our evolutionary equations v^*, s^* – see Eqs. (51)–(52). In Beretta’s equations, fluxes of non-equilibrium state parameters also appeared. They are marked by him by the letter \mathbf{J}_γ . They have the same status as our $\mathbf{h}_v, \mathbf{h}_s$ vectors, and they have nothing to do with the “thermodynamic fluxes” of LIT. According to Beretta, \mathbf{J}_γ fluxes are subjected to various constraints, for example, the fluxes of state parameters should satisfy symmetry conditions similar to

the Onsager symmetry condition supposed on “thermodynamic fluxes”. The essence of Beretta’s proposal is the introduction of a metric G_γ field and an intrinsic dissipation time τ_γ , which span over the non-equilibrium space of energy at the point of contact. This metric and time allow the evolution of the non-equilibrium state to the optimal equilibrium state according to the fourth law of thermodynamics (SEA).

In conclusion, Beretta’s concept goes further than our assumption about the possible evolution of non-equilibrium state parameters. His concept assumes the existence of a non-equilibrium energy spanning over a tangent space that has its own Riemannian metric and “intrinsic time”.

However, in thermodynamical practice, there are no numerous connotations with the notion of “non-equilibrium internal energy” in the literature. Casas-Vázquez and Jou [37] have extensively discussed this problem, and they remark that in practice the internal energy cannot be a function of non-equilibrium state parameter.

11 The case of a solid

A solid continuum, like heat resistance steels [5], can be as good a working medium as liquids and gases. For heat engines, alloys that have high hidden heat of phase transition, e.g. austenite-martensite [42], are frequently used and the Carnot cycle has also four transformations.

In a solid body, state parameters and internal energy can also be successfully defined. The intrinsic energy of a solid state was first proposed by de Saint Venant and later by Poisson [42]. It has been called: “storage energy” and was a function of a generalized change in the specific volume of deformation and a generalized change in specific entropy. Both of these state parameters are denoted today by: $\mathbf{v} = v_{ij}\mathbf{e}_i \otimes \mathbf{e}_j$ and $\mathbf{s} = s_{ij}\mathbf{e}_i \otimes \mathbf{e}_j$, respectively. From a mathematical point of view, these are tensors; let us also assume that they are symmetric objects. Specific internal energy is therefore a function of both: $\varepsilon = \varepsilon(\mathbf{v}, \mathbf{s})$. For isotropic materials, the internal energy is a function of the invariants of both tensors [5]. If we accept Kirchhoff’s assumption that the entropy tensor is simplified to be a spherical tensor, it is enough to use the entropy scalar $s = \frac{1}{3}\text{tr}(\mathbf{s})$.

The equations of evolution of state parameters have a structure similar to our Eqs. (9)–(10):

$$\rho \overbrace{\mathbf{v}}^{\Delta} = \text{div } \mathbf{h}_v + \rho \mathbf{n}_v, \quad \rho \overbrace{\mathbf{s}}^{\Delta} = \text{div } \mathbf{h}_s + \rho \mathbf{n}_s, \quad (56)$$

where $\mathbf{h}_v = h_{ijk}^v \mathbf{e}_i \otimes \mathbf{e}_j \otimes \mathbf{e}_k$, $\mathbf{h}_s = h_{ijk}^s \mathbf{e}_i \otimes \mathbf{e}_j \otimes \mathbf{e}_k$, are the volume and entropy fluxes, and \mathbf{n}_v , \mathbf{n}_s are the uncompensated transformation of work and heat, in analogy to σ_v and σ_s in Eqs. (9)–(10).

Due to the fact that we deal with tensors, not with scalars, additional elements appear. The \mathbf{h}_v , \mathbf{h}_s fluxes are third-order tensors, and their evolution is subjected to the Zaremba principle of relativity and must use an objective time derivative [5, 20]. Additionally, the Gibbs equation now has an objective form:

$$\frac{d}{dt}\varepsilon(\mathbf{v}\mathbf{s}) = \frac{\partial\varepsilon}{\partial\mathbf{v}} \cdot \overbrace{\mathbf{v}}^{\Delta} + \frac{\partial\varepsilon}{\partial\mathbf{s}} \cdot \overbrace{\mathbf{s}}^{\Delta}. \quad (57)$$

This equation allows us, ultimately, to introduce the equation of evolution of state parameters into the energy balance. Let us note additionally that non-equilibrium parameters ξ_α in solid continuum are also tensors, which in the case of Prandtl-Reuss rate of plasticity can easily be interpreted physically [4, 5].

12 Conclusions

In the literature, there are several approaches to modelling of continua in non-equilibrium state (see: [4–6, 36–38]). Evidently, the main difficulty of this physical concept lies in these basic questions: how to define the “internal state”, i.e. what are the variables to be chosen for this definition? Which variables can be taken to be: independent or dependent [24, 25]? Which variables can influence the dissipation of energy? Which thermodynamic law is first (more primitive)? Why most of the existing literature on thermodynamics does not admit an entropy balance but postulates an entropy inequality such as the Clausius-Duhem or similar inequalities? [29, 30, 39, 40].

The main purpose of this note was to demonstrate another line of reasoning leading to a more consistent model of continuum with a non-equilibrium state. Two aspects of the present derivation are worth emphasising. First, the inclusion of balances of specific entropy and specific volume in the primitive form of balance of total energy provided a clearer interpretation of Kelvin’s principle of desegregated energy. Second, the balance of entropy, which within the framework of inviscid fluid model plays an independent role, in the present development emerges naturally instead of being a separate postulate motivated by Carnot and Clausius.

The paper is based on the Beretta and Gyftopoulos exposition of thermodynamics [10, 38]. It means that “heat”, as well as “work”, plays no

role in our statement of the first law, also in the definition of internal energy where the intensive state parameters are primary objects. “Heat” and “work” notions are not present in our statement of the second law, and in the definition of entropy and specific volume. Our concept of “the energy flux” is based on collecting particular physical fluxes into one resulting balance. The most important are the momentum, volume and entropy flux exchanges between interacting systems. They are defined using these concepts and laws, after they have been independently and unambiguously introduced. In other words, “heat” and “work” are not the energy exchanged between systems, since we assume them to be more fundamental: heating and working processes. Does not exist “a heat interaction” but only “the flux of entropy”.

Finally, let us note that in this paper, we develop and illustrate the general definition of equilibrium and non-equilibrium intensive state parameters within the Carnot working fluid. In view of the importance of non-equilibrium states for a wide range of applications of thermodynamics, we hope our efforts will help to remove obstacles to understating numerous physical phenomena (like the action of laser), yet not described within the framework of thermodynamics.

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References

- [1] Carnot S.: *Réflexions sur la puissance motrice du feu*, Paris: Bachelier 1824, (critical edition by R. Fox, Vrin, Paris, 1978).
- [2] Carnot L.: *Essai sur les machines en général*, Dijon: Defay 1783 (Ital. transl. and critical edition by S.D. Manno and A. Drago, Naples: CUEN 1994).
- [3] Ochrymiuk T., Banaszkiwicz M., Lemański M., Kowalczyk T., Ziółkowski P., Ziółkowski P.J., Hyrzyński R., Stajnke M., Bryk M., Kraszewski B., Kruk-Gotzman S., Froissart M., Badur J.: *Fluid solid interactions – a novelty in industrial applications*. Arch. Thermodyn. **43**(2022), 2, 75–96.

- [4] Ochrymiuk T., Dudda W., Froissart M., Badur J.: *Principles of stress-strength modelling of the highly loaded materials – the influence of an effect of strength differential on the material effort*. Materials (Basel) **14**(2021), 23, 7449. doi: [10.3390/ma14237449](https://doi.org/10.3390/ma14237449)
- [5] Dudda W.: *Problems of Thermal Effort of a Heat-Resistant Material*. Wyd. UWM, Olsztyn 2021.
- [6] Gyftopoulos E.P., Beretta G.P.: *Thermodynamics, Foundations and Applications* (2nd Edn.). Dover, Mineola New York 2005.
- [7] Kjelstrup S., Bedeaux D.: *Non-equilibrium Thermodynamics of Heterogeneous Systems*, Word Sci., Singapore 2008.
- [8] Feidt M.: *Thermodynamique et optimization énergétique des systèmes et procédés*. Technique et Documentation, Paris, 1987 (in French).
- [9] Zanchini E., Beretta G.P.: *Removing heat and conceptual loops from the definition of entropy*. Int. J. Thermodyn. **13**(2010), 67–76.
- [10] Beretta G.P., Gyftopoulos E.P.: *A novel sequence of exposition of engineering thermodynamics*. J. Energ. Res. Technol. **137**(2015), 021009-1. doi: [10.1115/1.4026385](https://doi.org/10.1115/1.4026385)
- [11] Natanson W.: *On the laws of viscosity*. Phil. Mag. **2**(1901), 342–356.
- [12] Maldenstam L., Leontovich M.: *A theory of sound absorption in liquids*. J. Exp. Theor. Phys. **7**(1937), 438–449.
- [13] Szaniawski A.: *Relaxation phenomena in flow problems*. Arch. Mech. **10**(1958), 671–698.
- [14] Meixner J.: *TIP has many faces*. In: Irreversible aspects of continuum mechanics (H. Parkus, L. Sedov, Eds.). Springer Verlag 1968, 237–249.
- [15] Kestin J.: *Local-equilibrium formalism applied to mechanics of solids*. Int. J. Solids Struct. **29**(1992), 1827–1836.
- [16] Brey J.J., Santos A.: *Non-equilibrium entropy of a gas*. Phys. Rev. A, **45**(1992), 8566–8572.
- [17] Sieniutycz S.: *Conservation Laws in Variational Thermo-Hydrodynamics*. Kluwer Academic, Dordrecht 1994
- [18] Bilicki Z., Kestin J.: *Physical aspects of the relaxation model in two-phase flow*. Proc. Royal. Soc. London A **428**(1990), 379–397.
- [19] Bilicki Z., Badur J.: *A thermodynamically consistent relaxation model for turbulent binary mixture undergoing phase transition*. J. Non-Equil. Thermodyn. **28**(2003), 145–172.
- [20] Badur J., Nastalek L.: *Thermodynamics of thermo-deformable solids*. In: Encyclopaedia of Thermal Stresses (1st Edn.), (R. Hetnarski, Ed.). Springer Verlag, Dordrecht, 2014.
- [21] Badur J., Ochrymiuk, T., Kowalczyk, T., Dudda, W., Ziółkowski P.: *From fluid mechanics backgrounds to modern field theory*. Acta Mech. **233**(2022), 8, 3453–3465.
- [22] Gaggioli R.A.: *Principles of thermodynamics*. In: Thermodynamics: Second Law Analysis (R.A. Gaggioli, Ed.); Washington, Washington DC 1980, 1–13.

- [23] Fülöp T., Ván P., Csatar A.: *Elasticity, plasticity, rheology and thermal stress – an irreversible thermodynamical theory*. In: Proc. 12th Joint European Thermodynamics Conf., JETC 2013 (M. Pilotelli, G.P. Beretta, Eds.), Brescia, July 1-5, 2013. Snoopy, Brescia 2013, 525–530.
- [24] Grmela M., Öttinger H.C.: *Dynamics and thermodynamics of complex fluids. I. Development of a general formalism*. Phys. Rev. **56**(1997), 6620–6632.
- [25] von Spakovsky M.R.: *Intrinsic quantum thermodynamic; what it is and what can be done with it*. In: Proc. 12th Joint European Thermodynamics Conf., JETC 2013 (M. Pilotelli, G.P. Beretta, Eds.), Brescia, July 1-5, 2013. Snoopy, Brescia 2013, 359–369.
- [26] Palazzo P.: *Proposal for generalized exergy and entropy properties based on stable equilibrium of composed system-reservoir*. J. Mod. Phys. **4**(2013), 52–58.
- [27] Ván P.: *Weakly non-local irreversible thermodynamics – The Guyer-Krumhal and the Chan-Hillard equations*. Phys. Lett. A **290**(2001), 88–91.
- [28] Lebon G., Jou D., Casas-Vázquez J.: *Understanding Non-equilibrium Thermodynamics*. Springer, Berlin 2008.
- [29] Bejan A.: *Entropy Generation Through Heat and Fluid Flow*. Wiley, New York 1982.
- [30] Mieczyski M.: *The Essence of Symmetry in Classical and Contemporary Thermodynamics*. Oficyna PW, Wrocław 2002 (in Polish).
- [31] Born M.: *Kritische Betrachtungen zur traditionellen Darstellung der Thermodynamik*. Phys. Zeitschr. **22**(1921), 210–230.
- [32] Bridgeman P.W.: *The Logic of Modern Physics*. Willey, New York 1960.
- [33] Kestin J.: *Thermodynamics (An essay)*. In: Fluid-Flow Machinery Problems (Z. Bilicki, at al. Ed.), 319–252, Wydawn. IMP PAN, Gdańsk 1993.
- [34] Eglit M.E.: *Generalization of the model of an ideal compressible fluid*. PMM **32**(1965), 771–785.
- [35] Badur J., Banaszkiwicz M.: *Model of the ideal fluid with scalar microstructure, An application to flashing flow of water*. Trans. Inst. Fluid-Flow Mach. **105**(1999), 115–152.
- [36] Lebon G., Casas-Vazquez J., Jou D.: *On the definition of non-equilibrium*. J. Phys. A: Math. Gen. **15**(1982), 565–584.
- [37] Casas-Vázquez J., Jou D.: *Temperature in non-equilibrium states: a review of open problems and current proposals*. Rep. Prog. Phys. **66**(2003), 1937–2023.
- [38] Beretta G.P.: *Steepest entropy ascent model for far-non-equilibrium thermodynamics. Unified implementation of the maximum entropy production principle*. Phys. Rev. E **90**(2014), 042113.
- [39] Ván P. 2020 *Non-equilibrium thermodynamics: emergent and fundamental*. Phil. Trans. R. Soc. A 378, 20200066. doi: [10.1098/rsta.2020.006](https://doi.org/10.1098/rsta.2020.006)
- [40] Lucia U., Grisolia G.: *Non-equilibrium temperature: An approach from irreversibility*. Materials (Basel) **14**(2021), 8, 2004. doi: [10.3390/ma14082004](https://doi.org/10.3390/ma14082004)
- [41] Gujrati P.D.: *Generalized non-equilibrium heat and work and the fate of the Clausius inequality*. UATP **1103**(2011), 1–4.
- [42] Badur J.: *Evolution of the Energy Notion*. Wydawn. IMP PAN, Gdańsk 2009.