

Article

Duhem and Natanson: Two Mathematical Approaches to Thermodynamics

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Abstract: In this article, the previously unrecognized contributions of Pierre Duhem and Ladislavus Natanson in thermodynamics are shown. The mathematical remodelling of a few of their principal ideas is taken into consideration, despite being neglected in the literature. To emphasize these ideas in an appropriate epistemological order, it would be crucial to first revalue and reconstruct some underrepresented parts of the proceedings process through which Duhem and Natanson created their thermodynamics. Duhem and Natanson's scientific works are against the background of modern continuum mechanics, presenting relevant approaches. In line with the long-held beliefs of many French and Polish researchers, the article mentions that Duhem and Natanson's ideas dated back to one century ago. Both scientists were qualified in the same Royal Way, which in this case includes chemistry, mechanic of fluid and solid, electro-chemistry, thermodynamics, electrodynamics, and relativistic and quantum mechanics. Therefore, it is possible to connect and then compare the results of their conceptions and approaches. Duhem and Natanson are both in firm opposition with Newtonian mechanisms. Thus, the Maupertuis least action principle created the ground for their efforts, in which they flourished as an elementary quantum.



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Keywords: thermo-chemistry thermodynamics of hidden parameters; Duhem inequality; Natanson's fundamental equation; non-linear evolution equations; logical structure of the extended thermodynamics; Maxwell–Natanson un-objectivity; Zaremba relativity; co-rotational time derivative; objective thermodynamics; nonlocal thermodynamics of Navier–Stokes–Fourier fluid

1. Introduction

Cimmelli, Jou, Ruggeri, and Ván [1] recently elaborated concise versions of the modern mathematical methods used in thermodynamics. To do this, they surveyed numerous results from classical, irreversible, extended, and statistical thermodynamics in order to obtain a summary of the current methods and their usefulness as scientific tools. Here, we take a similar approach, but instead outline the state of thermodynamics at the end of the 19th century. We begin by introducing the state-of-art for the period of 1870–1880, before describing the thermodynamic models developed by Duhem and Natanson.

Here, we aimed to reconstruct and revalorize two extremely abstract, potential-based thermodynamic models that were created simultaneously by two independent scientists: Pierre Duhem (Lille, Bordeaux, and Toulouse) and Ladislavus Natanson (Cracow). We specifically wanted to show the important developments that were made during the last decades of the 19th century, and restrict ourselves to some selected not yet published mathematical ideas devoted to Duhem and Natanson [2–5]. Thus, we could rediscover an original construction of a very general approach, which started from the established unification of thermodynamics and mechanics. Sometimes we present the original results without

explanation of the original symbols in the equation, if nowadays those are well-known. The authors would like to mention that a historical reorganization of the theoretical thermodynamics in the second half of the 19th century was given by S. Bordoni [6]. Natanson and Duhem belong to that historical context, and Duhem has been widely analyzed in this paper.

Stefano Bordoni recently proposed [6] a finer arrangement would demand at least five branches, which can be divided concerning their conceptual distance from mechanics, as follows:

- 1 an entirely phenomenological approach, in which thermodynamics counted on its own filars;
- 2 the energetism approach, in which a science of energy is implemented into thermodynamics;
- 3 a macroscopic approach, which appears as a structural analogy with analytical mechanics;
- 4 the consolidation of macroscopic and microscopic approaches, where thermodynamics relies on a similar analogy;
- 5 the last branch—a microscopic one—is based on specific mechanical approaches of forces and/or collisions coming from statistical assumptions that are beyond the tradition of mechanics.

Most would agree that the tradition of classical field theory finally began with Lagrange's *Mécanique analytique*. Similarly, we agree that Carnot's roots of rational thermodynamics also have the same origin. Lazare Carnot's statement, shared in the form of advice to his son Sadi, is well-known (this advice was given in Warsaw—one of the countries where Lazare Carnot had migrated to): "In order to find a base for thermodynamics you have to prolongate the mathematics of Analytic Mechanics". Therefore, the overall aim of Sadi Carnot was to create a science of caloric balance, similar to the established structures of analytical mechanics. Thus, it is unsurprising that Carnot's equation of motion of substantial caloric possesses the same mathematical structures as the balance of entropy.

However, Carnot's abstractive approach to energy conversion from heating to working is very mysterious. Truly speaking, Sadi Carnot provided a germ of a mathematical model that is actually a specific mechanical model, completely hidden in footnotes. This Carnot approach blossomed slowly over about ten decades across Britain and Europe. Owing to the efforts of Clapeyron, Lamè, Hoëné-Wroński, Ferdinand Reech, and James Thomson (older brother of Lord Kelvin), some elements of Carnot's idea were retained in the foundation of the Second Law of thermodynamics. Unfortunately, none of the three foundations of thermodynamic laws (Clausius, Thomson, and Helmholtz) borrowed from Carnot's concept of rational thermodynamics.

After the 1850s, some researchers occasionally turned towards rational thermodynamics (e.g., Mikhail Okatov, Francois Massieu, Josiah Willard Gibbs, Franz Neumann, Arthur von Oettingen, and the young Max Planck). Thus, Pierre Duhem and Ladislavus Natanson were the first among the chemists to explore the connections between the contents of thermo-chemistry and the formal structures of analytical mechanics.

Energetism began with William Macquorn Rankine and Ferdinand Reech's researches in the mid-19th century. Unfortunately, this science was a kind of reaction to a powerful paradigm that assumed a mechanical nature of every physical phenomenon. A few scientists were entirely involved in the project of presenting this by transferring physical theory to the mechanical approach. Both Duhem and Natanson were against a direct interpretation of the Rankine–Reech approach to a clear and adequate foundation for thermodynamics. They especially rejected the orthodox vision developed by the German school of energetism. It is important to note that in Germany, the three well-known people, Georg Helm, Wilhelm Ostwald, and Ernst Mach, had been promoting a theory of energetic affected by thermodynamics in the last years of the 19th century, with quite different motivations.

In 1911, Duhem [7] directly criticized the understanding of energetism. He disagreed with Ostwald's perspective about assuming energy as the only eternal element (also known as Helm's phenomenal attitude). Even though Duhem accepted Ostwald and Helm opposition to reduce all physical phenomena to mechanics, he did not develop his own line of



reasoning, and never appealed to their writings. However, Mach's concept of relativity, as well as his criticism of Newton, were appreciated by both Duhem [8] and Natanson [9].

Based on the atomistic version of nature and the philosophical fundamentals given by Democritus, Lucretius, and Rudolf Clausius in the middle of 19th century, a new version of thermodynamics and traditions of research emerged from the kinetic theory of gases. Other "mechanical theories of heat" were demonstrated at the end of the 19th century, and the very meaning of the adjective "mechanical" was in doubt. Between 1860 and 1870, Krönig, Meyer, James Clerk Maxwell, and Ludwig Boltzmann enhanced the synthesis of the thermodynamics into the kinetic theory of gases.

The concept of irreversibility likely originated from Leonardo da Vinci, who was the first to make a distinction between the first and second type perpetuum mobile. Unfortunately, from the extensive writings about the irreversible phenomena, only a few concepts have been translated into precise mathematical meaning. In the time of Duhem and Natanson, irreversibility, relative to reversibility, had a poor mathematical understanding. However, interest in irreversibility was renewed following discoveries by Jaumann, Lippmann, Eckart, Onsager, Prigogine, Meixner, Reik, Lohr, de Groot, Garmathy, Klutenberg, Liukov, Ziegler, Biot, Machlup, and others [10]. With regard to recent trends in the thermodynamics of irreversible processes of rational thermodynamics, the authors would like to mention the excellent paper of Ingo Müller and Wolf Weiss [10].

Although extended irreversible thermodynamics formally began with Maxwell's much celebrated paper, it was only developed after a resurrection inspired by Ingo Müller's 1969 dissertation. G. Lebon, David Jou, José Casas-Vázquez, Péter Ván, and Vito Cimmelli and Tommaso Ruggeri are among the researchers that addressed the various types of extended thermodynamics [1,11].

The concept of hidden parameters is typically considered to have arisen from the efforts of pioneers and veterans such as Josef Kestin, Wolfgang Muschik, Miroslav Grmela, Gerard Maugin, Witold Kosiński, Lilliana Restuccia, and Bogdan Maruszewski. Unfortunately, authors such as Herman Helmholtz, Edward Routh, Kálmán Szily von Nagy-Szigeth, Hans Reissner, and Pierre Duhem are rarely recognized [12–14].

Contemporary related literature about internal variables are classified into two groups according to Maugin and Muschik [12,13]. Internal variables of state with a relaxation type of evolution are generated by thermodynamics and dynamic degrees of freedom with variational evolution. The two kinds of evolution are actually the same when one uses dual internal variables and weakly nonlocal theory [14].

The aim of the article is to show the previously unrecognized contributions of Pierre Duhem and Ladislavus Natanson in thermodynamics. The mathematical remodeling of a few of their principal ideas is taken into consideration, despite being neglected in the literature. To emphasize these ideas in appropriate epistemological order, it would be crucial to first revalue and reconstruct some underrepresented parts of the proceedings process through which Duhem and Natanson created their thermodynamics. In Section 2, the review of Duhem's work comprises thermodynamic potentials, hidden parameters, energy balance, nonlocal theories, constitutive relations, and supplementary equations. Section 3 considers Natanson's contributions and derivation of balance laws, which have a striking similarity with approaches nowadays known as extended thermodynamics. Objectivity of the evolution equations studied by S. Zaremba is discussed in Section 4. Conclusions and a peculiar recap of the scientific evolution of P. Duhem and L. Natanson are given in Section 5.

2. Duhem and His Thermodynamics of Hidden Parameters

2.1. Duhem: Thermodynamic Potentials

As many authors have noted [2,6,15], Duhem started with his concept of *Le potential Thermodynamique*. His success in discovering the thermodynamic potential for many phenomena encouraged him to dismantle Berthelot's thermo-chemistry, which had enjoyed an unquestionable authority in France. Duhem's numerous remarks on experimental

evidence for the third principle of Berthelot's thermo-chemistry has taken a variety of forms. Briefly, we now outline Duhem's original contributions to the following domains:

- capillarity is reconstructed according to Equation (5) in article [16]:

$$\Phi = \sum_{p=1}^{p=n} \left\{ M_p [E(u_p - Ts_p) + p\sigma_p] + \sum_q A_{p,q} \theta_{p,q} \right\}, \quad (1)$$

where M is the mass of component $p = 1, \dots, n$, E describes the coefficient, u_p defines the internal specific energy of component $p = 1, \dots, n$, T represents the temperature, s_p concerns the specific entropy, p means the pressure, σ_p characterizes the specific volume, $A_{p,q}$ expresses the surface tension, and $\theta_{p,q}$ shows the surface between the phases.

- dissociation [17] p. 390:

$$\Phi = \mu_2 \theta_2(T) + m_1 \psi_1(S, T) + m_2 \psi_2(S, T), \quad (2)$$

where μ_2 means the chemical amount, $\theta_2(T)$ represents the chemical potential, m_1 and m_2 are the input and output fluxes (1 and 2, respectively), and $\psi_1 \psi_2$ defines the conjugate thermodynamic forces.

- phase transition is defined according to Equation (55) in article [18]:

$$\Phi = m_A F_A + m_B F_B + m_C F_C + \mu_A \Phi_A(p_A, T) + \mu_B \Phi_B(p_B, T) + q\Theta, \quad (3)$$

where m_A, m_B, m_C are the mass, F_A, F_B, F_C describe the specific free energy, $\Phi_A(p_A, T)$ and $\Phi_B(p_B, T)$ characterize the chemical potential, μ_A, μ_B express the number of moles, q concerns the order parameter, and Θ means the square gradient parameter. Additionally, Duhem's other original contributions produced different forms of thermodynamic potential that were discovered and applied. In Duhem's equations above, many abstractive denotations appear, like $s_p, \sigma_p, \theta_{p,q}, \mu_A$. Nowadays, those symbols, due to their abstractive character, cannot be used as adequate notions from equilibrium thermodynamics—many concepts of Duhem's ideas have been forgotten. Nevertheless, the full reconstruction of the details of potentials given by Equations (1)–(3) is theoretically possible. For instance, most important is Duhem's generalization of the Young–Laplace equation with addition electrical tension which according to reconstructed Equation (46) in paper [19] is as follows:

$$(A_{12} + A_{21}) \left[\left(\frac{1}{R_1} + \frac{1}{R'_1} \right) + \left(\frac{1}{\rho_1} + \frac{1}{\rho_2} \right) \right] + (D_1 - D_2)g(z - \zeta) = -L_{12}(i_{12} - j_{12}) - L_{21}(i_{12}^2 - j_{12}^2). \quad (4)$$

where A_{12} is the affinity from 1 to 2 and A_{21} means the affinity from 2 to 1, R_1, R'_1 are the radii of the principal curves, ρ_1, ρ_2 represent the radii of the secondary curves, z, ζ concerns the level of concentration, g defines the gravity force, D_1, D_2 is the diffusion coefficients, i_{12} is the local current density, j_{12} is the local components density flux, L_{12} is the linear coefficient matrix, and L_{21} is the nonlinear coefficient matrix.

We can see that Duhem presented the general idea of the thermodynamic potential in a specific sense, as an analogy between certain formulas of mechanics and thermodynamics. His understanding of Reech, Gibbs, Maxwell, and Helmholtz gave him the ability to see analogies between the concept of potential and the function available energy termed by Gibbs and W. Thomson, and the free energy named by Helmholtz in a chemical reaction. Additionally, his idea to treat the theories of thermodynamic statics with methods very similar in form to those of Lagrange, in mechanical statics was, as seen in the future, powerful.

2.2. Duhem: Thermo-Chemistry of Hidden Parameters

In 1890, Duhem began to explore the foundations of thermo-chemistry, and treated it as an analogy to Lagrange's analytical mechanics. The results of Duhem's efforts were published in "The Fundamental Equations of Thermodynamics" [20] and were next extended in Duhem's three-part study, "Commentary on the Principles of Thermodynamics" [21–23]. Yet, in his 1903 essay, Duhem presented [8] his first rigorous definition of the notion of a reversible process that was in some aspects analogous to the peripatetic motion. In chemistry, this reasoning was problematic, because chemical equilibrium reactions have a form of thermo-statics that provide the characterization of matter at equilibrium.

In the analyses of the chemical reaction process connecting two equilibrium states that gather equilibrium states, Duhem assumed that, at the limit (nowadays called a quasi-static process), where the imbalance is step by step decreased, every level is treated as an equilibrium state. Whereas it indicates that the sum of such levels cannot itself represent a process, however this phenomenon need to be slow.

Thus, Duhem introduced a concept of a reversible change (*transformation réversible*), described by fields of hidden parameters α_a . Early in his physical chemistry textbooks, with this kind of peripatetic motion, he began his analytical description referring to reversible change (*modification réversible*), focusing on real changes that are never reversible [7,24].

With hidden parameters, these are related the following conjugate variables in reconstructed Equation (1) according to paper [20] is as follows:

$$A_a = \frac{\partial F}{\partial \alpha_a}, \quad a = 1, 2, 3, \dots, n. \quad (5)$$

where F is a generalized potential of Helmholtz' type (now known as free energy potential), which takes part in the evolution equations for hidden parameters in reconstructed Equation (2) from paper [20] in Duhem notation:

$$\begin{cases} R_a = \frac{\partial \Theta}{\partial \alpha_a} - \frac{A_a}{E} \\ C = \frac{\partial F}{\partial \vartheta} - \frac{\Theta}{E} \end{cases} \quad (6)$$

where R_a is viscous friction (generalized thermal capacity), C is thermal friction, and E is the heat equivalent. By this approach, Duhem describes an increment of chemical heat [20], p. 234, to be:

$$dQ = -(R_a d\alpha_a + C d\vartheta). \quad (7)$$

Thus, arriving at constitutive relations for viscous friction (or generalized thermal capacity), R_a , with an internal chemical dissipation, Θ , and absolute temperature, ϑ in reconstructed Equation (8) from paper [20]:

$$R_a = \frac{1}{E} \frac{F(\vartheta)}{\dot{F}(\vartheta)} \left(\frac{\partial \Theta}{\partial \alpha_a} - \frac{\partial A_a}{\partial \vartheta} \right). \quad (8)$$

This thermo-statics chemistry has been further extended in the last thermodynamic model of Duhem's book *Traite d'énergetique ou thermodynamique générale* [2]. Unfortunately, a revalorization of this fundamental book is, presently, beyond our scope, as it should be considered as an independent work.

2.3. The Vis Viva Integral in Thermodynamics (1898)

The problem of a general condition required for the kinetics of a fluid–solid phase transition was stated by Gibbs (1877) and Natanson (1896). In his 1898 paper, Pierre Duhem [25] returned to this problem in a more general fashion, by describing a system of two chemically reacting flowing bodies [(1) and (2)] in a surface contact whose various parts are at different absolute temperatures (T_1 and T_2 , respectively). The first part (solid) is described by the vector of state variables $\alpha_a^1 = \{\alpha^1, \beta^1, \dots, \lambda^1\}$, $a = 1, 2, 3, \dots, n^1$. Duhem



assumes that if only T_1 varies, then α_a^1 will remain invariable, whereas the different material elements that consist of part 1 will remain stable.

Similarly, part 2 (fluid) is indicated as having the normal variables $\alpha_b^2, b = 1, 2, 3, \dots, n^2$ and temperature T_2 . Usually, a solid state requires more state variables than a fluid: $n^1 > n^2$. The interphase surface leads to the existence of k bilateral constraints between variables according to reconstructed Equation (1) from paper [25]:

$$M_a^{(1)r} \delta \alpha_a^1 + M_b^{(2)r} \delta \alpha_b^2, \quad r = ', ', ', \dots, k, \quad (9)$$

where the constants $M_a^{(1)r}$ and $M_b^{(2)r}$ are functions of the parameters α_a^1, α_b^2 however, not T_1, T_2 . The form of internal thermodynamic potential according to reconstructed Equation (2) from paper [25] is as follows:

$$F = F^1(\alpha_a^1, T_1) + F^2(\alpha_b^2, T_2) + E\Psi(\alpha_a^1, \alpha_b^2), \quad (10)$$

where F^1, F^2 are the internal thermodynamic potentials of part 1 and part 2, considered in isolation, and $E\Psi$ is the potential for the interaction between bodies 1 and 2. The conditions in Equation (9) give the k relations according to reconstructed Equation (3) from paper [25]:

$$M_a^{(1)r} \dot{\alpha}_a^1 + M_b^{(2)r} \dot{\alpha}_b^2 = 0, \quad (11)$$

between parameters $\dot{\alpha}_a^1$ and $\dot{\alpha}_b^2$.

Next, Duhem supposed that the system did not have any internal viscosity and friction (external viscosity), giving the following form of the n^1 constitutive equations according to reconstructed Equation (4) from paper [25]:

$$A_a^1 - \frac{\partial}{\partial \dot{\alpha}_a^1} (F^1 + E\Psi - T) - \frac{d}{dt} \frac{\partial T}{\partial \dot{\alpha}_a^1} + \Pi^{1r} M_a^{1r} = 0, \quad a = 1, 2, 3, \dots, n^1. \quad (12)$$

For part 1 and according to reconstructed Equation (5) from paper [25]:

$$A_b^2 - \frac{\partial}{\partial \dot{\alpha}_b^2} (F^2 + E\Psi - T) - \frac{d}{dt} \frac{\partial T}{\partial \dot{\alpha}_b^2} + \Pi^{2r} M_b^{2r} = 0, \quad b = 1, 2, 3, \dots, n^2, \quad (13)$$

where T is the *vis-viva* of the system, and A_a^1 and A_b^2 are the total action that the system exerts upon body 1 and body 2, respectively. The internal reactions Π^{1r}, Π^{2r} depend on $\alpha, \dot{\alpha}$, but not on $\ddot{\alpha}$. The inertia-less state parameters $\ddot{\alpha}$ was developed in 2001 by Zbigniew Bilicki, who introduced a "second order in time differential equation on state parameters" [26].

The quantity of the evolution Equations (9), (12) and (13), is $(k + n^1 + n^2)$, however, it is necessary to define: the n^1 variables α_a^1 , the n^2 variables α_b^2 and the k auxiliary variables $\Pi^{1r} = -\Pi^{2r}$.

Next, Duhem supposed that the actions A_a^1, A_b^2 , that force the system by the bodies that are unfamiliar to the system, depend on a potential: $\Omega(\alpha_a^1, \alpha_b^2)$. From this position, it is not difficult to prove that the evolution (Equations (4) and (5)) and constrains (Equation (1)) fulfilled the following principle of energy creating from nothing which is reconstructed according to Equation (6) from paper [25]:

$$\frac{d}{dt} (\Omega + F^1 + F^2 + E\Psi + T) - \frac{\partial F^1}{\partial T_1} \frac{dT_1}{dt} - \frac{\partial F^2}{\partial T_2} \frac{dT_2}{dt} = 0 \quad (14)$$

Duhem then provided the statement: *In order for the relation (6) to immediately yield a first integral (viz., a vis viva integral) of the Equations (4) and (5), it is necessary and sufficient that the expression: $\frac{\partial F^1}{\partial T_1} \frac{dT_1}{dt} - \frac{\partial F^2}{\partial T_2} \frac{dT_2}{dt}$ must represent the total differential of a function of $\alpha_a^1, T_1, \alpha_b^2, T_2$, either by itself or by virtue of the supplementary condition $T_1 = T_2 = 0$.*

Finally, some systems can determine a vis viva integral by virtue of additional relations. When one is not correlated with an established system, the above formula will no longer be a total differential. On the other hand, equality of the following form can arise according to reconstructed Equation (21) from paper [25]:

$$\frac{\partial F^1}{\partial T_1} \frac{dT_1}{dt} - \frac{\partial F^2}{\partial T_2} \frac{dT_2}{dt} = \frac{dF(t)}{dt} \quad (15)$$

For this specific example, the system will indicate a vis viva integral, which will have the expression according to reconstructed Equation (22) from paper [25]:

$$\Omega + F^1 + F^2 + E\Psi + T - F(t) = \text{const} \quad (16)$$

This is a Daniel Bernoulli type vis viva integral in chemical statics. One of the complementary equations (15) implies that each of the constituent parts does not receive or release heat during any real modification of the system. These are specifically the additional relations that were stated by Laplace in his work on the propagation of sound in a material of air. On the other hand, if one admits that every part of the system has an invariable temperature, whereas the system is being reformulated, then Duhem's supplementary relation is reduced to the form: $\Omega + F^1 + F^2 + E\Psi + T = \text{const}$. $\Omega + F_1 + F_2 + E\Psi + T = \text{const}$, which will then be in the formula of the vis viva integral for isothermal modifications. This form of additional relations was eventually formulated by Newton and the geometers during the decades of the 18th century through the theory of sound.

Ultimately, Duhem underlined the power of thermodynamic principles in the following quote: "These considerations show that the questions that relate to thermodynamics will have to come to the attention of physicists before they can begin the study of systems other than classical systems, and in fact, it was the theory of the propagation of sound in air that provoked Laplace to create thermodynamics".

2.4. Duhem: Thermodynamics of Nonlocal Elastic Fluids

Typically, for French scientists, having little in common with the Newtonian mechanics, Pierre Duhem started from a variational formulation of the Lagrangean mechanics in the following exact and general (*exacte en général*) form, which is reconstructed according work [27] in issue I in Equation (2) as follows:

$$\Omega + F^1 + F^2 + E\Psi + T - F(t) = \text{const}. \quad (17)$$

Duhem's aim was to demonstrate the power of variational formulation, therefore, he went beyond the classical Navier–Stokes model of thermal, conductible, and viscous fluid and instead considered a fluid, nonlocal in space, based on the nonlocal free energy concept. Using same line of reasoning, Duhem repeated this for constructing a theory of three-dimensional elasticity nonlocal in time and nonlocal in space theory [28]. A few years later, a weekly-nonlocal model with an additional internal degree of freedom developed using quantum thermodynamics was proposed. Quantum mechanics is considered as a (strongly) nonlocal theory, at least regarding the role of quantum mechanical hidden variables. On the other hand, its Schrodinger–Madelung formulation is a weekly nonlocal fluid theory. However, the theory of Duhem that is presented here is a strongly nonlocal continuum theory.

In the above Equation (17), Lagrangian's four contributions to energy are as follows:

- variation of internal potential, which is reconstructed according to work [27] in issue I in Equation (67):

$$R_a = \frac{1}{E} \frac{F(\vartheta)}{\dot{F}(\vartheta)} \left(\frac{\partial \Theta}{\partial \alpha_a} - \frac{\partial A_a}{\partial \vartheta} \right) \quad (18)$$

where, due to the nonlocal potential (see Equation (34)), it appears as a definition pressure π and condition from nonlocality $A_{(i)}$, A_c (see Equations (31) and (36)), as well as a con-

tribution from an internal body force $X_{(i)}$ (see Equation (35)). Equations (31) and (34)–(36) will be defined in Section 2.4.1. Set of Governing Equations.

- variation of external actions, which is reconstructed according to work [27] in issue I in Equation (70):

$$dT_c = \int \rho X_{(c)} \cdot \delta x d\omega + \int P \cdot \delta x dS, \quad (19)$$

- variation of kinetic energy, which is reconstructed according to work [27] in issue I in Equation (3) as follows:

$$dT_j = \int \rho a \cdot \delta x d\omega, \quad (20)$$

- variation of viscous power, which is reconstructed according to work [27] in issue I in Equations (41), (45) and (47) as follows:

$$dT_v = \int \text{tr}(\tau \cdot \delta e) d\omega = - \int n\tau \cdot \delta x dS + \int \text{div} \tau \cdot \delta x d\omega. \quad (21)$$

Above, Duhem applied the following component notation:

- placement of particle:

$$x = x e_x + y e_y + z e_z \quad (22)$$

- body force, which can be reconstructed according to work [27] in issue I in Equation (70) as follows:

$$X_{(c)} = X_c e_x + Y_c e_y + Z_c e_z, \quad (23)$$

- surface forces, which can be reconstructed according to work [27] in issue I in Equation (70) as follows:

$$P = P_x e_x + P_y e_y + P_z e_z, \quad (24)$$

- vector of d'Alembert–Euler acceleration, which can be reconstructed according to work [27] in issue I in Equation (78) as follows:

$$a = \gamma_x e_x + \gamma_y e_y + \gamma_z e_z = \dot{v} = \partial_t v + (\text{grad} v)v, \quad (25)$$

- velocity vector, which can be reconstructed according to work [27] in issue I in Equation (55) as follows:

$$\delta x = v dt = (u e_x + v e_y + w e_z) dt, \quad (26)$$

- normal vector, which can be reconstructed according to work [27] in issue I in Equation (57) as follows:

$$n = \cos(n, x) e_x + \cos(n, y) e_y + \cos(n, z) e_z, \quad (27)$$

- diade of viscous stresses, which can be reconstructed according to work [27] in issue I in Equation (44) as follows:

$$\tau = v_x e_x \otimes e_x + v_y e_y \otimes e_y + v_z e_z \otimes e_z + \tau_x (e_z \otimes e_y + e_y \otimes e_z) + \tau_y (e_z \otimes e_y + e_y \otimes e_z) + \tau_z (e_y \otimes e_z + e_z \otimes e_y), \quad (28)$$

- diade of rate of deformation, which can be reconstructed according to work [27] in issue I in Equation (44) as follows:

$$d = D'_1 e_x \otimes e_x + D'_2 e_y \otimes e_y + D'_3 e_z \otimes e_z + G'_1 (e_z \otimes e_y + e_y \otimes e_z) + G'_2 (e_z \otimes e_y + e_y \otimes e_z) + G'_3 (e_z \otimes e_y + e_y \otimes e_z) = \frac{1}{2(\text{grad} v + \text{grad}^T v)} \text{ and } \delta e \equiv d dt \quad (29)$$

It should be noted that Duhem was the first to identify the role of the “rate of deformation” tensor d and also the Cosserats relation: $d = FEF^T$.

2.4.1. Set of Governing Equations

Using numerous variational identities, which have since become well-known, Duhem finally obtained a set of equations, as follows:

- motion, which can be reconstructed according to work [27] in issue I in Equation (74) and (79) as follows:

$$\rho \mathbf{a} + \text{grad} \pi = \text{div}(\boldsymbol{\tau}) + \rho(\mathbf{X}_{(c)} + \mathbf{X}_{(i)}), \quad (30)$$

- nonlocal state equation, which can be reconstructed according to work [27] in issue I in Equation (75) as follows:

$$\pi + \rho^2(A_{(i)} + A_{(e)}) - \rho^2 \zeta_{,\rho} = 0, \quad (31)$$

- continuity, which can be reconstructed according to work [27] in issue I in Equation (60) as follows:

$$\frac{d}{dt} \rho + \text{div}(\rho \mathbf{v}) = 0, \quad (32)$$

- Cauchy–Poisson condition on boundary, which can be reconstructed according to work [27] in issue I in Equation (77) as follows:

$$\mathbf{P} = (-\pi \mathbf{I} + \boldsymbol{\tau}) \mathbf{n} + \text{div}_2(\gamma \mathbf{I}_2), \quad (33)$$

where the surface force consists of: $\mathbf{P} = v_D \mathbf{t} + v_N \mathbf{v} + v_B v^2 \mathbf{t}$, from which the Duhem, Navier, and Du Buat coefficients of surface viscosity, respectively, and γ is the elastic surface tension. The tangent unit vector \mathbf{t} is defined as $\mathbf{t} = \frac{\mathbf{v}}{|\mathbf{v}|}$. By \mathbf{n} , a unit vector normal to the boundary surface is denoted, and by $\text{div}_2(\cdot)$, the surface (two-dimensional) divergence is introduced, as well as $\mathbf{I}_2 = \mathbf{I} - \mathbf{n} \otimes \mathbf{n}$, which is a two-dimensional surface metric.

2.4.2. Constitutive Equations

The hyper-thermodynamics of a nonlocal fluid is based on Duhem's potential (Helmholtz free energy) which was defined in work [27] in Equation (66) reconstructed as follows:

$$F = \int \zeta(\rho, T) d\omega + \frac{1}{2} \int \int \psi(\rho, \rho', r) dm' dm. \quad (34)$$

where ζ is the specific free energy, $dm = \rho d\omega$ is the mass element, T is the temperature field, and ρ is the density. The nonlocal free-energy ψ is a function of dm' acting on a distance of $r = |\mathbf{x} - \mathbf{x}'|$ which was described in work [27] in Equation (67) reconstructed with an additional nonlocal body force:

$$\mathbf{X}_{(i)} = - \int \frac{\partial \psi}{\partial r} \text{grad} r dm', \quad (35)$$

and an additional nonlocal pressure

$$A_{(i)} = - \int \frac{\partial \psi}{\partial \rho} dm'. \quad (36)$$

However, concerning the constitutive relation for viscous stresses, Duhem proposed using the dissipation function of Thomson–Tait [*dissipativité*] which is reconstructed according to work [27] in issue I in Equation (55) as follows:

$$d\tau_v = -2dt \int D d\omega = -2f dt, \quad (37)$$

where $f = \int Dd\omega$ is a function of the diade \mathbf{d} which is reconstructed according to work [27] in issue I in Equation (54) as follows:

$$D = \frac{\lambda(\rho, T)}{2}\theta^2 + \mu(\rho, T) \left[(u_{,x})^2 + (v_{,y})^2 + (w_{,z})^2 + (v_{,z} + w_{,y}) + (w_{,x} + u_{,z}) + (u_{,y} + v_{,x}) \right] \quad (38)$$

and according to work [27] in issue I in reconstructed Equation (51) as follows:

$$\tau = \frac{\partial D}{\partial \mathbf{d}} |_{\rho, T = \text{const}} = -\lambda(\rho, T)\mathbf{I}\theta - 2\mu(\rho, T)\mathbf{d} \quad (39)$$

where θ is reconstructed according to Equation (52) in work [27] in issue I in the form:

$$\theta = \text{div}(\mathbf{v}) = u_{,x} + v_{,y} + w_{,z} \quad (40)$$

2.5. The Duhem Inequality [1901,§6]

Strikingly, Duhem, probably for the first time, proposed an entropy field *ex cathedra* to be a scalar $\sigma(t, \mathbf{x})$:

$$S = \int \sigma \, dm \quad (41)$$

Next, starting from the global Clausius (in time and space), Duhem went on to describe a local Clausius' inequality reconstructed according to Equation (89) in work [27] in issue I as:

$$\sum \frac{dQ}{T} + \frac{dS}{dt} dt \geq 0 \quad (42)$$

In local variables, this took a form that depended on the free energy according to work [27] in issue I at page 346 as follows:

$$\frac{dS}{dt} = \frac{d}{dt} \int \sigma \, dm = \int \frac{d\sigma}{dt} \, dm = \int \left[-\frac{1}{E} \frac{\partial^2 \zeta(\rho, T)}{\partial T^2} \frac{dT}{dt} + \frac{\partial^2 \zeta}{\partial \rho \partial T} \frac{d\rho}{dt} \right] \, dm \quad (43)$$

Duhem then described how the local form of the heat flux dQ , in works [27] in issue I in Equation (80), which is reconstructed as follows:

$$EdQ = -E T dS - d\tau_v \quad (44)$$

and global entropy which is reconstructed according to work [27] in issue I in Equation (81) as follows:

$$ES = - \int \frac{\partial \zeta(\rho, T)}{\partial T} \, dm \quad (45)$$

Expressing the uncompensated working $d\tau_v$ in terms of the dissipation potential, Duhem defines the entropy flux which is reconstructed according to work [27] in issue I in Equation (86) as:

$$\frac{EdQ}{T} = \frac{\int \left\{ ET \frac{d\sigma}{dt} \, dm - 2Dd\omega \right\} dt}{T} \quad (46)$$

And, finally, as according to reconstructed Equation (90) from paper [27] in issues I is presented:

$$\det \begin{bmatrix} \mu & 0 & 0 & 0 & 0 & 0 \\ 0 & \mu & 0 & 0 & 0 & 0 \\ 0 & 0 & \mu & 0 & 0 & 0 \\ 0 & 0 & 0 & \lambda + 2\mu & \lambda & \lambda \\ 0 & 0 & 0 & \lambda & \lambda + 2\mu & \lambda \\ 0 & 0 & 0 & \lambda & \lambda & \lambda + 2\mu \end{bmatrix} \geq 0 \quad (47)$$

At this point, the principal difference between Clausius and Duhem is that the Clausius inequality (in terms of zero-dimensional model) states that the un-compensated heating is >0 , while for Duhem, the inequality (three-dimensional) states that the un-compensated

working is >0 . This inequality leads to $D \geq 0$, if coefficients λ and μ , according to work [27] in issue I at page 328, are as follows:

$$\mu \geq 0, \mu^2 \geq 0, \mu^3 \geq 0, \mu^2(\lambda + 2\mu) \geq 0, \mu^4(\lambda + \mu) \geq 0, \mu^5(3\lambda + 2\mu) \geq 0. \quad (48)$$

From above, it follows that only two are independent which is reconstructed according to work [27] in issue I in Equations (62) and (63):

$$\mu \geq 0, \mu^2 \geq 0, \mu^3 \geq 0, \mu^2(\lambda + 2\mu) \geq 0, \mu^4(\lambda + \mu) \geq 0, \mu^5(3\lambda + 2\mu) \geq 0. \quad (49)$$

2.6. La Relation Supplémentaire (1901)

The above set of nonlocal Navier–Stokes equations is incomplete, as the field of local temperature is not yet determined. Moreover, the balance of energy cannot be further used, as it is responsible for starting the variational energy in the Lagrangean equations. Therefore, Duhem, maintaining a line of Fourier reasoning, proposed a supplementary relation for the temperature field. Even now, the status of this supplementary relation remains unclear. First, Duhem defined heat flux dQ on the surface as dS which is reconstructed according to work [27] in issue I in Equation (93):

$$\mu dQ = dt \int k(\rho, T) \frac{\partial T}{\partial n} dS = - \int \left\{ k\Delta T + \left[\frac{\partial k}{\partial \rho} \text{grad} \rho + \frac{\partial k}{\partial T} \text{grad} T \right] \cdot \text{grad} T \right\} d\omega \quad (50)$$

Next, balancing internal efforts, Duhem obtained his *la relation supplémentaire* which is reconstructed according to work [27] in issue I in Equation (94) in the form:

$$k(\rho, T) \nabla^2 T + \frac{\partial k}{\partial T} (\text{grad} T)^2 + \frac{\partial k}{\partial \rho} (\text{grad} T) \cdot (\text{grad} \rho) + \frac{T}{E} \rho \frac{\partial^2 \zeta}{\partial T^2} \left(\frac{d}{dt} T \right) + \frac{T}{E} \rho^2 \frac{\partial^2 \zeta}{\partial \rho \partial T} (\text{div} \mathbf{v}) + D = 0 \quad (51)$$

which can be considered a generalized thermal equation of motion. D is defined in Equation (38).

The above set of governing equation is likely the first example of an original extension of the so-called Navier–Stokes–Fourier equations, written for general fluids found in the literature. The novelty of these equations is located in three points:

- 1 in the literature, nonlocal formulation, not only momentum, but also entropy equation;
- 2 a new kind of the momentum boundary condition Equation (33);
- 3 explicit use of an inequality for the restriction of values of the first and second viscosity coefficient.

With reference to Equations (47)–(49), note that it is not Clausius' inequality of entropy—this inequality deals with energy as Duhem introduces the novel concept of un-compensate working. Importantly, in the context of the current literature, some authors like Truesdell and Toupin have wrongly interpreted the un-compensate working in terms of: “entropy inequality”. Therefore, proposed by Truesdell, the expression “Clausius–Duhem inequality” has no deeper historical background.

In our opinion, the reconstruction of Duhem achievements within the framework of thermodynamics, made 60 years ago by Clifford Truesdell are incomplete and in the section of energy balance, it can be developed in another way. Much better is a revalorization of Duhem's thermodynamics made by Brouzeng [2], however he is strongly influenced by the framework of “the truesdellian school of rational thermodynamics”. Similarly, Duhem's concept of internal variables was significantly developed by Maugin and Muschik [12,13], nevertheless, their treatment is too far from Duhem's original, because it is under the strong influence of Coleman. Probably, it was Josef Kestin who understood better and developed the original Duhem model of internal variables [10,11].

3. Natanson's Nonlinear Extended Thermodynamics

Referring to Natanson's achievements nowadays, he is mainly recognized as a pioneer of the quantum thermodynamics [3–5]. People also considered him as a veteran

of science of linear non-equilibrium thermodynamics. Less is known about pioneering works of Natanson on the subject of “nonlinear extended thermodynamics”. Natanson’s papers [29–34], published simultaneously in four languages, are the first probe in the literature to establish exact (nonlinear) foundations of the kinetic theory of gases. Note that Natanson had learned the Maxwell’s approach [35] to modelling of gases at Cavendish Laboratory during his private visit in years 1887–1889. The results of his researcher was published firstly in the monograph *Introduction to Theoretical Physics* [9] and next in series of publications [36–42].

3.1. Natanson’s Velocity Vectors

Following Maxwell’s approach, Natanson implemented the employment of two types of velocity vectors: molar \mathbf{u} and molecular \mathbf{c} [9,33,34]:

$$\mathbf{u} + \mathbf{c} = (ue_x + ve_y + we_z) + (\xi e_x + \eta e_y + \zeta e_z) \quad (52)$$

Additionally, the body force \mathbf{f} was taken into account by Natanson, revalorizing Maxwell’s original approach [35], therefore it was possible to expand the Maxwell fundamental Equation (12) obtained in [9], which can be reconstructed as follows:

$$\frac{d}{dt}(\overline{Qn}) + \text{div}(nc \otimes Q) + \text{div}(\mathbf{u})Qn = \frac{\delta}{\delta t}(Qn) + n \left(\mathbf{f} \cdot \frac{\delta Q}{\delta \mathbf{u}} \right) \quad (53)$$

This is now the familiar beginning for the kinetic theory of gases.

3.2. Continuity Equation

Referring to Maxwell’s reasoning, in exactly the same way, Natanson acquired a governing evolution equation for another balanced quantities Q (topological charges). By initially taking $Q = m$, and the next identities [36]:

$$\overline{\mathbf{c} \otimes Q} = \overline{m\mathbf{c}} = 0, Qn = \rho, Q = m, \frac{\delta Q}{\delta \mathbf{u}} = 0 \quad (54)$$

Natanson arrived at the Euler mass continuity:

$$\frac{d}{dt}\rho + \rho \text{div} \mathbf{u} = 0 \quad (55)$$

Then, by establishing (54) into (53), a non-conservative formula of the basic equation was gained according to Equation (5) in Paragraph 1 of [37], which can be reconstructed as follows:

$$\rho \frac{d}{dt}Q + \text{div}(\rho \overline{\mathbf{c} \otimes Q}) = \rho \frac{\delta}{\delta t}Q + \rho \left(\mathbf{f} \cdot \frac{\delta Q}{\delta \mathbf{u}} \right) \quad (56)$$

in which the d’Alembert–Euler material derivative is indicated as follows:

$$\frac{d}{dt}(\cdot)_{X=\text{const}} = \frac{\partial}{\partial t}(\cdot)_{x=\text{const}} + \text{grad}(\cdot)\mathbf{u} \quad (57)$$

3.3. Balance of Linear Momentum

Next, putting $Q = \mathbf{u} + \mathbf{c}$ and using the following identities:

$$Q = \mathbf{u}, \quad \overline{\mathbf{c} \otimes Q} = \overline{\mathbf{c} \otimes \mathbf{c}}, \quad \frac{\delta}{\delta t}Q = 0, \quad \frac{\delta Q}{\delta \mathbf{u}} = \mathbf{I} \quad (58)$$

Natanson obtained the evolution of the linear momentum according to Equation (5) in Paragraph 4 of [37], which can be reconstructed in the following form:

$$\rho \frac{d}{dt} \mathbf{u} + \operatorname{div}(\rho \overline{\mathbf{c} \otimes \mathbf{c}}) = \rho \mathbf{f} \quad (59)$$

where, according to Gabriel Stokes and the British traditional instance of the Cauchy tension tensor \mathbf{t} , Natanson introduced a Stokes–Reynolds pressure tensor, denoted as: $\mathbf{p} = \rho \overline{\mathbf{c} \otimes \mathbf{c}}$ (note that $\mathbf{t} = -\mathbf{p}$).

3.4. Balance of Total Energy

It was more difficult and time consuming for Natanson to balance the total energy. Taking $Q = (\mathbf{u} + \mathbf{c}) \cdot (\mathbf{u} + \mathbf{c}) = (u + \xi)^2 + (v + \eta)^2 + (w + \zeta)^2$ and a few not trivial identities

$$Q = \overline{\mathbf{u} \cdot \mathbf{u} + 2\mathbf{c} \cdot \mathbf{u} + \mathbf{c} \cdot \mathbf{c}} = \overline{u^2 + c^2} = \overline{u^2} + \overline{\xi^2} + \overline{\eta^2} + \overline{\zeta^2} \quad (60)$$

$$\mathbf{c} \otimes Q = \overline{\mathbf{c} \mathbf{u} \cdot \mathbf{u}} + \overline{\mathbf{c} \cdot \mathbf{u} \mathbf{c}} + \overline{\mathbf{u} \cdot \mathbf{u} \mathbf{c}} + \overline{\mathbf{c} \cdot \mathbf{c} \mathbf{c}} = 2\overline{\mathbf{u} \cdot \mathbf{c} \mathbf{c}} + \mathbf{q} \quad (61)$$

$$\begin{aligned} \operatorname{div}(\rho \overline{\mathbf{c} \otimes Q}) &= \operatorname{div}(\rho \mathbf{q}) + 2\operatorname{div}(\rho \overline{\mathbf{c} \otimes \mathbf{c}} \cdot \mathbf{u}) \\ &= \operatorname{div}(\rho \mathbf{q}) + 2\operatorname{div}(\rho \overline{\mathbf{c} \otimes \mathbf{c}}) \cdot \mathbf{u} + 2(\rho \overline{\mathbf{c} \otimes \mathbf{c}}) \cdot \mathbf{u} \otimes \nabla \end{aligned} \quad (62)$$

as well as

$$\frac{\delta}{\delta t} Q = \frac{\delta}{\delta t} \overline{\xi^2} + \frac{\delta}{\delta t} \overline{\eta^2} + \frac{\delta}{\delta t} \overline{\zeta^2} = 0 \quad (63)$$

and

$$\rho \mathbf{f} \cdot \frac{\delta Q}{\delta \mathbf{u}} = 2\rho \mathbf{f} \cdot \mathbf{u}, \quad \mathbf{p} = \rho \overline{\mathbf{c} \otimes \mathbf{c}}, \quad \operatorname{grad} \mathbf{u} \equiv \mathbf{u} \otimes \nabla, \quad d = \frac{1}{2}(\nabla \otimes \mathbf{u} + \mathbf{u} \otimes \nabla) \quad (64)$$

Natanson, defined the heat energy flux as $\mathbf{q} = \overline{\mathbf{c} \cdot \mathbf{c} \mathbf{c}}$, arriving at:

$$\rho \frac{d}{dt} (\overline{u^2 + c^2}) + \operatorname{div}(\rho \mathbf{q}) + 2\operatorname{div}(\mathbf{p}) \cdot \mathbf{u} + 2\mathbf{p} \cdot d = 2\rho \mathbf{f} \cdot \mathbf{u} \quad (65)$$

and after removing a contribution coming from momentum, ultimately arrived at the Equation (4) in Paragraph 2 of work [36], which can be reconstructed in the form:

$$\rho \frac{d}{dt} (\overline{c^2}) + \operatorname{div}(\rho \mathbf{q}) + 2\mathbf{p} \cdot d = 0 \quad (66)$$

This is the part of the balance of the whole energy that is called the vis viva balance. It should be mentioned that the concept of vis viva balance comes from Galileo Galilei (1636) where this approach was used for the single mass (a stone falling from a tower). Therefore, Equation (66) presents a simple extension of the vis viva balance into a continuum of massive particles.

3.5. Evolution of Heat Flux

Furthermore, by considering $Q = (\mathbf{u} + \mathbf{c}) \otimes (\mathbf{u} + \mathbf{c}) \otimes (\mathbf{u} + \mathbf{c})$, Natanson decided to take a source of energy flux as follows: $Q = (\mathbf{u} + \mathbf{c})(\mathbf{u} + \mathbf{c}) \cdot (\mathbf{u} + \mathbf{c})$ by exploring the non-trivial identities:

$$Q = \mathbf{u} \mathbf{u}^2 + \mathbf{u}(\mathbf{c} \cdot \mathbf{c}) + \overline{\mathbf{c} \mathbf{u} \cdot \mathbf{c}} + \overline{\mathbf{c} \mathbf{c} \cdot \mathbf{u}} + \overline{\mathbf{c} \mathbf{c} \cdot \mathbf{c}}, \quad (67)$$

$$\overline{\mathbf{c} \otimes Q} = 2\overline{(\mathbf{c} \cdot \mathbf{u}) \mathbf{c} \otimes \mathbf{u}} + \overline{c^2 \mathbf{c} \otimes \mathbf{u}} + \overline{u^2 \mathbf{c} \otimes \mathbf{c}} + 2\overline{\mathbf{c} \cdot \mathbf{u} \mathbf{c} \otimes \mathbf{c}} + \overline{(\mathbf{c} \cdot \mathbf{c}) \mathbf{c} \otimes \mathbf{c}}, \quad (68)$$

$$\frac{\delta}{\delta t} Q = \mathbf{u} \frac{\delta}{\delta t} \overline{c^2} + \frac{\delta}{\delta t} (\overline{\mathbf{u} \cdot \mathbf{c}}) \mathbf{c} + \frac{\delta}{\delta t} \mathbf{q}, \quad (69)$$

$$\overline{\mathbf{f} \frac{\delta Q}{\delta \mathbf{u}}} = \overline{\mathbf{f}(\mathbf{u} + \mathbf{c}) \cdot (\mathbf{u} + \mathbf{c})} + 2\overline{\mathbf{f}(\mathbf{u} \otimes \mathbf{u} + \overline{\mathbf{c} \otimes \mathbf{c}})}, \quad (70)$$

3.6. Evolution of the Heat Flux and Linear Momentum Flux

Natanson according to Equation (2) in Paragraph 3 of [37] obtained the evolution equation for energy heat flux vector q , which can be reconstructed as follows:

$$\begin{aligned} \rho &= \frac{d}{dt} \left[\left(u^2 + \overline{c^2} \right) u + 2 \overline{(u \cdot c)} c + q \right] \\ &+ \operatorname{div} \left[\begin{aligned} &2 \rho \overline{(u \cdot c)} u \otimes c + \rho u \otimes q + \rho u^2 \overline{c} \otimes c + \\ &\quad + 2 \overline{(u \cdot c)} c \otimes c + \overline{(c \cdot c)} c \otimes c \end{aligned} \right] \\ &= \rho \frac{\delta}{\delta t} \left[\overline{c^2} u + 2 \overline{(c \cdot u)} c + q \right] + \rho f \left(u^2 + \overline{c^2} \right) \\ &+ 2f \left[\rho u \otimes u + \rho c \otimes c \right] \end{aligned} \quad (71)$$

This fully geometrically nonlinear equation that appeared in Natanson's original paper required 26 pages. Natanson found this equation suddenly in following papers [34,36–39]. Thus, the process of creating this formula can be divided into stages, namely: the part designated with index 1 was created in paper [34], the part numbered with index 2 was developed in paper [36], then the part numbered assigned with index 3 was derived in paper [38], the part named with index 4 was established in paper [39] and the last part with index 5 was formed in paper [37]. It is worth noting that a linear version of this equation was discovered by Cattaneo in 1948 [11]:

$$\frac{\partial}{\partial t} q + \frac{q}{\tau} = \kappa \operatorname{grad} T. \quad (72)$$

Next, taking $Q = (u + c) \otimes (u + c)$ and the appropriate identities:

$$Q = u \otimes u + \overline{c} \otimes c \equiv u \otimes u + p \quad (73)$$

$$\overline{c} \otimes Q = \overline{c} \otimes u \otimes c + \overline{c} \otimes c \otimes u + \overline{c} \otimes c \otimes c \quad (74)$$

$$\begin{aligned} \operatorname{div}(\overline{\rho c} \otimes Q) &= \operatorname{div}(p \otimes u^{2,3} + p \otimes u + \rho \overline{c} \otimes c \otimes c) \\ &= (\operatorname{grad} p)u + p(\operatorname{div} u) + (\operatorname{div} p) \otimes c + p \operatorname{grad}^T u + \operatorname{div}(\rho \overline{c} \otimes c \otimes c) \end{aligned} \quad (75)$$

$$\rho \frac{\delta}{\delta t} Q = \frac{\delta}{\delta t} p, \quad \rho \left(f \cdot \frac{\delta Q}{\delta u} \right) = \rho(u \otimes f + f \otimes u) \quad (76)$$

Natanson obtained the nonlinear evolution equation for momentum flux:

$$\begin{aligned} &\frac{d}{dt} p + (\operatorname{grad} u)p + p(\operatorname{grad}^T u) + (\operatorname{div} u)p + \operatorname{div}(\rho \overline{c} \otimes c \otimes c) \\ &+ u \otimes (\rho \delta_t u + \rho u \operatorname{grad}^T u + \operatorname{div} p) + (\rho \delta_t u + \rho u \operatorname{grad}^T u + \operatorname{div} p) \otimes u \\ &= \frac{\delta}{\delta t} p + \rho(u \otimes f + f \otimes u) \end{aligned} \quad (77)$$

By next omitting parts $u \otimes (\cdot)$, $(\cdot) \otimes u$ and $(u \otimes f + f \otimes u)$:

$$\operatorname{grad} u = u \otimes \nabla = \frac{1}{2}(\nabla \otimes u + u \otimes \nabla) + \frac{1}{2}(u \otimes \nabla - \nabla \otimes u) = d + w \quad (78)$$

Natanson arrived at Equation (12) in work [40], which is reconstructed as follows:

$$\frac{\partial}{\partial t} p + (\operatorname{grad} p)u + (d + w)p + p(d + w^T) + (\operatorname{div} u)p + \operatorname{div}(\rho \overline{c} \otimes c \otimes c) = \frac{\delta}{\delta t} p \quad (79)$$

Note that in comparison to Maxwell [35], the above equation of linear momentum balance possessed a nonlinear contribution, which was developed due to an additional

part in the basic Equation (53). It is the last term with the force f . This force was introduced by Natanson to execute the Galilean principle of relativity, not only for a single material point but for continuum of the material points.

Going further, by averaging Maxwellian's procedure of "gas continuation", Natanson found a special form of a Galilean-non-objective derivative. Helpfully, Stanislaw Zaremba, a professor of Jagiellonian University, after reading the paper [39], discovered, for the first time in 1903, a new principle of relativity that was based on local in time transformations.

3.7. Evolution of Mass Flux Vector

According to Maxwell, by considering an evolution equation for a diffusion flux $\mathbf{j} = \rho\mathbf{u}$, Natanson was able to formulate the following equation, which is reconstructed according to Equation (4) in Paragraph 6 of [41]:

$$\frac{\partial}{\partial t}\mathbf{j} + \text{div}(\rho\mathbf{u} \otimes \mathbf{u} + \overline{\rho\mathbf{c} \otimes \mathbf{c}}) = \frac{\delta}{\delta t}\mathbf{j} + \rho f_A \quad (80)$$

where f_A is a diffusion force.

3.8. Hypothesis of Coertia

With the aim of determining a source of irreversibility in nature, Natanson stated the definition of Coertia that is analogous to inertia. Coertia, specified by Natanson, can be treated as a fundamental property of space, which is a reason for the irreversible phenomena in matter, additionally in the electromagnetic and gravitational areas. Due to this point of view, the irreversible changes assumed in the Maxwell mathematical approach are defined as relaxation times [42]:

$$\frac{\delta}{\delta t}\mathbf{q} = -\frac{\mathbf{q}}{\tau_q}, \quad \frac{\delta}{\delta t}\mathbf{p} = -\frac{\mathbf{p}}{\tau_p}, \quad \frac{\delta}{\delta t}\mathbf{j} = -\frac{\mathbf{j}}{\tau_j}, \quad (81)$$

in which τ_q, τ_p, τ_j are relaxation times for heat, momentum, and mass fluxes, respectively.

3.9. Logical Structure of Extended Thermodynamics (1901)

By focusing on the Maxwell procedure of determined moments of the fundamental relation, Natanson quickly noticed the need for cutting the moment, thus establishing the right closure equations. He suggested the crucial logical structure which takes Q as a balanced quantity and the f_Q flux of Q and F_Q as a super-flux of f_Q , the set of equations could be specified [37]:

- Balance equation

$$\frac{\partial}{\partial t}Q + \text{div}f_Q = 0 \quad (82)$$

- Evolution equation

$$\frac{\partial}{\partial t}f_Q + \frac{1}{\tau_f}f_Q + \text{div}F_Q = 0 \quad (83)$$

- Algebraic closure for F_Q

$$F_Q = a^2 \text{grad}Q \quad (84)$$

- Resulting equation for Q

$$\frac{\partial^2}{\partial t^2}Q + \frac{1}{\tau_f} \frac{\partial}{\partial t}Q - a^2 \text{div}(\text{grad}Q) = 0 \quad (85)$$

According to Natanson, the set of equations mentioned above refers to a whole real phenomenon of nature, in which reversibility is connected with irreversibility by Equation (81) in the relaxation time. Therefore, if $\tau_f = \infty$ (inertia), it is a reversible term, whereas if $\tau_f = 0$ (coertia), it is an irreversible phenomenon.

4. Objectivity of the Evolution Equations (1903)

At around 1903, yet another professor of Jagellonian University, Stanisław Zaremba, started a general discussion on the possibility of Galileian relativity extension to continua, other than Maxwellian electromagnetic aether. From this position, Zaremba proposed a group of transformations beyond the Lorentzian. Zaremba started from a clear argument [43–45] that: “Natanson’s evolution equation does not fulfill the principle of Galileian relativity”. Zaremba was especially interested in Natanson’s fully nonlinear evolution equation for the linear momentum flux (Equation (79)), rewritten in the new form:

$$\frac{d_{M-N}}{dt} \mathbf{p} + \operatorname{div}(\overline{\rho \mathbf{c} \otimes \mathbf{c} \otimes \mathbf{c}}) = \frac{\delta}{\delta t} \mathbf{p} \quad (86)$$

where the Maxwell–Natanson (un-objective) time derivative is given as:

$$\frac{d_{M-N}}{dt} \mathbf{p} = \frac{\delta}{\delta t} \mathbf{p} + (\operatorname{grad} \mathbf{p}) \mathbf{u} + (\mathbf{d} + \mathbf{w}) \mathbf{p} + \mathbf{p} (\mathbf{d} + \mathbf{w}^T) + (\operatorname{div} \mathbf{u}) \mathbf{p} \quad (87)$$

Here, our revalorization, called “The Maxwell–Natanson Derivative”, is in opposition to Truesdell’s reconstruction, which he called “The Maxwell–Zaremba Derivative” [46]. Such an expression erroneously suggests that the original Maxwell fundamental equation is objective; it only becomes an objective after Zaremba’s correction. Assuming that

$$\operatorname{div}(\overline{\rho \mathbf{c} \otimes \mathbf{c} \otimes \mathbf{c}}) = 2n\mathbf{d}, \quad \frac{\delta}{\delta t} \mathbf{p} = -\frac{1}{\tau} \mathbf{p}, \quad (88)$$

where τ is relaxation time. Zaremba obtains the geometrically nonlinear, un-objective, Natanson equation:

$$\tau \frac{d_{M-N}}{dt} \mathbf{p} + \mathbf{p} = -2\mu \mathbf{d}. \quad (89)$$

In order to remove un-objectivity, Zaremba [44] proposed an interesting extension of Galilean’s relativity, that has its roots in the Leibnitz–Berkeley relativity principle, which had been earlier rediscovered by Pierre Duhem in his “ΣΩΖΕΙΝΤΑΦΑΙΝΟΜΕΝΑ” [47]. As Michał Heller mentioned [48], the special relativity theories based on the mechanical approach are always more consistent than the special relativity theories based only on a one single Lorentzian (i.e., electromagnetical) group of symmetry transformations. Even in Cracow, Zaremba’s relativity theory was strongly opposite to Einstein’s fashionable theory of special relativity, which was published at around the same time.

The Zaremba procedure [44] is mathematically extremely simple. Zaremba started by comprising a new transformation between two observers. Letting the second observer $x_\alpha(t)$ be related to the first x_i , $i = x, y, z$ observer by the following:

$$x_\alpha(t) = Q_{\alpha j}(t)x_j + b_\alpha(t) \quad (90)$$

where the orthogonal tensor $Q^{\alpha j}$ describes a time dependent rotation in which the bases e_j to e_α and b_α form a time dependent connecting vector. In this procedure, a spin between the observers is defined as follows:

$$W_{\alpha\beta} = \partial_t Q_{\alpha j} Q_{\beta j}^{-1} = -W_{\beta\alpha}, \quad \mathbf{W} = W_{\alpha\beta} \mathbf{e}_\alpha \otimes \mathbf{e}_\beta. \quad (91)$$

Now, rewriting the fundamental Natanson Equation (53) in the second (non-inertial) observer system:

$$\frac{\partial}{\partial t} (nQ) + \operatorname{div} [n(\mathbf{u} + \mathbf{c}) \otimes Q] = \frac{\delta}{\delta t} (nQ) + n\mathbf{f}_r \cdot \frac{\partial Q}{\partial (\mathbf{u} + \mathbf{c})}, \quad (92)$$

one obtains a relative force f_r :



$$\begin{aligned} f_r &= \mathbf{b} + \mathbf{z} + 2\mathbf{W}(\mathbf{u} + \mathbf{c}) = \\ &= f_\alpha \mathbf{e}_\alpha + [-W_{\alpha\beta}(x_\alpha - b_\alpha) - 2W_{\alpha\beta}\partial_t b_\beta + \partial_t W_{\alpha\beta}(x_\beta - b_\beta) + \partial_t \partial_t b_\alpha] \mathbf{e}_\alpha + 2W_{\alpha\beta}(u_\beta + c_\beta) \mathbf{e}_\alpha \end{aligned} \quad (93)$$

Considering (92) the case of momentum flux, we consequently obtain:

$$nQ = \overline{\rho(\mathbf{u} + \mathbf{c}) \otimes (\mathbf{u} + \mathbf{c})} = \overline{\rho \mathbf{c} \otimes \mathbf{c}} + \rho \mathbf{u} \otimes \mathbf{u} = \mathbf{p} + \rho \mathbf{u} \otimes \mathbf{u}, \quad (94)$$

$$n(\mathbf{u} + \mathbf{c}) \otimes Q = \overline{\rho(\mathbf{u} + \mathbf{c}) \otimes (\mathbf{u} + \mathbf{c}) \cdot (\mathbf{u} + \mathbf{c})} = \rho \mathbf{u} \otimes \mathbf{u} \otimes \mathbf{u} + \mathbf{u} \otimes \mathbf{p} + (\mathbf{p} \otimes \mathbf{u})^{2,3} + \mathbf{J}, \quad (95)$$

$$\overline{nf_r \cdot \frac{\partial Q}{\partial(\mathbf{u} + \mathbf{c})}} = \rho[(f + z) \otimes \mathbf{u} + \mathbf{u}(f + z)] + 2(\mathbf{W}\mathbf{p} + \mathbf{p}\mathbf{W}^T) + 2(\mathbf{W}\mathbf{u} \otimes \mathbf{u} + \mathbf{u} \otimes \mathbf{u}\mathbf{W}^T), \quad (96)$$

where $\rho = n m$ and $\mathbf{J} = \overline{\rho \mathbf{c} \otimes \mathbf{c} \otimes \mathbf{c}} = J_{\alpha\beta\gamma} \mathbf{e}_\alpha \otimes \mathbf{e}_\beta \otimes \mathbf{e}_\gamma$. Next, using the following identities:

$$\partial_t \rho + \text{div}(\rho \mathbf{u}) = 0, \quad \mathbf{l} = \text{grad} \mathbf{u} = \mathbf{u} \otimes \nabla, \quad (97)$$

$$\partial_t nQ = \partial_t \mathbf{p} + \mathbf{u} \otimes \mathbf{u}(\partial_t \rho) + \rho(\partial_t \mathbf{u}) \otimes \mathbf{u}, \quad (98)$$

$$\text{div}(\rho \mathbf{u} \otimes \mathbf{u} \otimes \mathbf{u}) = \mathbf{l}\mathbf{u} \otimes (\rho \mathbf{u}) + (\rho \mathbf{u}) \otimes \mathbf{u}\mathbf{l}^T - \mathbf{u} \otimes \mathbf{u}(\partial_t \rho), \quad (99)$$

$$\text{div}(\mathbf{u} \otimes \mathbf{p}) = (\text{grad} \mathbf{u})\mathbf{p}^T + \mathbf{u} \otimes \text{div} \mathbf{p}, \quad (100)$$

$$\text{div}(\mathbf{p} \otimes \mathbf{u}) = (\text{grad} \mathbf{p})\mathbf{u} + \mathbf{p} \text{div} \mathbf{u}, \quad (101)$$

$$\text{div}(\mathbf{p} \otimes \mathbf{u})^{2,3} = (\text{div} \mathbf{p}) \otimes \mathbf{u} + \mathbf{p} \text{grad}^T \mathbf{u}, \quad (102)$$

$$\begin{aligned} &\partial_t \mathbf{p} + (\text{grad} \mathbf{p})\mathbf{u} + \mathbf{l}\mathbf{p} + \mathbf{p}\mathbf{l}^T + (\text{tr} \mathbf{l})\mathbf{p} - 2(\mathbf{W}\mathbf{p} + \mathbf{p}\mathbf{W}^T) + \text{div} \mathbf{J} \\ &+ \mathbf{u} \otimes (\rho \partial_t \mathbf{u} + \rho \mathbf{u}(\text{grad}^T \mathbf{u}) + \text{div} \mathbf{p}) + (\rho \partial_t \mathbf{u} + \rho \mathbf{u}(\text{grad}^T \mathbf{u}) + \text{div} \mathbf{p}) \otimes \mathbf{u} \\ &= \frac{\delta}{\delta t} \mathbf{p} + \mathbf{u} \otimes [-2\rho \mathbf{u}\mathbf{W}^T + \rho(\mathbf{b} + \mathbf{z})] + [2\rho \mathbf{W}\mathbf{u} + \rho(\mathbf{b} + \mathbf{z})] \otimes \mathbf{u}, \end{aligned} \quad (103)$$

by removing the independently fulfilled momentum balance from the above equation, we obtain a general form of the evolution equation able to obtain an evolution equation within the non-inertial frame:

$$\left(\dot{\mathbf{p}} - \mathbf{W}\mathbf{p} - \mathbf{p}\mathbf{W}^T\right) + (\mathbf{d} + \mathbf{w} - \mathbf{W})\mathbf{p} + \mathbf{p}(\mathbf{d} + \mathbf{w}^T - \mathbf{W}^T) + (\text{tr} \mathbf{l})\mathbf{p} + \text{div} \mathbf{J} = \frac{\delta}{\delta t} \mathbf{p}, \quad (104)$$

with a decomposition of $\mathbf{l} = \mathbf{d} + \mathbf{w}$ and denotation of $d/dt(\mathbf{p}) = \dot{\mathbf{p}}$.

Now, the Zaremba principle of relativity can be formulated as a postulate according to Equation (7) in Paragraph 2 of [45], which can be reconstructed in the form: “**passive transformations = active transformations**”.

Which leads to equality

$$\mathbf{W} = \mathbf{w}, \quad (105)$$

which is the so-called the co-rotational Zaremba derivative, which can be summarized as follows:

$$\frac{d_*}{dt} \mathbf{p} = \dot{\mathbf{p}} = \frac{d}{dt} \mathbf{p} - \mathbf{w}\mathbf{p} - \mathbf{p}\mathbf{w}^T. \quad (106)$$

By inserting the Zaremba derivative, we arrive at an objective evolution equation for the flux of the linear momentum:

$$\dot{\mathbf{p}} + \text{div} \mathbf{J} = \frac{\delta}{\delta t} \mathbf{p} - (\mathbf{d}\mathbf{p} + \mathbf{p}\mathbf{d} + \mathbf{p} \text{div} \mathbf{u}). \quad (107)$$

Thus, from the point of Zaremba’s investigations, it follows that the fundamental equations within an arbitrary version (e.g., Maxwell, Boltzmann, and Natanson) should fulfill some principle of relativity, which is formulated in terms of an appropriate group of transformations. The equality of results of passive (motion of observer) and active (motion of continua) transformations ultimately leads to the correct mathematical procedure and the best way for obtaining the objective thermodynamics [6]. It should be added that the

name objective thermodynamics does not appear in the historical studies that we have cited, however, T. Fülöp proposed the term objective thermodynamics [49].

5. Conclusions

There are a few common features that strongly connect both scientists under consideration. Firstly, Duhem and Natanson were strongly influenced by Aristotelian thermodynamics; especially his concept for the conservation of two special parameters: *energeia* and *entelechia*. The conservation of *energeia* and *entelechia* were a starting point for building the concept of “perpetuum mobile” in the Renaissance, and, next in 19th-century, the concept of First and Second Laws of Thermodynamics. It is unusual that Duhem and Natanson, independently, developed a new concept of energy that was nothing like the first (main) invariant of a general kind of motion, called peripatetic motion by Aristotle. From this point of view, the notion of energy obeys the entire changes in nature.

Secondly, Duhem and Natanson had a common approach to the Second Law of Thermodynamics, which could be interpreted as requirements stated for quality of energy. If one interpreted the *entelechy* as a second invariant of peripatetic motion measuring the energy quality, then the Aristotelian principle of *entelechy* conservation can be treated as the pattern for the Duhem–Natanson principle of energy quality conservation. Contemporary, this version of the Second Law of Thermodynamics could be related to the conservation or the destruction of exergy (available energy) [50–59].

Thirty, both Duhem and Natanson had a specific approach to entropy and its balance. Both started from a Boltzmannian concept of “entropy element” described by the Boltzmann constant k_B . If k_B is an independent fundamental constant of physics, then, entirely, the entropy and temperature are state parameters of more fundamental fields [60–62]. In the Duhem reasoning taken from the old concept of caloric, it was some kind of “disconnected” electromagnetic field that was hidden inside of matter. This means that Duhem’s entropy indicates a certain field not a kind of matter. Another way in Natanson’s approach that his treatment of entropy was similar to Maxwell [35] was related to the matter as a “specific measure of collective motion of particles”. Therefore, Duhem photons can transport the entropy, but for Natanson.

In modern thermodynamics, generally, Clausius entropy inequality plays the fundamental role. Thus, the relevance of Duhem’s and Natanson’s results is very weak in comparison to contemporary studies. For instance, the principle of least action, so preferred by Duhem and Natanson, in modern thermodynamics, is not popular as a basic tool; most scientists prefer a phenomenological approach. Another example is non-equilibrium thermodynamics, where, owing to the so-called Coleman–Noll procedure [63–66], the whole system of governing equations is always finally reduced to the entropy production and is presented as the Clausius–Duhem inequality. This was not satisfied from Duhem’s view, as, originally, he assumed the inequality in the energy not entropy frame.

Generally speaking, for Duhem and Natanson, the sector of energy (quantity and quality) was the place where the entire laws of thermodynamics needed to be formulated, however, the balance of entropy was a second-rate balance equation that played a similar role to the balance of mass or the balance of linear momentum. A quite different theory structure is observed in modern thermodynamics, where the balance of entropy is the most important among the other equations and, simultaneously, the balance of energy is degraded and reduced to a simple equation only describing the field of temperature [67–70]. It is our general reflection that thermodynamics paradigms change very slowly, therefore, both Duhem and Natanson’s achievements and original lines of reasoning should be remembered and treated just as a part of history.

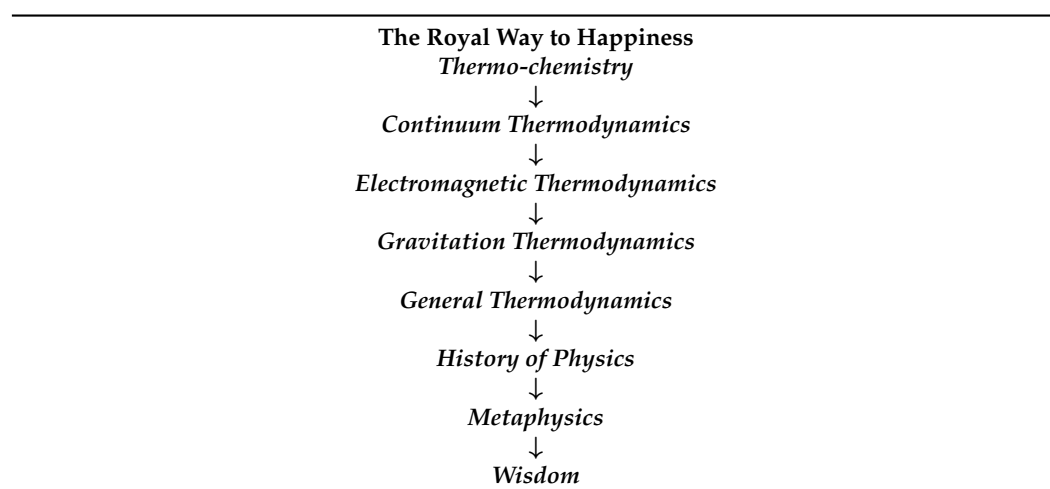
Among thermodynamics researchers, there is a deeply rooted belief in the impossibility of fitting, taking the laws of thermodynamics as a precise mathematical framework. This leads to the impression that the mathematical foundations of our sciences have “shallow roots” [71,72]. Looking at the theoretical base from a mathematical perspective, and especially at the first law of thermodynamics, it is impossible to identify a unique framework

among the collection of numerous incomplete, restrictions on real energy conversion and questionable mathematical equations [73,74]. There has been no experimental violation of the first law of thermodynamics for more than 200 years, yet there remains no intellectual ambition to develop a single mathematically consistent statement of the first and second laws of thermodynamics. Therefore, the laws continue to be understood pragmatically and taken by us “on faith”.

Most investigators are not interested in the mathematical foundation of nature, simply because the foundations must first be extended and this is, as of yet, beyond our knowledge limits. Referring to Josef Kestin, from a purely mathematical standpoint, we have a Babel-like understanding of the foundations. This problem Maxwell undertakes in his *Matter and Motion*, saying that “**the foundation of the first law of thermodynamics requires a knowledge of the whole of physics, chemistry, biology and even sociology**”. While at the end of 19th century this was possible, given the current volume of the literature, today it is impossible to achieve such knowledge. The best examples of those that have come close to achieving such a pinnacle are the subjects of this article, Pierre Duhem and Ladislavus Natanson. Both invested much time and effort into building a mathematical framework of generalized thermodynamics. Here, our aim was to reconstruct, in a way that is understandable for a contemporary reader, a singular example of their original mathematical approaches to thermodynamics.

Finally, we stress that there are many of similarities between these two scientists. They both had a love of Aristotle and Maxwell, both were overcome by Cartesian’s approach to the description of gravitation and light, and both developed the Maxwellian electrodynamics into a thermodynamic frame (Duhem—hidden, polycyclic thermodynamics; Natanson—the quantum thermodynamics). However, perhaps the most impressive similarity between these two is their unique scientific evolution. Both scientists started as chemists—Pierre Duhem at the Stanislaw College at Paris under the supervisor of the largely underestimated Jules Moutier, and Ladislavus Natanson in a private laboratory of Jerzy Bogucki (Marie Curie’s uncle) at Warsaw; both had excellent starting points. In Table 1, we present a scheme outlining the steps in their evolution of knowledge, from chemical practice to the thermodynamics, history of physics and, ultimately, to Aristotelian metaphysics and wisdom. These unusual ways (Table 1) sciences developed were frequently reported by Natanson in his philosophical papers, where he mentioned that the best pattern to follow was that of P. Duhem. We completely agree with this statement.

Table 1. The frame of knowledge and scientific activity of Duhem and Natanson.



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