Article

J.J. Thomson and Duhem's Lagrangian Approaches to Thermodynamics [†]

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Abstract: In the last decades of the nineteenth century, different attitudes towards mechanics led to two main theoretical approaches to thermodynamics: an abstract and phenomenological approach, and a very different approach in terms of microscopic models. In reality some intermediate solutions were also put forward. Helmholtz and Planck relied on a mere complementarity between mechanical and thermal variables in the expressions of state functions, and Oettingen explored the possibility of a more demanding symmetry between mechanical and thermal capacities. Planck refused microscopic interpretations of heat, whereas Helmholtz made also recourse to a Lagrangian approach involving fast hidden motions. J.J. Thomson incorporated the two mechanical attitudes in his theoretical framework, and put forward a very general theory for physical and chemical processes. He made use of two sets of Lagrangian coordinates that corresponded to two components of kinetic energy: alongside macroscopic energy, there was a microscopic energy, which was associated with the absolute temperature. Duhem put forward a bold design of unification between physics and chemistry, which was based on the two principles of thermodynamics. From the mathematical point of view, his thermodynamics or *energetics* consisted of a Lagrangian generalization of mechanics that could potentially describe every kind of irreversible process, explosive chemical reactions included.

1. Introduction

In the second half of the nineteenth century, the recently emerged thermodynamics underwent a process of mathematisation, and new theoretical frameworks were put forward. Moreover a widespread philosophical and cosmological debate on the second law also emerged. On the specific physical side, two main traditions of research were at stake: the refinement of the kinetic theory of gases, and a questionable alliance between mechanical models and statistical procedures, on the one hand, and the attempt at recasting thermodynamics in accordance with the mathematical structures of Analytical mechanics, on the other. Both research traditions attempted to bridge the gap between the mechanical and thermal domains (Some conceptual aspects of the theoretical pathway leading from Clausius to Duhem are developed in [1,2]. A detailed mathematical account of the emergence of abstract thermodynamics can be found in [3]. For the methodological and philosophical debate that stemmed from the second principle of thermodynamics, see [4]).

James Clerk Maxwell and Ludwig Boltzmann pursued the integration of thermodynamics with the kinetic theory of gases and statistics. At the turn of the twentieth century, the alliance between microscopic mechanical models and probabilistic laws was successfully applied to the field of electromagnetic radiation [5]. Other scientists relied on a macroscopic and abstract approach in term of continuous variables, setting aside specific mechanical models. The second research tradition was based on the mathematical and physical concept of *potential*, and had its roots in Rudolf Clausius and William Macquorn Rankine's researches in the mid-nineteenth century. Nevertheless the simplified picture of two traditions of research in thermodynamics overshadows the existence of many nuances and different theoretical streams. Different "mechanical theories of heat", and different meanings of the adjective *mechanical* were on stage. In the abstract approach we can find at least three conceptual streams, which corresponded to different attitudes toward mechanics:

(1). a macroscopic and phenomenological approach,
(2). a macroscopic approach based on a structural analogy with abstract mechanics,
(3). a combination of macroscopic and microscopic approaches.

The third stream represented an attempt to bridge the gulf between the two main traditions. It is worth remarking that even Clausius had followed a twofold pathway: a very general mathematical approach to thermodynamics in some memoirs, and an attempt at devising kinetic models of gases in other memoirs. Some scientists contributed to different streams: Max Planck and Arthur von Oettingen contributed to the first and second, Hermann von Helmholtz developed the second and third, and Joseph John Thomson was also at ease along the second and third. Pierre Duhem developed the second stream in an original way: at first he recast thermochemistry, where the second principle of thermodynamics and the concept of free energy were in prominence. Subsequently he attempted to set up a mathematical theory for hysteresis and other irreversible processes. In the meantime he had developed a generalized Lagrangian theory where geometrical, thermal, and other kinds of generalised coordinates were at stake. After some reference to the early developments of the abstract pathway, I will focus on J.J. Thomson and Duhem's Lagrangian approaches. They had different attitudes towards a Lagrangian approach to thermodynamics. J.J. Thomson looked upon Lagrange's equations as a powerful language that could unify microphysics and macrophysics, whereas Duhem refused any reference to microscopic structures. The latter looked

upon Lagrange's equations as a model for a more general mathematical framework that could account for a wide set of physical and chemical processes.

2. The Second Research Tradition

The first tradition was pursued and refined by Ludwig Boltzmann. He tried to go far beyond Maxwell's microscopic interpretation of equilibrium in rarefied gases: he aimed at clarifying the processes leading to equilibrium. In a long paper he published in 1872 he assumed that molecules were continuously in motion, and those microscopic undetectable motions gave rise to "well-defined laws" at the macroscopic level, which involved the observed average values. A thermodynamic theory required therefore two different levels: a microscopic invisible, and a macroscopic visible one. Statistics and probability could bridge the gap between the two levels. According to Boltzmann, probability did not mean uncertainty: probabilistic laws were ordinary mathematical laws as certain as the other mathematical laws. In 1877, in an even longer paper, he stressed the structural similarity between his function Ω, representing the probability of a given state, and the entropy dQ/T in any "reversible change of state" [6,7] (Dugas reminded us that Boltzmann's theoretical representation of atoms and molecules evolved over time. In the first volume of his *Vorlesungen über Gastheorie* (1895–1898), we find molecules as "elastic spheres", and then molecules as "centers of force", whereas in the second volume molecules are represented as "mechanical systems characterized by generalized coordinates" [8]).

With regard to the second tradition and its theoretical roots, it is worth remarking that in 1854 Clausius had looked upon the second law of thermodynamics as a law of equivalence between "transformations," in order to maintain a sort of symmetry in the axiomatic structure of thermodynamics. This formulation of the second law, pivoted on the concept of "equivalence value" dQ/T, where T was a function of temperature. From the linguistic and conceptual points of view, the two laws of thermodynamics were two principles of the same kind: while the first stated the equivalence between heat and work, the second stated the equivalence between mathematically well-defined "transformation values". In the case of "reversible cyclic processes", the sum or the integral vanished, namely $\oint dQ/T = 0$. A formal analogy between mechanics and thermodynamics was thus established. The sum of the "transformation content" [*Verwandlungsinhalt*] had to vanish in pure, "reversible" thermodynamic processes, as well as the sum of mechanical works along a closed path had to vanish in non-dissipative mechanics. When the processes were irreversible, there was a loss of the transformation content, and the above integral became positive: the initial conditions could not be restored, and the transformation was "uncompensated" [9].

Another formal development was put forward by the Scottish engineer Rankine in 1855. The concept of "*Actual energy*" became a generalization of the mechanical *living force*: it included "heat, light, electric current", and so on. The concept of "*Potential energy*" was extended far beyond gravitation, elasticity, electricity and magnetism. It included "chemical affinity of uncombined elements", and "mutual actions of bodies, and parts of bodies". In general, work was the result of a sum of different terms, where every "variation" of a generalized variable was multiplied "by the corresponding effect" [10]:

$$W = Xdx + Ydy + Zdz + ...$$
(1)

In 1869, the mining engineer François Massieu took the path of a mathematical generalization of thermodynamics. After having chosen the volume *v* and the temperature *t* as independent variables, and

after some computations, he arrived at a function ψ whose differential was an exact differential of the same variables. Massieu labeled "*characteristic function of the body*" the function ψ. The most important mathematical and physical step consisted in deriving "all properties dealing with thermodynamics" from ψ and its derivatives. More specifically, the internal energy U and the entropy S could be expressed in terms of the function ψ:

$$U = T^2 \frac{\partial \psi}{\partial t} \text{ and } S = \psi + T \frac{\partial \psi}{\partial t}, \text{ or } S = \frac{\partial}{\partial t}(T\psi) \text{ and } \psi = S - \frac{U}{T} \tag{2}$$

He also introduced a second *characteristic function* ψn in terms of the two variables t and pressure p. Besides U, p, v, Q and S, even the specific heats at constant pressure or volume, and the coefficient of dilatation at constant pressure or volume could be derived from ψ and ψn. According to Massieu, this "mechanical theory of heat" allowed mathematicians and engineer to "settle a link between similar properties of different bodies". Thermodynamics could rely on a consistent set of general and specific laws, and his "characteristic functions" could be looked upon as the mathematical and conceptual link between general and specific laws. In Massieu's theoretical and meta-theoretical context, the adjective "mechanical" did not mean microscopic mechanical models in the sense of Maxwell and Boltzmann, but a mathematical approach on the track of abstract mechanics [11–13].

An abstract approach and wide-scope generalizations were also the hallmarks of Josiah Willard Gibbs's researches on thermodynamics, which he published in the years 1875–1878. The American scientist put forward three "fundamental" thermodynamic functions:

$$\psi = \varepsilon - t\eta , \ \chi = \varepsilon + pv , \ \zeta = \varepsilon - t\eta + pv \tag{3}$$

The adjective "fundamental" meant that all "thermal, mechanical, and chemical properties" of a physical-chemical system could be derived from them. Under specific conditions, the functions ψ, χ, and ζ led to specific conditions of equilibrium [14] (The modern names and symbols for Gibbs's functions ψ, χ, ζ are *free energy* $F = U - TS$, *enthalpy* $H = U + pV$, and *free enthalpy* or *Gibbs free energy* $G = U - TS + pV$ [15,16]).

In 1880, the young German physicist Max Planck remarked that the theory of elasticity had been put forward without any connection with the thermal properties of bodies, and the thermal actions on them. He aimed at filling the gap between thermodynamics and the theory of elasticity, and outlined a mathematical theory where the mechanics of continuous media merged with thermodynamics. Both mechanical work and heat flow could act on the body: under those actions, both the reciprocal of density [*spezifische Volumen*] and temperature could change from $(v;T)$ to $(v\text{n};T\text{n})$. In particular the geometrical co-ordinates of a point inside the body, and its temperature, underwent a transformation in accordance with the equations

$$x = x_0 + \xi; y = y_0 + \eta; z = z_0 + \zeta \text{ and } T\text{n} = T + \tau \tag{4}$$

where x_0, y_0, z_0 and T were the initial values and ζ, η, ζ, and τ the infinitesimal variations. Energy depended on τ and Cauchy's six strain components. Planck showed that energy, entropy, and elastic stresses depended on a combination of mechanical and thermal variables, which were multiplied by a combination of mechanical and thermal coefficients. The two elastic constants could be expressed in terms of those coefficients [17].

After two years, the physicist and physiologist Helmholtz put forward a mathematical theory of heat pivoted on the concept of "free energy". Helmholtz labeled ϑ the absolute temperature, and p_α the parameters defining the state of the body: they depended neither on each other nor on temperature. If P_α was the external force corresponding to the parameter p_α, and $P_\alpha \cdot dp_\alpha$ the corresponding work, then the total external work was $dW = \sum_\alpha P_\alpha \cdot dp_\alpha$. Provided that U was the internal energy of the physical system, S its entropy, and J the mechanical equivalent of heat, the function $F = U - J \cdot \vartheta \cdot S$ played the role of a generalized potential for the forces P_α:

$$P_\alpha = -\frac{\partial F}{\partial p_\alpha}.$$ (5)

According to Helmholtz, the function F represented the potential energy in the thermodynamic context. The functions U and S could be derived from F by simple derivation. The function F also represented "the free energy", namely the component of the internal energy that could be transformed into every kind of work. If U represented the total internal energy, the difference between U and F, namely $J \cdot \vartheta \cdot S$, represented "the bound energy", namely the energy stored in the system as a sort of *entropic heat* [18] (Helmholtz did not seem aware of Massieu's result, which had probably not crossed the France borderlines).

In 1884 Helmholtz attempted to give a microscopic representation of heat, but without any recourse to specific mechanical models. He introduced a global microscopic Lagrangian coordinate, corresponding to a fast, hidden motion, and a set of macroscopic coordinates, corresponding to slow, visible motions. The energy associated with the first coordinate corresponded to thermal energy, whereas the energy associated with the others corresponded to external thermodynamic work [19].

In 1885 Oettingen undertook an even more ambitious design: a formal theory, where mechanical work and heat flows represented the starting point of a dual mathematical structure. The whole body of knowledge of thermodynamics could be based on four "main variables" and two kinds of energy. Temperature and entropy corresponded to "the actual energy [*actuelle Energie*]" Q, or in other words the exchanged heat. Volume and pressure corresponded to "the potential energy S", namely the mechanical energy that actually appeared under the form of mechanical work. In brief

$$dQ = t \cdot du, \; dS = -p \cdot dv$$ (6)

where t was "the absolute temperature", u "the entropy or Adiabate", p the pressure, and v "the specific volume". He insisted on the physical and linguistic symmetry between thermal and mechanical variables and functions. He put forward a list of "energy coefficients" or "capacities": both "heat capacities [*Wärmecapacitäten*]" and "work capacities [*Arbeitscapacitäten*]" were at stake. In particular, "thermal heat capacities" and "thermal work capacities" [20] corresponded to

$$\left(\frac{dQ}{dt}\right)_v = C_v, \; \left(\frac{dQ}{dt}\right)_p = C_p; \; \left(\frac{dS}{dt}\right)_u = \Phi_u, \; \left(\frac{dS}{dt}\right)_p = \Phi_p.$$ (7)

3. J.J. Thomson's "Applications of Dynamics"

In 1888 Joseph John Thomson published a book, *Applications of Dynamics to physics and Chemistry,* where he put forward a very general approach to physical and chemical problems. From the outset he remarked that physicists had at their disposal two different methods of establishing "the connection between two different phenomena": a detailed mechanical description of the physical system, or a more general description, "which does not require a detailed knowledge of the mechanism required to produce the phenomena". The second method depended on "the properties of a single function of quantities fixing the state of the system", and had already been "enunciated by M. Massieu and Prof. Willard Gibbs for thermodynamic phenomena". The structure of Lagrange's equations was suitable for dealing with a set of generalized coordinates q_i, and generalized forces Q_i; $L = T - V$ was the difference between kinetic and potential energy. Temperature or a distribution of electricity could be interpreted as "coordinates" in a very general sense. Thomson insisted on this opportunity: "any variable quantities" could be considered as coordinates if the corresponding Lagrangian function could be expressed "in terms of them and their first differential coefficients" [21].

He applied the method to those cases "in which we have to consider the effects of temperature upon the properties of bodies": temperature was a measure of "the mean energy due to the translatory motion of the molecules of the gas". In the general structure

$$\frac{d}{dt}\frac{dL}{d\dot{q}_i} - \frac{dL}{dq_i} = Q_i \qquad i = 1, \ldots, n \tag{8}$$

he introduced kinetic terms of the kind $(1/2)K\,\dot{u}^2$, where u was a Lagrangian coordinate "helping to fix the position or configuration of a molecule". There was "an essential difference" between this kind of coordinates and those "which fix the geometrical, strain, electric, and magnetic configuration of the system". If the latter could be labelled "controllable coordinates" because they were "entirely under our control", the former were much more elusive and "individually" unattainable. Only "the average value of certain functions of a large number of these coordinates" was actually observable or measurable: he labeled them "unconstrainable" coordinates. He could not exclude that the above kinetic terms depended on some "controllable coordinate ϕ", namely

$$\frac{1}{2}K\,\dot{u}^2 + \ldots\ldots = \frac{1}{2}f(\phi)\Big[(uu)'\,\dot{u}^2 + \ldots\ldots\Big] \tag{9}$$

where "the coefficients (uu)n do not involve ϕ". On the contrary, the temperature θ, which was proportional to those kinetic expressions, did not involve "controllable coordinates" [21].

Thomson found convenient to "divide the kinetic energy of a system into two parts": the first part T_u depended on "the motion of unconstrainable coordinates", and was proportional to the absolute temperature θ, whereas the second part T_c depended on the motion of "controllable coordinates". He stressed that T_c corresponded to what Helmholtz had called "die freie Energie [free energy]". He also assumed that the generalized velocities $\dot{u}$ and $\dot{\varphi}$ could not mix, and in particular

$$\frac{dT_u}{d\dot{\phi}} = 0 \tag{10}$$

As already pointed pout, T_u might contain ϕ, and Lagrange's equations for the coordinates ϕ was

$$\Phi = \frac{d}{dt}\frac{dL}{d\dot\phi} - \frac{dL}{d\phi} = \frac{d}{dt}\frac{d(T_c+T_u-V)}{d\dot\phi} - \frac{d(T_c+T_u-V)}{d\phi} = \frac{d}{dt}\frac{dT_c}{d\dot\phi} + \frac{d}{dt}\frac{dT_u}{d\dot\phi} - \frac{dT_c}{d\phi} - \frac{dT_u}{d\phi} + \frac{dV}{d\phi} \quad (11)$$

where Φ was "the external force of this type acting on the system". Taking into account the above mentioned assumptions, the equation could be written [21] as

$$\Phi = \frac{d}{dt}\frac{dT_c}{d\dot\phi} - \frac{dT_c}{d\phi} - \frac{dT_u}{d\phi} + \frac{dV}{d\phi} \quad (12)$$

The last equation was the starting point of a mathematical derivation which led to a differential relationship between the invisible kinetic energy T_u and the applied forces Φ, and then between heat fluxes and Φ. In the end, simple relationships between thermal and mechanical effects in elastic bodies could be derived. The first step consisted in computing

$$\frac{dT_u}{d\phi} = \frac{d}{d\phi}\left\{\frac{1}{2}f(\phi)\left[(uu)\,\mathrm{n}\,\dot u^2 + ... \right]\right\} = \frac{1}{2}f\,\mathrm{n}(\phi)\left[(uu)\,\mathrm{n}\,\dot u^2 + ... \right] =$$
$$\frac{1}{2}\frac{f\,\mathrm{n}(\phi)}{f(\phi)}f(\phi)\left[(uu)\,\mathrm{n}\,\dot u^2 + ... \right] = \frac{f\,\mathrm{n}(\phi)}{f(\phi)}T_u \quad (13)$$

As a consequence, Equation (l) became

$$\Phi = \frac{d}{dt}\frac{dT_c}{d\dot\phi} - \frac{dT_c}{d\phi} - \frac{f\,\mathrm{n}(\phi)}{f(\phi)}T_u + \frac{dV}{d\phi} \quad (14)$$

When no purely mechanical transformation took place, and only the energy depending on "uncontrollable" coordinates could change, the last equation yielded

$$\frac{d\Phi}{dT_u} = -\frac{f\,\mathrm{n}(\phi)}{f(\phi)} \quad (15)$$

This was the second equation involving the ratio $f\,\mathrm{n}(\phi)/f(\phi)$: the comparison between the two equations gives [21]

$$-\frac{d\Phi}{dT_u} = \frac{1}{T_u}\frac{dT_u}{d\phi} \text{ or } \frac{dT_u}{d\phi} = -T_u\frac{d\Phi}{dT_u} \quad (16)$$

Now a flux of heat δQ was called into play, and the conservation of energy required that

$$\delta Q + \sum \Phi \cdot \delta\phi = \delta T_c + \delta T_u + \delta V \quad (17)$$

The term δV depended only on $\delta\phi$, and therefore

$$\delta V = \sum \frac{dV}{d\phi}\delta\phi \quad (18)$$

whereas the term δT_c required some computations, which led to

$$\delta T_c = \sum\left(\frac{d}{dt}\frac{dT_c}{d\dot\phi} - \frac{dT_c}{d\phi}\right)\delta\phi \quad (19)$$

The expression corresponding to the conservation of energy thus became

$$\delta Q = \sum \left(\frac{d}{dt} \frac{dT_c}{d\dot{\phi}} - \frac{dT_c}{d\phi} \right) \delta\phi - \sum \Phi \cdot \delta\phi + \delta T_u + \sum \frac{dV}{d\phi} \delta\phi \qquad (20)$$

Equation (l) offered an expression for the generalized forces Φ, which allowed Thomson [21] to simplify the expression for δQ:

$$\delta Q = \sum \left(\frac{d}{dt} \frac{dT_c}{d\dot{\phi}} - \frac{dT_c}{d\phi} \right) \delta\phi - \sum \left(\frac{d}{dt} \frac{dT_c}{d\dot{\phi}} - \frac{dT_c}{d\phi} - \frac{dT_u}{d\phi} + \frac{dV}{d\phi} \right) \cdot \delta\phi + \delta T_u + \sum \frac{dV}{d\phi} \delta\phi =$$
$$= \sum \left(\frac{dT_u}{d\phi} \right) \cdot \delta\phi + \delta T_u \qquad (21)$$

Now Equation (p) was called into play, and therefore

$$\delta Q = \sum \left(-T_u \frac{d\Phi}{dT_u} \right)_{\phi=const} \cdot \delta\phi + \delta T_u \qquad (22)$$

When he took into account isothermal transformations, he assumed that "the quantity of work communicated to the system" was "just sufficient to prevent T_u from changing", where T_u was "proportional to the absolute temperature θ. As a consequence,

$$\delta Q = \sum \left(-T_u \frac{d\Phi}{dT_u} \right)_{\phi=const} \cdot \delta\phi$$
$$\left(\frac{dQ}{d\phi} \right)_{\theta=const} = \left(-T_u \frac{d\Phi}{dT_u} \right)_{\phi=const} \quad \text{or} \quad \left(\frac{dQ}{d\phi} \right)_{\theta=const} = -\theta \left(\frac{d\Phi}{d\theta} \right)_{\phi=const} \qquad (23)$$

Thomson stressed the importance of the last equation, which linked the dependence of heat fluxes on mechanical coordinates to the dependence of external forces on temperature. A deep connection between thermal and mechanical effects was at stake. He made use of this equation in order to tackle "the relations between heat and strain", and in particular the "effects produced by the variation of the coefficients of elasticity *m* and *n* with temperature" [21] (In 1845 George Gabriel Stokes had introduced two distinct kinds of elasticity, "one for restoration of volume and one for restoration of shape" [22,23]).

The Greek letters α, β, γ corresponded to "the components parallel to the axes x, y, z of the displacements of any small portion of the body". Six Latin letters corresponded to longitudinal and transverse strains:

$$e = \frac{d\alpha}{dx}, f = \frac{d\beta}{dy}, g = \frac{d\gamma}{dz}, \ a = \frac{d\gamma}{dy} + \frac{d\beta}{dz}, b = \frac{d\alpha}{dz} + \frac{d\gamma}{dx}, c = \frac{d\beta}{dx} + \frac{d\alpha}{dy} \qquad (24)$$

He assumed that Φ corresponded to "a stress of type e", and therefore

$$\Phi = m(e+f+g) + n(e-f-g) \frac{d\Phi}{d\theta} = \frac{dm}{d\theta}(e+f+g) + \frac{dn}{d\theta}(e-f-g) \qquad (25)$$

What had been labeled ϕ in Equation (w) corresponded now to the coordinate e, and δQ corresponded to the amount of heat which had to be supplied to the unit volume of a bar "to keep its temperature from changing when e is increased by δe" [21]:

$$\frac{dQ}{de} = -\theta \frac{d\Phi}{d\theta} = -\theta \left[\frac{dm}{d\theta}(e+f+g) + \frac{dn}{d\theta}(e-f-g) \right] \text{ or}$$

$$\delta Q = -\left[\frac{dm}{d\theta}(e+f+g) + \frac{dn}{d\theta}(e-f-g) \right] \theta \delta e \tag{26}$$

If the coefficients of elasticity decreased as the temperature increased ($dm/d\theta < 0$ and $dn/d\theta < 0$) then the equation showed that $\delta Q > 0$: a given amount of heat had to be supplied in order "to keep the temperature of a bar constant when it is lengthened". In other words, "a bar will cool when it is extended", if no heat is supplied from outside.

In the case of twist, Φ represented "a couple tending to twist the bar about the axis of x", and a was the corresponding twist:

$$\Phi = na \,, \ \frac{d\Phi}{d\theta} = \frac{dn}{d\theta} a \tag{27}$$

The amount of heat that assured the temperature to be preserved was

$$\delta Q = -\frac{dn}{d\theta} \theta \, \delta a \tag{28}$$

The physical interpretation was not different from the previous one: when a rod is twisted, "it will cool if left to itself", provided that "the coefficient of rigidity diminishes as the temperature increases", which is what usually happens (Thomson reminded the readers that William Thomson had first obtained those results "by means of the Second Law of thermodynamics" [21]).

4. Duhem's "General Equations"

In 1891, Pierre Duhem began to outline a systematic design of mathematisation and generalization of thermodynamics. He took into account a system whose elements had the same temperature: the state of the system could be completely specified by its temperature ϑ and n independent coordinates α, β, …, λ. He then introduced some "external forces", which depended on α, β, …, λ and ϑ, and held the system in equilibrium. At the thermodynamic equilibrium, a series of equations of the kind

$$\frac{\partial A}{\partial \beta} - \frac{\partial B}{\partial \alpha} = 0 \tag{29}$$

could be derived. The equations suggested that "a uniform, finite, and continuous function $F(\alpha, \beta, ..., \lambda, \vartheta)$ of $n+1$ coordinates α, β, …, λ, and ϑ does exist". In other words, apart from Θ, which was "independent of the function F", generalized forces could be written as the components of F gradient:

$$A = \frac{\partial}{\partial \alpha} F(\alpha, \beta, ..., \lambda, \vartheta), \ B = \frac{\partial}{\partial \beta} F(\alpha, \beta, ..., \lambda, \vartheta), \ ... \ L = \frac{\partial}{\partial \lambda} F(\alpha, \beta, ..., \lambda, \vartheta) \tag{30}$$

The function F was nothing else but Helmholtz's free energy of Gibbs' first potential [24].

In 1892 Duhem put forward Lagrange's equations for a physical system at the thermodynamic equilibrium. When $dQ = 0$,

$$\frac{d}{dt}\frac{\partial T}{\partial \alpha'} - \frac{\partial T}{\partial \alpha} + E\frac{\partial U}{\partial \alpha} = A, \quad ..., \quad ..., \quad \frac{d}{dt}\frac{\partial T}{\partial \lambda'} - \frac{\partial T}{\partial \lambda} + E\frac{\partial U}{\partial \lambda} = L \tag{31}$$

where T was the kinetic energy, U the internal energy, and E the mechanical equivalent of heat. In 1894 he generalized the equations, and introduced a perturbation, which represented a source of irreversibility for the physical system:

$$\frac{d}{dt}\frac{\partial T}{\partial \alpha'} - \frac{\partial T}{\partial \alpha} + \frac{\partial F}{\partial \alpha} = A' + f_\alpha, \quad ..., \quad ..., \quad \frac{d}{dt}\frac{\partial T}{\partial \lambda'} - \frac{\partial T}{\partial \lambda} + \frac{\partial F}{\partial \lambda} = L' + f_\lambda \tag{32}$$

The new functions $f_\alpha, f_\beta, ..., f_\lambda$ represented "passive resistances to be overcome by the system", and depended on the coordinates α, β, …, λ, ϑ, their time derivatives $\alpha', \beta', ..., \lambda'$, and time t. Equilibrium was *perturbed* by physical or chemical actions that represented the generalization of mechanical *viscosity* [25,26].

In the meantime Duhem was committed to updating thermochemistry. In 1893 he focused on experiments performed at high temperatures, and in particular the phenomenon of "false equilibrium". Thermodynamics forbade some transformations, and they did not really happen, but sometimes even permitted transformations did not take place. Duhem qualified the first case as "true equilibrium", and the latter as "false equilibrium". The concept of "false" equilibrium allowed Duhem to interpret chemical reactions that were associated with "a powerful release of heat" or explosions. When mixtures of hydrogen and oxygen, or hydrogen and chlorine, reached their "true" equilibrium, namely water and muriatic acid, they released such a great amount of heat as to trigger off an explosion. In Duhem's theoretical framework, an explosion was therefore a passage "from a state of false equilibrium to a state of true equilibrium", where "a remarkable amount of heat" was released [27].

From 1894 onwards he published a series of papers dealing with mechanical and magnetic hysteresis, and other kinds of physical and chemical irreversible transformations. He started from a simplified physical system defined by a temperature T and a single "normal variable x", and applied to it "the classic propositions of thermodynamics". The condition of equilibrium under an external force X was $X = \partial \mathcal{F}(x,T)/\partial x$. If the differentiation of the external force required in general that

$$dX = \frac{\partial^2 F(x,T)}{\partial x^2}dx + \frac{\partial^2 F(x,T)}{\partial x \partial T}dT \tag{33}$$

a more general expression

$$dX = \frac{\partial^2 F(x,T)}{\partial x^2}dx + \frac{\partial^2 F(x,T)}{\partial x \partial T}dT + f(x,T,X)\cdot|dx| \tag{34}$$

was required in order to describe the presence of permanent deformations. The function $f(x,T,X)$ was an unspecified "*uniform* and *continuous* function of the three variables x, T, X". It was the existence of a term depending on $|dx|$ that assured that "*a continuous series of states of equilibrium of the system is not, in general, a reversible transformation*". The mathematical model became sensitive to the direction of transformations. At that stage, Duhem confined himself to isothermal transformations, for he was interested mainly in mechanical deformations. The simplified equation yielded [28]

$$dX = \frac{\partial^2 F(x,T)}{\partial x^2}dx + f(x,T,X)\cdot|dx| \tag{35}$$

He assumed the existence of a new kind of closed cycle, a cycle of hysteresis, which was the fundamental entity of the new thermodynamics of permanent, irreversible transformations. When a force dX was applied to the physical system, and then applied in the opposite direction, the sum of forces vanished, but the sum of the corresponding strains dx_1 and dx_2 did not. According to the simplified equation,

$$0 = dX - dX = \frac{\partial^2 F(x,T)}{\partial x^2} \sum_{k=1}^{2} dx_k + f(x,T,X) \sum_{k=1}^{2} |dx_k| \quad \text{or} \quad \sum_{k=1}^{2} dx_k = -\frac{f(x,T,X)}{\dfrac{\partial^2 F(x,T)}{\partial x^2}} \sum_{k=1}^{2} |dx_k| \qquad (36)$$

The physical system did not return to its initial conditions: it experienced an irreversible strain. Duhem made use of the non-simplified equation in order to describe simple mechanical systems: "a homogeneous cylinder submitted to a traction", or "torsion", or "flexion". Other kinds of permanent deformations corresponded to processes like quenching. If traction, torsion and flexion represented the mechanical side, quenching represented the thermal side of Duhem's theory of permanent deformations [28].

In 1896, he put forward a further generalization of his Lagrangian equations, which relied on the structural analogy between chemical "false" equilibrium and mechanical "friction". From the mathematical point of view, the condition of unstable equilibrium that preceded an explosive chemical reaction was not so different from the equilibrium experienced by a body at rest on a rough inclined plane when the tilt angle was slowly increased. Only after having crossed a critical value of the inclination, the body suddenly slid down. The new equations involved a set of functions $g_a, g_b, \ldots\ldots, g_l$, and terms of the kind $g_a \cdot a'/|a'|$ that represented the generalization of static friction:

$$\frac{d}{dt}\frac{\partial T}{\partial \alpha'} - \frac{\partial T}{\partial \alpha} + \frac{\partial F}{\partial \alpha} = A' + f_\alpha + g_\alpha \frac{\alpha'}{|\alpha'|}, \quad \ldots, \quad \ldots, \quad \frac{d}{dt}\frac{\partial T}{\partial \lambda'} - \frac{\partial T}{\partial \lambda} + \frac{\partial F}{\partial \lambda} = L' + f_\lambda + g_\lambda \frac{\lambda'}{|\lambda'|} \qquad (37)$$

The generalized frictional terms depended on generalized coordinates, velocities, and forces. Differently from the "viscous" forces, the new terms did not vanish when the velocities vanished: on the contrary, they tended to the limiting functions $\gamma_\alpha, \gamma_\beta, \ldots\ldots, \gamma_\lambda$, which depended only on coordinates and forces. In this case, every equation gave rise to two different sets of forces that corresponded to two thresholds for the physical-chemical system [29]:

$$A' \pm \gamma_\alpha, \quad \ldots, \quad \ldots, \quad L' \pm \gamma_\lambda \qquad (38)$$

Duhem set up a general and pliable mathematical structure that could be further widened in order to account for phenomena of increasing complexity. When he took into account chemical false equilibrium and explosions, he dropped the traditional "inertial" Lagrangian terms. After having widened the scope and the mathematical structure of traditional mechanics, he disregarded the original component of that structure, and focused on the complementary terms, which corresponded to a sort of complementary mechanics. It was a chemical mechanics or a new kind of mechanics suitable for chemical reactions. The thermodynamic potential $H = F + PV$ (Duhem's potential H corresponded to Massieu's potential φ' and Gibb's potential ζ) was the suitable potential for physical-chemical processes taking place at constant pressure, and the general equations were reduced to a mathematical structure [29] of the kind

$$\frac{\partial H(P,\alpha,T)}{\partial \alpha} - f(P,\alpha,T,\alpha') - g(P,\alpha,T,\alpha')\frac{\alpha'}{|\alpha'|} = 0 \tag{39}$$

Duhem had added dissipative terms to Lagrange's equations in order to generalize analytical mechanics. In the new mathematical structure, no inertial terms appeared, while dissipative terms were in prominence: traditional Analytical mechanics and Chemistry represented two opposite poles in the new formal framework.

The equation described a chemical mixture: the three coordinates represented the degree of combination α, "a uniform and constant pressure P", and "a variable temperature T". The time derivative α represented "the velocity of transformation of the system", or in other words, the velocity of the chemical reaction. Some approximations allowed Duhem to derive that velocity, which was in some way the solution of the mathematical procedure. He assumed that $g(P,\alpha,T,\alpha')$ did not depend on α,

$$g(P,\alpha,T,\alpha \text{n}) \approx \gamma(P,\alpha,T) \tag{40}$$

and $f(P,\alpha,T,\alpha')$ was a linear function of α':

$$f(P,\alpha,T,\alpha') \approx \varphi(P,\alpha,T) \cdot \alpha' \tag{41}$$

The simplified *equation of motion*

$$\frac{\partial H(P,\alpha,T)}{\partial \alpha} - \varphi(P,\alpha,T) \cdot \alpha' \pm \gamma(P,\alpha,T) = 0 \tag{42}$$

yielded the "velocity" of reaction [29]

$$\alpha' = \frac{\dfrac{\partial H(P,\alpha,T)}{\partial \alpha} \pm \gamma(P,\alpha,T)}{\varphi(P,\alpha,T)} \tag{43}$$

Duhem's complementary or chemical mechanics led to results that were paradoxical from the point of view of traditional mechanics but consistent with explosive chemical reactions. When the viscous term vanished, the velocity of reaction became infinite. Pure mechanics and chemical reactions represented the opposite poles in Duhem's generalized mechanics, which could encompass physics and chemistry in a very general mathematical structure.

5. Concluding Remarks

In the context of an abstract approach to thermodynamics, late nineteenth-century Lagrangian theories represented one of the most interesting theoretical streams. J.J. Thomson put forward a bold mathematical framework that could host microscopic motions, macroscopic stresses, and macroscopic heat fluxes. Duhem put forward an even bolder mathematical framework where traditional Lagrangian terms stood alongside dissipative terms that could account for irreversible processes. The concept of motion underwent a deep transformation: it corresponded to any variation of a Lagrangian coordinate. It does not seem that the two authors were influenced by one another. Duhem put forward the first historical reconstruction of the emergence of an abstract approach to thermodynamics. In general he acknowledged the scientific contributions of other scholars: he explicitly mentioned Massieu, Gibbs, Helmholtz, and

Oettingen, but not J.J. Thomson. This is a weak clue about the non-influence of Thomson on Duhem, but stronger evidence is given by the fact that Duhem sharply opposed any microscopic approach. It is definitely more evident that Duhem could not influence Thomson because Duhem's systematic research programme was put forward after 1888.

Today we know that J.J. Thomson's approach did not leave disciples whereas Duhem is acknowledged as the creator of modern phenomenological thermodynamics or the theory of continuous media based on thermodynamics (For the role played by Duhem in the emergence of twentieth-century thermodynamics of nolinear irreversible processes, see [30]. He was the first scholar to put forward a general thermodynamic framework for widespread dissipative processes such as hysteresis and explosions.

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Conflicts of Interest

The author declares no conflict of interest.

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